OPTICAL DETECTION OF SPIN-BATH RELAXATION IN Eu$^{2+}$ DOPED CALCIUM FLUORIDE

by

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ABSTRACT

The magneto-optical Faraday effect was used to observe the spin-bath relaxation in Europium doped CaF$_2$ crystals at helium temperatures from 1.5 to 4.2° K. Theory shows that the magnitude of the Faraday rotation is proportional to the difference in population of the ground state doublet. The experimental method used in this thesis is the same as that which was successfully used by Glättli and by Griffiths. Pulsed microwave power at X-band frequencies was employed to disturb the equilibrium between the spin system and the bath.

The observed relaxation time $T$ was expected to have a $T^{-1}$ temperature dependence but because of the orientation of the crystal in our dc magnetic field which resulted in the seven transition lines being close together, cross-relaxation effects produced a temperature dependence of approximately $T^{-x}$. It is suggested that exchange coupled pairs of Eu$^{2+}$ and clusters involving Eu$^{3+}$ may account for this temperature dependence rather than there being a phonon bottleneck present.

The field dependence of the relaxation time was found not to be directly related to the resonance spectrum.

The Eu$^{2+}$ concentration of the crystals used in this thesis was .2%. 
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Chapter One
INTRODUCTION

Spin-bath relaxation is the way in which energy is exchanged between a system of paramagnetic ions of a crystal and a constant temperature bath.

Kronig (1939) suggested that a direct energy transfer from the spin system to the lattice phonons could take place due to the modulation of the crystal field by the lattice vibrations through the interactions of spin-orbit coupling.

Kastler (1951) put forth the idea that the magneto-optical Faraday rotation should be influenced by electron spin resonance due to differences in population of the various spin states. He reasoned that the rotation should be influenced by the resonance conditions under which microwaves of the appropriate frequency change the distribution of the electrons over these levels.

A quantum mechanical treatment of the dependence of magneto-optical effects in general upon paramagnetic resonance was developed by Opechowski (1953) and the influence was first found experimentally by Daniels and Wesemeyer (1958).

This thesis is an extension of the research done by Glättli (1966) on Europium doped Calcium Fluoride crystals. The Europium doped Calcium Fluoride crystals used in this thesis were cut and oriented in an external magnetic field in such a way that the seven transition lines were as close together as possible while in Glättli's crystals the lines were far apart to avoid possible effects of cross-relaxation. We were interested to observe what effects if any maximum cross-relaxation would have on the relaxation time of our crystals.
Chapter 2 gives the background theory about the relaxation process and accompanying effects. In Chapter 3 the experimental arrangements and procedures are outlined and the results and discussion are presented in Chapter 4.
A) Spin-Lattice Relaxation

Spin-lattice relaxation is used in this thesis to describe the process of energy transfer from a single paramagnetic spin to the surrounding lattice phonons by modulation of the crystal field by the vibration of the lattice.

There are three different processes by which a spin in the upper level of a ground Kramers doublet can relax to the lower level.

a) The Direct Process

In this process, the fluctuating crystal field interaction with the orbital moment of the electron (orbital-lattice interaction) acts as a time dependent perturbation on the spin-phonon system producing a spin flip from the upper state to the lower state which simultaneously creates a phonon of energy $\delta$, equal to the energy difference between the two states. The phonon system can be characterized by $\bar{p}$, the average phonon excitation number whose equilibrium value is given by:

$$\bar{p}_s = (e^{\frac{\delta}{kT}} - 1)^{-1}$$

(2.1)

The number of oscillators in the crystal with energy between $\delta$ and $d\delta$ is given by its classical value:

$$\rho(\delta)d\delta = \frac{3\sqrt{3}v^3 d\delta}{2\pi^2 \hbar v}$$

(2.2)

where $V$ is the crystal volume and $v$ is the velocity of sound in the crystal. The transition probability per second
for a spin flip from \( |b> \) to \( |a> \) is:

\[
W_{b \rightarrow a} = \frac{2\pi}{\hbar} |\langle b | H'_c | a \rangle| ^2 \mathcal{O}(s)
\] (2.3)

where \( H'_c \) is the crystal field Hamiltonian. The relaxation perturbation \( H'_c \) is that part of \( H'_c \) which is time dependent due to the thermal lattice strains \( \epsilon \). Scott and Jeffries (1962) show that for the direct process the relaxation perturbation is approximately given in form and magnitude by:

\[
H'_c = \epsilon \sum_{n,m} \mathcal{U}^{nm}
\] (2.4)

where \( \mathcal{U}^{nm} \) is an operator involving combinations of components of the total angular momentum operator \( J \).

The matrix elements of \( \epsilon \) are given by: (Abragam 1961)

\[
|\langle p_\epsilon (\xi) | \epsilon | \bar{p}_\epsilon (\xi) + 1 \rangle| ^2 = \frac{s(\bar{p}_\epsilon (\xi) + 1)}{2M\sqrt{2}}
\] (2.5)

where \( M \) is the mass of the crystal.

Therefore from first order time dependent perturbation theory the transition probability per second for transition of the combined spin-phonon system from initial state \([|b>, \bar{p}_\epsilon (\xi)|\) to the final state \([|a>, \bar{p}_\epsilon (\xi) + 1|\) is given by:

\[
W_{b \rightarrow a} = \frac{3\epsilon^3}{2\pi\hbar^2 \rho \sqrt{\mathcal{O}(s)}} (\bar{p}_\epsilon (\xi) + 1) |\langle b | \sum_{n,m} \mathcal{U}^{nm} | a \rangle| ^2 \text{ sec}^{-1}
\] (2.6)

where \( \rho = M/V \) is the crystal density.

