Durham E-Theses

Mechanisms of paramagnetic relaxation

Dugdale, D. E.

How to cite:

Dugdale, D. E. (1967) *Mechanisms of paramagnetic relaxation*, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/8632/

MECHANISMS OF PARAMAGNETIC

RELAXATION

by

D.E. DUGDALE B.Sc. M.sc.

Thesis presented in candidature for the degree of

Doctor of Philosophy of the University of Durham.

ACKNOWLEDGEMENTS.

ABSTRACT.

An experimental study has been made of the paramagnetic spin-lattice relaxation properties of some transition metal ions. Three trivalent metal ions were studied, namely those of titanium, chromium and ruthenium, in the form of acetyl-acetonate compounds of the general formula $M(C_5H_7O_2)_3$. By the use of the corresponding diamagnetic aluminium or cobalt compounds, mixed single crystals were grown with various paramagnetic concentrations. Measurements were made at low temperatures in the liquid helium range, at X band microwave frequencies (9.3 KMc/s). Some measurements were also made at higher microwave frequencies (35.5 KMc/s).

In all cases the relaxation behaviour observed in magnetically dilute crystals is in good agreement with the well established theories relating to single ion relaxation. Particular attention has been given however to the study of the relaxation processes in more concentrated crystals, where concentration dependent relaxation is found. The results obtained have been compared with the two theoretical suggestions that have been proposed to account for these effects. Although neither proposal is entirely satisfactory, the one involving exchange interactions within paramagnetic ion clusters is shown to account in a qualitative way for the observed behaviour. A detailed study of the E.P.R. spectrum of chromium doped crystals has been made which shows that significant exchange interactions do exist in these materials.

CONTENTS.

INTRODUCTION

The magnetic properties of dielectric materials may be considered to arise from a localised array of microscopic magnetic dipoles. If, to a first approximation, the magnetic properties can be described without considering exchange interactions between neighbouring dipoles the material is said to be paramagnetic. When the mutual interactions are important ferromagnetism or antiferromagnetism is found, depending upon the exact nature of the exchange interactions.

This thesis is concerned with paramagnetic materials in which the magnetic properties are due to the presence of ions of the transition group elements. Ions of these elements contain unfilled electronic shells with unpaired electrons, giving the ion a non zero total angular momentum and a consequent non zero magnetic moment. In the crystalline state the magnetic properties of such ions are due almost entirely to the electron spins rather than their orbital angular momentum. A collection of such ions is therefore often referred to as a "spin system". By the use of a diamagnetic material which forms crystals isomorphous with those of some related paramagnetic material mixed single crystals can be grown containing various amounts of paramagnetic material.

In this way studies can be made over a range of paramagnetic concentrations.

Paramagnetic relaxation is concerned with the study of the mechanisms by which such a spin system achieves a state of thermal equilibrium within itself and with its surroundings. The first process, that of achieving internal thermal equilibrium, is referred to as spin-spin relaxation. It may be thought of as energy transfer within the spin system so as to achieve the Boltzman of population distribution among the various spin energy levels necessary for the system to be described by a unique temperature (the "spin temperature"). In the second process the surroundings with which the spin system interacts most strongly are the lattice vibrations of the crystal. This process, which is the main concern of this thesis, is called "spin-lattice relaxation" and consists of exchange of energy between the spin system and lattice so that a common temperature is established. Spin-spin relaxation is strongly dependent on the strength of the interactions between neighbouring spins compared with the Zeeman energy of a single spin in the applied magnetic field. For the magnetic fields and paramagnetic concentrations used in this work it is, apart from possible "cross-relaxation", a very slow process and is of negligible importance compared with spin-lattice relaxation.

Relaxation phenomena of this kind fall strictly within the domain of irreversible thermodynamics. The simplest theoretical description of such irreversible effects consists of the calculation, by perturbation theory methods, of transition probabilities to describe the rate at which the various spin energy level populations change with time, due to the transfer of energy within the spin system and the absorption,

emission and inelastic scattering of phonons. In this way rate equations can be obtained to describe the spin energy level populations as thermal equilibrium between the spin system and lattice returns following some disturbance. For the simplest paramagnetic system, that due to ions with a total spin $S = \frac{1}{2}$, having only two spin energy levels (Zeeman levels) the populations return to their thermal equilibrium values in an exponential manner. The time constant of this exponential is referred to as the "spin-lattice relaxation time". For multilevel systems the rate equations predict that a sum of different exponential functions is necessary to describe the relaxation process. Very often one of these exponentials, usually the longest time constant, is dominant, in which case its time constant is again called somewhat loosely the "spin-lattice relaxation time".

As a vehicle for the study of irreversible phenomena a paramagnetic system is uniquely suitable. The spin system (if not the lattice vibrations) is relatively simple to describe quantum mechanically, having only a small number of discrete energy levels. At low temperatures the relaxation times are long and easily measured, and range from microseconds to seconds. Very large temperature differences between the spin system and the lattice can also be achieved. Thus, with modern microwave techniques, it is a simple matter to equalise the populations of two spin energy levels (infinite spin temperature) and even to produce an inversion of the normal population distribution. Such population inversions, in which higher energy levels have a greater population than lower energy ones, corresponds to negative spin temperatures.

The original investigations in this field were conducted in the 1930's, mainly by Dutch physicists at Lieden University. They used a non resonant method involving magnetic field modulation to determine the frequency range over which the induced magnetisation was able to follow the applied field. At the same time detailed theories of the relaxation processes were evolved. Apart from the intrinsic interest in these relaxation effects these studies arose from the importance of spin-lattice interactions in the detailed understanding of adiabatic demagnetisation of paramagnetic salts. Interest in these studies increased after the war when radar equipment became readily obtainable. New experimental techniques were used involving the direct stimulation of transitions within the spin system by the use of resonant electro-magnetic radiation of microwave frequencies. Most relaxation studies since this time, including the present work have used this resonant microwave technique.

The experimental results have shown that the relaxation phenomena are quite complicated and in general not in agreement with the theories that have been developed by Van Vleck and others. The most significant discrepancy between theory and experiment lies in the observed concentration dependence of the relaxation times. The theories so far developed (single ion theories) consider each ion relaxing independently to thermal equilibrium with the lattice and so predict no concentration dependence. It is generally found that these single ion theories are only valid in very dilute paramagnetic systems. Above one or two molar percent paramagnetic concentration other processes dominate the relaxation behaviour. In this concentration range relaxation times are found which

can be up to several orders of magnitude shorter than those found at low concentrations. Temperature and magnetic field dependencies are also found which, judged by the predictions of the single ion theories, are somewhat anomalous. Some suggestions have been put forward to show how concentration effects could arise. This thesis is concerned mainly with the study of these concentration dependent relaxation times to discover which, if any, of these