This equation can be rewritten as:

\[
W_{b \rightarrow a} = K[\bar{p}_\epsilon (\xi) + 1] \text{ sec}^{-1}
\] (2.7)

For the reverse process the equation is:

\[
W_{a \rightarrow b} = K \bar{p}_\epsilon (\xi) \text{ sec}^{-1}
\] (2.8)
The rate equation for the spin system can be written as:

\[-\dot{N}_a = \dot{N}_b = -N_b W_{ba} + N_a W_{ab} = \kappa \left[ -N_b \overline{\rho}_b(\delta) - N_b + N_a \overline{\rho}_a(\delta) \right] \tag{2.9}\]

where the three terms on the right represent stimulated emission, spontaneous emission, and absorption of phonons respectively.

By introducing \( n = N_a - N_b \) and its thermal equilibrium value \( n_0 = N \text{tanh}(\frac{\delta}{kT}) \) where \( N \) is the total number of paramagnetic ions we obtain:

\[ \dot{n} = -T_d^{-1}(n - n_0) \tag{2.10}\]

where

\[ T_d^{-1} = K \coth(\frac{\delta}{kT}) \]

Our measurements were performed at X-band frequencies thus allowing us to make the approximation \( \delta \ll kT \). Hence \( T_d^{-1} \) can be rewritten as:

\[ T_d^{-1} = \frac{2AAT}{\delta} = AT \tag{2.11}\]

where

\[ A = \frac{3\delta^2 A}{\pi^2 \nu^2 \nu} \left| \langle b | \sum_{n} U_n | a \rangle \right|^2 \]

Scott and Jeffries finally arrived at the equation for the relaxation rate for a Kramers salt to be:

\[ T_d^{-1} = \frac{3}{2\pi^2 \nu^2 \nu} \left( \frac{\delta}{kT} \right)^3 \sum_{n,m} \left| \sum_{i} \left( \frac{2\delta A}{\delta_i} \right) \langle a | H \cdot \mathcal{I} | i \rangle \langle i | U_n | b \rangle \right|^2 \]

\[ + \left| \langle a | U_n | i \rangle \langle i | H \cdot \mathcal{I} | b \rangle \right|^2 \frac{2AAT}{\delta} \equiv A'T \tag{2.12}\]

where \( \beta \) is the Bohr magneton, \( A \) is the Lande \( g \) factor, \( |i\rangle \) is one of the states for each higher Kramers doublet, \( H \) is the dc magnetic field, and the sum \( \sum_i \) is over all the excited doublets. This can be written in a form which shows the
temperature and field dependence of the direct process.

\[ T_d' = H' T \]  \hspace{1cm} (2.13)

b) **The Raman Process**

One phonon of energy \( \varepsilon_b \) is scattered inelastically into another phonon of energy \( \varepsilon_a \) while the spin makes simultaneously a transition from \( |b\rangle \) to \( |a\rangle \). \( \varepsilon \) is the energy difference between the states \( |b\rangle \) and \( |a\rangle \) with \( \varepsilon_a = \varepsilon + \varepsilon_b \).

The Raman process is always stronger than the direct process at high temperatures, but the direct process is usually dominant at helium temperatures. For Kramers salts the relaxation rate is given by:

\[ T_r' = \frac{9! \hbar^2}{\pi^2 \alpha^2 V \varepsilon^5} \left( \frac{\hbar}{\varepsilon} \right)^9 \sum \Delta_i \sum |\langle a| U_i^m |i\rangle|^2 \sum |\langle i| U_i^m |b\rangle|^2 T^9 \]  \hspace{1cm} (2.14)

\[ = C T^9 \]

c) **The Orbach Process**

In cases where the crystal field splitting \( \Delta_i \) (ergs) is less than the maximum phonon energy \( \Delta \theta \) (\( \theta = \) Debye temperature) then relaxation between \( |a\rangle \) and \( |b\rangle \) may proceed by the two stage process developed by Finn, Orbach, and Wolf. i.e.

Relaxation proceeds via the intermediate occupation of state \( |c\rangle \). It is possible for the relaxation perturbation \( H_c' \) to induce a spin flip from \( |b\rangle \) to \( |c\rangle \) simultaneously with the absorption of a phonon of energy \( \Delta_i \), thus conserving energy.

Scott and Jeffries (1962) consider the rate equations for such a process and deduce the Orbach relaxation rate to be given by:

\[ T_o' = \frac{3}{2 \pi^2 \sqrt{\hbar}} \left( \frac{\hbar}{\Delta_i} \right)^9 \sum |\langle a| U_i^m |c\rangle|^2 e^{-\frac{\Delta_i}{T}} = C e^{-\frac{\Delta_i}{T}} \]  \hspace{1cm} (2.15)
B) **Phonon Bottleneck**

The calculated spin-lattice relaxation time $T_1$ is, to be correct, the spin-phonon relaxation time. What we measure is the spin to bath relaxation time. There is, therefore, a two step process present; spin via phonons to lattice and then lattice to helium bath. If the spin to lattice relaxation time is very short then it may be that the lattice oscillators are incapable of conducting the spin energy to the bath in a time shorter than the spin-lattice relaxation time $T_1$. If $T_1$ is short enough then the lattice to bath relaxation time may be related to the spin-bath relaxation time that we measure instead of the spin-lattice relaxation time we want. This effect is called the phonon bottleneck.

The main effect of the phonon bottleneck is to change the spin-bath relaxation rate to: (Shulz and Jeffries, 1966)

$$ \frac{1}{\tau} \approx \frac{12 \pi \nu^2 \Delta \nu}{T_{ph} \nu^2 c} \coth^2 \left( \frac{\hbar \nu}{2 k T} \right) \approx D T^2 $$

(2.16)

where $\Delta \nu$ is the spin resonance linewidth, $T_{ph}$ is the phonon-bath relaxation time, $c$ is the number of paramagnetic ions per cubic centimeter, and $\nu$ is the velocity of sound. The bottleneck is distinguished from the direct process by its different temperature dependence, concentration dependence, and possibly a sample size dependence through $T_{ph}$.

A phonon bottleneck would not be expected in our crystals because our value of $T_1$ is very long. i.e. The rate of energy transfer from spins to lattice is very slow. Glättli (1966)
Figure 2.1  Crystal structure of CaF$_2$
C) Europium Doped Calcium Fluoride

a) Crystal Structure

The position of the fluorine and calcium ions in a CaF$_2$ crystal lattice is shown in Figure 2.1. (from Wykoff: Crystal Structure). Each unit cell contains 8 F$^-$ and 4 Ca$^{2+}$ ions. The fluorine ions form a simple cubic lattice with a lattice constant of $\frac{1}{2}a_c = 2.72 $ Å. The calcium ions form a face centered cubic lattice with a lattice constant of $a_c$. Each Ca$^{2+}$ ion has 12 Ca$^{2+}$ nearest neighbors at a distance of 3.86 Å and 8 F$^-$ nearest neighbors at 2.36 Å. Each F$^-$ ion has 6 F$^-$ nearest neighbors at 2.72 Å and 4 Ca$^{2+}$ nearest neighbors at 2.36 Å. The Eu$^{2+}$ ions replace the calcium ions in CaF$_2$ without causing noticeable distortion to the crystal field symmetry. It remains cubic. Trivalent rare earth ions, however, can be found at sites of lower than cubic symmetry.

b) Ground State and Paramagnetic Resonance

The Eu$^{2+}$ free ion has a $^8S_{7/2}$ ground state. The cubic field of the fluoride lattice can split the 8-fold degenerate ground state only in higher order through the interplay of spin-orbit coupling of the $^6P_{7/2}$ multiplet in first order and the multiplets $^6D_{7/2}$ and $^4D_{5/2}$ in second order. (Lacroix, 1957) In a magnetic field of a few KOe, the ground state is split into eight nearly equidistant levels which can be described approximately by the magnetic quantum numbers: $M = \pm 7/2, \pm 5/2, \pm 3/2, \pm 1/2$. Magnetic dipole transitions of the form $\Delta m = 1$ can be induced by our X-band microwave radiation as well as the forbidden transitions $\Delta m = 2$ and $\Delta m = 3$. The seven paramagnetic resonance lines
resulting from these $\Delta m = 1$ transitions are separated due to the crystal field by an amount which depends upon the relative orientation of the external magnetic field with respect to the crystallographic directions. Our crystals were cut so that our magnetic field was parallel to a direction which was approximately $30^\circ$ from the [001] direction. This direction gives the maximum cross-relaxation within the single spin system since the crystal field splitting is at a minimum. For a complete treatment of this refer to Glättli (1966).

c) Cross-Relaxation

At high concentrations spin-spin interactions can play an important role in the redistribution of the populations of the different levels in the spin system which can lead to cross-relaxation effects. The three different cross-relaxation mechanisms which can have an effect on the relaxation times of our Eu$^{2+}$:CaF$_2$ crystals are:

i) Cross-relaxation between different hyperfine components of an electronic transition

The hyperfine structure is not resolved if the hyperfine splitting of a given electronic transition is not large as compared to the dipolar width of the single components. This occurs when the resonance line is inhomogeneously broadened. This can result in a short microwave pulse saturating only parts of the line. The time it takes for the excitation to diffuse through the whole line is given by: (Bloembergen et al., 1959)

$$T_d = \frac{(\Delta \nu)^3}{(\Delta \nu)^4}$$

(2.17)
where $\Delta v^*$ is the width of the whole resonance line and $\Delta v$ is the width of its homogeneously broadened components.

ii) Cross-relaxation between different electronic transitions

There are several possibilities for multiple spin flips between the different electronic levels of Eu$^{2+}$:CaF$_2$. Two processes which conserve angular momentum while spreading the excitation from the center $+1/2 \rightarrow -1/2$ transition line to the other lines are a quadruple spin flip involving a double flip with flips from $-3/2 \rightarrow -1/2$ and $1/2 \rightarrow 3/2$ and a double spin flip involving a single flip from $+1/2 \rightarrow -1/2$ and $3/2 \rightarrow 5/2$. There are also triple spin flips which do not conserve angular momentum.

The actual calculation of the transition probabilities due to the above mechanisms is not possible without the knowledge of the line shapes and would be very involved due to the complicated hyperfine structure.

iii) Cross-relaxation to other spin systems

We have assumed non-interacting spins in calculating $T_1$. Dipolar and exchange interactions between spins can cause a redistribution in the populations of the different levels in the spin systems which can lead to cross-relaxation effects.

Consider two different spin systems made up of single ions and excited pairs. If we assume that the single ions have a spin-lattice relaxation time of $T_1$ and the excited doublet a spin-lattice relaxation time of $T_2$, then we have from Shulz and Jeffries 1966 for the case of $N_i > N_e$ the total rate equations for the population differences $n_i$ and $n_e$ given by:
\[ \dot{n}_i = -W_i(N_i^* n_i - N_i n_i) - T_i^*(n_i - n_i^*) \]
\[ \dot{n}_i = -W_i(N_i n_i - N_i^* n_i) - T_i^*(n_i - n_i^*) \]

where \( N_i \) and \( N_i^* \) are the populations in the two levels of each system, \( N_i^* \) is the total population of the excited pair doublet, and \( n_i^* \approx n_i^* \) are the equilibrium population differences. Rannestad and Wagner (1963) have solved these coupled rate equations and have shown that following saturation of \( n_i \), the population difference of the single ions and therefore the signal recovers at the rate \( T_i^{-} \) which is given by:

\[ \dot{\zeta}^{-} \approx T_i^{-} + \left[ \frac{T_{12}^{-} T_i^{-}}{(T_{12}^{-} + T_2^{-} - T_i^{-})} \right] \left( \frac{N_i^*}{N_i} \right) \]  

(2.19)

where \( T_{12}^{-} \) is the cross-relaxation time.

There are several values \( \zeta^{-} \) can take depending on the relative magnitudes of \( T_1^{-} \), \( T_2^{-} \), and \( T_{12}^{-} \).

1) \( T_1^{-} \gg T_2^{-} \) and \( T_{12}^{-} \gg T_2^{-} \)
\[ \zeta^{-} = T_2^{-} \]

(2.20)

where the rate is the spin-lattice relaxation rate of the single ions.

2) \( T_{12}^{-} \gg T_2^{-} \gg \frac{N_i^*}{N_i} T_1^{-} \)
\[ \zeta^{-} = \frac{N_i^*}{N_i} T_2^{-} \]

(2.21)

This is the case of strong cross-relaxation and weak spin-lattice relaxation of the single ions, therefore the relaxation rate for the single ions is observed to be equal to the spin-lattice rate of the excited pairs reduced by the factor \( N_i^* / N_i \), which is the
specific heat ratio of the two systems.

3) $T_2^{-1} \gg T_{12}^{-1} \gg \frac{N_2}{N_1} T_{12}^{-1}

\mathcal{L}^{-1} = \frac{N_2}{N_1} T_{12}^{-1}

(2.22)

Here we have strong spin-lattice relaxation of the excited pair which results in an observed relaxation rate equal to the cross-relaxation rate multiplied by the reducing factor $N_2/N_1$.

Shulz and Jeffries evaluate case 2 to arrive at the result:

$$\mathcal{L}^{-1} \propto C_1 \Delta' \text{csch} \left( \frac{\Delta'}{kT} \right)

(2.23)$$

for the concentration and temperature dependence and

$$\mathcal{L}^{-1} \propto C_1' \left[ 1 + e^{-\Delta'/kT} \right]^{-1}

(2.24)$$

for case 3. The result for case 3 is the same temperature dependence as in the Orbach process in the limit $\Delta' \gg kT$.

Because of the possibility of pairs or clusters with a distribution of values of $\Delta'$, the value of $\mathcal{L}^{-1}$ may differ from that calculated. The temperature dependence may be of the form $\mathcal{L}^{-1} \propto T^2$ as was found by Gill (1962), Shulz and Jeffries (1966), and Glättli (1966). It will be noted that this temperature dependence is similar to that found when a phonon bottleneck is present. From equation (2.19) it can be seen that cross-relaxation can lead to a wide variety of concentration and temperature dependences, i.e., $N_2/N_1$ depends on the relative concentrations of the two systems.
Single Ions

|a⟩

Pairs

Δ

|α⟩

N_a + N_b + N_i = N_2

N_a + N_i = N_2^*

N_a - N_i = n_2

N_a + N_b = N_1

N_a - N_b = n_1

Figure 2.2

Energy levels |a⟩ and |b⟩ of a single ion and levels |α⟩, |β⟩, |γ⟩ of a pair of ions.

Figure 2.3

Thermal block diagram of the system of Figure 2.2
D) **The Magneto-Optical Faraday Effect**

The magneto-optical Faraday effect is the change in the direction of polarization of linearly polarized light after passing through a medium as a function of an externally applied magnetic field.

It has been shown that the Faraday rotation $\phi$ (rotation of the plane of polarization) is proportional to the magnetization $M$ of the crystal under certain general conditions. The dependence of the light intensity $I(t)$ transmitted by an analyser can be measured and if the transmission law of the analyser $I(\phi)$ is known the magnetization can be calculated from the proportionality $\phi \propto M$. The response time of the light detection system is the only limit on the time resolution of this method.

A redistribution of the populations in the energy levels of paramagnetic ions can be caused, under certain conditions, by microwave radiation which induces magnetic dipole transitions between various levels. A change in population effects the magnetization and therefore the Faraday rotation.

Glättli (1966) shows that the proportionality $\phi \propto M$ holds for Eu$^{2+}$-doped CaF$_2$ crystals at the light frequencies used here.
Chapter Three
EXPERIMENTAL ARRANGEMENT

A) The Apparatus

The apparatus used in the optical detection of paramagnetic resonance and relaxation described in this thesis is nearly identical to that used by Glättli (1966), Griffiths (1965), and Rieckhoff (1962). We therefore review, only briefly, the general features and the few changes which were made during the course of our experiments and refer you to the detailed description by Griffiths (1965). A block diagram of the apparatus is shown in Figure 3.1.

a) The Cryostat

The inner dewar which contains the helium has a diameter large enough to fit over the microwave cavity and the adjusting rods. This dewar is then placed in an oversized nitrogen dewar which reduces the number of times it requires filling during a run. Both dewars are made of pyrex glass and strip silvered. To keep nitrogen bubbles out of the light path windows made of several layers of black plastic tape were cut out and these were secured in place at opposite sides of the inner dewar by a copper sleeve. This resulted in eliminating noise from our light signal. Except for a new dewar cap the mounting of the dewars is identical to the method used by Griffiths (1965). Our cap has the pumping line, the connections to the helium return line, and the manometers entering from the side. The cover which contains the openings for waveguide, transfer syphon, and adjusting rods is screwed on top of the brass cap. A
combination of Hg-diffusion pump and Hyvac 2 forepump was used to pump out the transfer siphon jacket, the oil and mercury manometers, and the "soft" wall of the inner dewar to a hard vacuum. A Kinney high speed pump was employed via a pumping line of one inch diameter to reduce the pressure above the liquid helium surface in order to obtain temperatures down to $1.5^\circ$K.

For a detailed description of the pumping system refer to Griffiths (1965).

b) The Magnet

The iron core watercooled electromagnet (series impedance of $3.6\,\Omega$) was especially designed for this work by Dr. J. M. Daniels and built by the Tateno Electric Mfg. Co., Tokyo, Japan. An axial hole through the magnet allows optical investigations with a light beam parallel to the magnetic field of up to 12 K0e at 40 amperes in a pole piece separation of 7.27 cm. This field is large enough at X-band frequencies to investigate substances with $g$ values as low as 0.5. The current through the magnet was produced by a dc generator and regulated by means of four watercooled rheostats. The ripple from the generator was minimized by two 5600 Mfd. capacitors in parallel. The magnet current was stabilized by power transistors, whose base current was regulated by a combination of voltage and current feedback loops. This stabilization has been described by Garwin et al (1959). A long term stability of at least $\pm 1$ gauss was achieved, which is certainly less than the line width of the hyperfine components of the Europium lines and is better than the resolution limit set by the inhomogeneity
of the magnetic field. The value of the magnetic field was taken from a calibration curve $H$ vs $I$ using the measured value of the current through the magnet. The magnet was mounted on a dolly which allowed it to be rolled into place around the dewar. The magnet could also be raised, lowered, or rotated in the horizontal plane via a set of worm gears. A diagram of the circuit is shown in Figure 3.2.

c) The Microwave System

Microwave power was produced by a reflex klystron (Sperry Gyroscope Co. Ltd., 2K39 velocity modulated reflex oscillator) which was capable of delivering 250 mW at X-band frequencies. The klystron heater current was provided by a 6 volt car battery and the high voltages by a homemade regulated power supply. The klystron was matched to the rectangular waveguide transmission line by a variable susceptance. A ferrite isolator protected the klystron from reflected power. Before reaching the sample crystal in the cavity the microwave power passed through a 30 db flap attenuator, two variable precision attenuators, and a magic T. The reflected power from the cavity was monitored in the fourth arm of the magic T, which contained a stub tuner and a crystal detector (1N23). A cavity wave-meter followed by a crystal detector was coupled to the microwave system with a 20 db directional coupler inserted just after the ferrite isolator. (See Figure 3.1) It was used to measure the resonance frequency of the sample cavity.

The cylindrical sample cavity was coupled to the waveguide by a circular iris. Two screws extending into the waveguide above the cavity were used to match the loaded
cavity to the transmission line at room temperature. The cavity was operated in the TE112 mode. The field configuration in a horizontal plane is shown in Figure 33. This mode permits a simple solution to the problem of adjusting the crystal at helium temperatures. A teflon plug which can be turned using a gear drive fills the lower half of the cavity. With CaF$_2$ crystals it was found necessary to only rotate the crystal and not also to tilt it as was the case for Cerium ethylsuphate crystals.

Stainless steel waveguide obtained from Superior Tube Co., Morristown, Pa. was used in the dewar from the brass cap to the cavity. Since the magnetic-dipole transitions are induced by a microwave magnetic field, the H-plane of the wave guide was set perpendicular to the dc magnetic field.

Pulse modulation of the microwaves was achieved by applying a pulse from a Tektronix 161 pulse generator to the reflector electrode of the klystron via a 1 Mfd. capacitor. The repetition rate used was at least (10) times the relaxation time so that complete recovery had taken place before applying a new pulse. To tune the microwave system, a sawtooth voltage from Tektronix 162 waveform generator was applied to the reflector. This allowed the klystron frequency to be swept through the cavity resonance. Both generators were powered by a Tektronix 160A regulated power supply.

d) The Optical System

The optical system including the Hg light source was rigidly attached to the magnet by means of sheets of 7 ply
which were bolted to angle aluminum frames which were in turn bolted to the magnet's yolk. This allowed the optical system to be raised, lowered, or rotated with the magnet.

The light source was a General Electric H100 A4/T mercury arc lamp which was inside a brass cylinder housing and cooled by forced air. The current was taken from a dc generator and passed through filter capacitors, a choke, and a current regulator tube (Amperite 10-4C) in order to keep the light intensity as constant and free from ripple as possible.

A series of lenses collimated the light to a narrow and nearly parallel beam at the crystal's position. A Corning glass filter C.S. No. 7-74 with transmitted wavelengths between 4300 - 4400 Å and 7 mm. thickness was used to select single lines from the Hg spectrum. Both analyser and polarizer were of the Glan-Thompson type and were mounted in a divided circle which made possible angle readings of five minutes of arc. A camera iris was installed between the light source and the first lens to adjust the light intensity so that the photomultiplier would always be operating in it's linear region. A second fixed iris was placed just before the photomultiplier to allow through only light which had come directly from the cavity and thus shut out scattered light.

e) Signal Detection

The light passing through the analyser was detected by an R.C.A. 6217 photomultiplier powered by twelve radio B batteries each giving 90 volts. The photocurrent was fed through a 10 KΩ resistor. The resulting photo signal $V_{ph}$
was found to be proportional to the light intensity up to $V_{ph} = 700 \text{ mV}$ and so care was taken to adjust the light intensity so that $V_{ph}$ never exceeded 600 mV. The relaxation signals were filtered with a variable RC network with a time constant long enough so as not to distort the signals but short enough to cut down the noise.

The signals were then displayed directly on a Tektronix 502 oscilloscope using a built in differential dc amplifier. The opposite bias needed to cancel the dc component of the photo signal was taken from a No. 6 dry cell regulated by a 10 KΩ helipot. The image on the oscilloscope was then photographed using a Polaroid Tektronix scope camera.
Figure 3.1  Block diagram for the apparatus
Figure 3.2 The current regulation
Figure 3.3 Field configuration in the microwave cavity

Figure 3.4 Crystal adjusting mechanism
Figure 3.5 The dewar cap
B) The experimental Procedures

a) Preparations for the Measurements

The Europium doped CaF$_2$ crystals were bought cut and oriented from Optovac Inc., North Brookfield and were polished by the author.

The crystals were cooled to liquid helium temperatures by standard low temperature techniques which are described in detail by Griffiths (1965). After having reached the desired low temperature, the crystal is aligned via the rotating rod for maximum light transmission. This alignment is not as critical as in Cerium ethylsulphate. (Glättli) A good check of the proper alignment is the Faraday rotation at low magnetic fields which should be linear with field.

b) Faraday Rotation

To determine the Faraday rotation, the analyser was adjusted to minimum light transmission for a given field. If the angle of the analyser is $\phi_{\text{min}}(H)$, then the total Faraday rotation is given by:

$$\rho_{\text{nt}}(H) = \phi_{\text{min}}(H) - \phi_{\text{min}}(H=0)$$

(3.1)

Each value of $\phi$ was averaged from several readings. $\rho_{\text{nt}}$ must be corrected by the Faraday rotation of the glass walls of the dewar $\rho_g$ and for the diamagnetic rotation of the sample $\rho_d$. Since $\rho_g + \rho_d$ are of opposite sign with respect to $\rho$, this gives:

$$|\rho_r| = |\rho_{\text{nt}}| + |\rho_g| + |\rho_d|$$

(3.2)

where $\rho_d$ is independent of temperature and has been
determined at room temperatures where $\rho$ is negligible. $\rho$ is also independent of temperature down to 1.5° K. The Faraday rotation of our dewar is shown in Figure 3.5.

c) **Determination of the Resonance Spectrum**

The relative change in the population difference of a two level spin system due to a microwave radiation field is usually called the saturation $S$.

$$S = \frac{\Delta n - \Delta n_0}{\Delta n} \quad (3.3)$$

where $\Delta n$ and $\Delta n_0$ are the population differences between the two levels in the presence and absence of microwaves respectively. The population difference of a two level spin system is proportional to the magnetization $M$ and can be written:

$$S = \frac{M - M_0}{M_0} \quad (3.4)$$

If the magnetization is in turn proportional to the Faraday rotation, the saturation can be put in the form:

$$S = \frac{\varphi - \varphi_0}{\varphi_0} \quad (3.5)$$

where $\varphi$ and $\varphi_0$ are the paramagnetic Faraday rotations in the presence and absence of the microwave radiation respectively.

In a multilevel system, equation 3.4 can be used to define the saturation $S$ since equation 3.3 does not, in general hold. The saturation of a spin system is defined as the relative change in magnetization due to microwave
radiation. \( S \) is a measure of the microwave absorption. To obtain the paramagnetic resonance spectrum \( S \) is plotted against the applied dc magnetic field \( H \). Equation 3.5 has been used to determine the resonance spectrum for Eu\(^{2+}\):CaF\(_2\). It requires reading the angles of minimum light transmission with microwaves on and then off for each field value. This method is sufficient to determine the spectra found in undiluted rare earth salts which exhibit broad resonance lines. If the microwave power required to produce a measurable saturation heats the sample a pulse method can be used to determine the saturation. The light intensity \( I \) transmitted by the analyser is given by:

\[
I(\phi) = (I_0 - I_{\pi/2})\cos^2 \phi + I_{\pi/2}
\]

(3.6)

where \( \phi \) is the angle of the analyser with respect to the plane of polarization of the light. \( I_0 \) is the maximum transmitted light intensity at \( \phi = 0 \) and \( I_{\pi/2} \) is the minimum light intensity at \( \phi = \pi/2 \). A small change \( \Delta \phi \) around the angles \( \phi = \pi/4, 3\pi/4, 5\pi/4 \), gives from equation 3.6:

\[
|\Delta I| = (I_0 - I_{\pi/2})\Delta \phi = (I_0 - I_{\pi/2})\Delta \phi
\]

(3.7)

since \( |\Delta \phi| = |\Delta \rho| \) if \( \Delta \rho \) is the change in Faraday rotation due to a microwave pulse.

The saturation due to a microwave pulse using equation 3.7 is:

\[
S = \frac{\Delta \rho}{\Delta I} = \frac{\Delta I_{\pi/2}}{\Delta \rho (I_0 - I_{\pi/2})}
\]

(3.8)

where \( \Delta I_{\pi/2} \) is the intensity at 45° to the minimum. Equation 3.8 was used to determine the saturation.
The dc photosignal $V_{ph}$ was measured for maximum and minimum light transmission and the angle for minimum light intensity was recorded. The microwaves were then pulsed into the cavity at long repetition rates (two seconds) to avoid heating the crystal. The saturation signal height $\Delta V_{ph}$ was determined from a polaroid picture of the saturation trace. We always kept the maximum $V_{ph} < 600 \text{ mV}$ to stay well within the linear range of the photomultiplier.

d) Relaxation Time Measurements

In Eu$^{2+}$:CaF$_2$ crystals the Faraday rotation is proportional to a change in magnetization and so the decay of the photosignal displayed on the oscilloscope screen after a microwave pulse is a linear measure of the recovery of the magnetization. For a detailed analysis refer to Glättli (1966). A polaroid photograph was taken of the image on the oscilloscope screen and the trace was then measured point by point with the values being plotted on semi-log graph paper. The slopes of the resulting straight lines give the value of $n$ in the equation for the observed relaxation time given by:

$$I' = AT^n \text{ sec}^{-1}$$

(3.9)

See Figure 4.4 for an example.

A second scope (Tektronix 545A with a CA plug in) was employed to observe the pulse response of the wavemeter and the cavity. This enabled us to tune the klystron to match the slowly changing cavity resonance by adjusting the pulse height applied to the reflector electrode.

A zero line of the experimental trace was obtained by
using the 545A to trigger the 502 oscilloscope a second time after the pulse had died out.

e) Temperature Measurements

From 1.5 to 4.2° K the crystal was immersed in liquid helium and the temperature could be calculated by measuring the helium vapour pressures from 1.5 to 2.3° K with an oil manometer and from 2.3 to 4.2° K by the change in Faraday rotation. For a detailed explanation of this procedure refer to Glättli (1966). Since the concentration of Eu\textsuperscript{2+} in the CaF\textsubscript{2} was less than 0.2% the signal to noise ratio deteriorated rapidly as the temperature was raised and so the highest temperature at which meaningful results were still obtainable was 4.2° K.
Figure 3.6 Rotation due to diamagnetic effects of dewar and crystal at room temperature
Chapter Four

EXPERIMENTAL RESULTS

A) **Faraday Rotation**

The change in the angle of polarization with field was measured in order to check that the Faraday rotation was proportional to the magnetization. The measured rotation was corrected in each case for the Faraday rotation due to the glass walls of the dewar and for the diamagnetic rotation of the crystal which was plotted in the third chapter. (Figure 3.6) The resulting paramagnetic rotation was compared to the Brillouin function $B_{\nu}$ and confirmed the proportionality between rotation and magnetization.

The saturation rotation per mm. thickness $\omega (=6^0/mm$ for our crystals) is proportional to the Eu$^{2+}$ concentration, if the effect of concentration dependence of the optical spectrum on the Faraday rotation is negligible. This effect would be strongest for light frequencies close to the optical transitions. Glättli found that the ratio of $\omega$ for different concentrations does not depend on the light frequency for CaF$_2$ crystals and is a direct measure for the relative concentrations of the different specimens.

It is known that Europium ions enter the fluoride lattice in both the divalent and trivalent state. (Shen, 1964) The Eu$^{3+}$ ion has a $^7F_0$ singlet groundstate and gives no paramagnetic contribution to the Faraday rotation. The ratio of Eu$^{2+}$ to Eu$^{3+}$ is very sensitive to the growing conditions. Europium added in the form of Eu$_2$O$_3$ will result in a higher Eu$^{2+}$ concentration than if it was added in the form of EuF$_3$. In our crystals it can be assumed that the Eu$^{3+}$ concentration is as great or greater than our Eu$^{2+}$ concentration of .2%. 
B) **Resonance Spectrum**

The saturation of the spin systems as a function of the external magnetic field was determined in the manner outlined in Chapter 3. The minimum step possible with our rheostat is approximately 30 gauss and therefore we cannot resolve the individual transition lines or hyperfine structure. We do however, obtain an envelope of the $\Delta m = 1, 2, \text{ and } 3$ transitions. The points shown in Figure 4.1 are from one run but the curve drawn through the points is a composite based on the results of several runs.

C) **Relaxation Times**

a) **Field Dependence**

The field dependence of the relaxation times are as shown in Figure 4.2. The readings were taken at $1.58^\circ K$ with a microwave frequency of 8591 Mc/s. The relaxation times in region A are for transitions $\Delta m = 1$, $B$; $\Delta m = 2$, and $C$; $\Delta m = 3$. Between the $\Delta m$ transitions the signals were too weak to evaluate any data.

b) **Temperature Dependence**

The spin-bath relaxation time temperature dependence was measured from $1.5^\circ K$ to the highest temperature which still gave a reasonable signal to noise ratio ($4.2^\circ K$). The points shown in Figure 4.3 are averages from several measurements. As was explained earlier the measurements were done with both the dc magnetic field and the light path parallel to the direction which was $30^\circ$ off the[100] direction. This results in minimum separation between electronic transitions and therefore maximizes cross-relaxations between different transition lines.
The experimental points can be fitted to the straight line:

\[ T'^{-1} = A T^n \]  

(4.1)

where the value of \( n \) is the slope of the line drawn on semi-log graph paper.

Our results were as follows:

<table>
<thead>
<tr>
<th>Crystal No.</th>
<th>Runs</th>
<th>Slope (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>E</td>
<td>2.12</td>
</tr>
<tr>
<td>2</td>
<td>E</td>
<td>1.99</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>1.88</td>
</tr>
</tbody>
</table>

It is observed that the absolute value as well as the functional dependence of the relaxation rate \( T' \) depends on the crystal. This is due to a slight difference in \( \text{Eu}^{2+} \) concentration between the crystals. The differences in values in crystal 2 for the E and F runs is due to our inability to orient the external magnetic field to the identical position each time thus effecting the line separation and hence the degree of cross-relaxation. Line E is in fact made up of two separate runs which did agree in magnitude and temperature dependence.

At these temperatures the accuracy of measurements is quite high (good signal to noise ratio) and the error of measurement does not exceed the size of the circles drawn in Figure 4.3.

No change in \( T \) was observed by varying the pulse length. Earlier work showed no change in \( T \) when the pulse length was changed by a factor of 30.
Figure 4.1: Composite Resonance Spectrum

0.2% Eu²⁺: CaF₂
1.58° K  8591 Mc/s
Figure 4.2 Field Dependence of $I_m$.
Figure 4.3 Relaxation rate of Eu$^{2+}$:CaF$_2$ as a function of temperature
Figure 4.4  
a) Typical relaxation photograph of Eu$^{2+}$ :CaF$_2$

b) Semi-logarithmic plot of trace in a)
Chapter Five
DISCUSSION OF RESULTS

A) Field Dependence of $I$

From the graph of $I$ vs the external magnetic field it appears that the field dependence of $I$ is not directly related to the spectrum as was the case for Neodymium ethylsulphate. (Griffiths, 1965) The field dependence may be due to cross-relaxation effects as were outlined by Bloembergen (1961) in which there is an energy transfer between different parts of the spin system. This could lead to a cross-relaxation process faster than the direct spin-lattice relaxation process.

B) Temperature Dependence of $I$

A comparison of our results with those of Glättli's for Eu$^{2+}$:CaF$_2$ shows that our values of relaxation times are faster than his. This can be explained by the cross-relaxation between different electronic transitions which is at a maximum in our crystals due to their orientations in our external dc magnetic field. Glättli's crystals were cut so that the separation between transition lines was a maximum. This cross-relaxation allows the spins to transmit their energy to the bath faster by having more transition lines available for the direct relaxation process to take place.

Our method of observing the change in paramagnetic rotation after a saturating microwave pulse enables us to measure the time dependence of the magnetization due to the Eu$^{2+}$ ions (to the extent that only they contribute to the Faraday rotation).

The occurrence of a $T^{-2}$ temperature dependence at first seems to indicate the presence of a phonon bottleneck, however
the values of $T$ are much faster than they should be if a bottle-
neck were present. It has been shown that pairs of ions might
be coupled together through exchange interaction to form
paramagnetic systems with energy levels which differ from those
of single ions. Cross-relaxation from single ions to exchange
coupled pairs (or larger clusters) has been proposed by many
authors to explain the $T^{-2}$ dependence; Van Vleck (1959 and 1961),
Gill (1961), Gill and Elliott (1961), Bloembergen and Pershan
(1961), Statz et al (1961), Ramestad and Wagner (1963), Shulz
and Jeffries (1966), and Glättli (1966).

Statz et al (1961) and Gill (1961) measured relaxation times
of transitions in the Cr$^{3+}$ pair spectrum in ruby. The pair
relaxation rates were found to be about three orders of magnitude
faster than the single ion relaxation rates. The above authors
qualitatively explained the strong spin-lattice coupling of pairs
as due to modulation of the exchange interaction by the lattice
vibrations. In our crystals as in two of Glattli's there is an
appreciable concentration of Eu$^{3+}$ ions. These ions have a
ground state singlet $^7F_0$. Since the exchange interaction acts
on the electronic spin rather than on the total angular momentum,
Eu$^{3+}$ ions could be coupled to nearby Eu$^{2+}$ pairs. It is possible
therefore, for either exchange coupled pairs and/or clusters
made up of Eu$^{2+}$ pairs and Eu$^{3+}$ ions to have a steeper $T^{-2}$
dependence and thus account for the $T^{-2}$ temperature dependence.
Since we only had one set of crystals with the same Eu$^{2+}$ and Eu$^{3+}$
concentration it was not possible to check as to which mechanism
was responsible.

Quantitative or even semi-quantitative explanations are
impossible, due to the very complicated structure of our system.
BIBLIOGRAPHY


Griffiths, D.J. (1965) Ph. D. Thesis, Univ. of British Columbia


Kronig, R. deL. (1939) Physica 6, 33


Low, W. Paramagnetic Resonance in Solids, Suppl. 2 Solid State Physics, Seitz and Turnbull ed.


Wyckoff, Crystal Structures, Interscience Publishers, New York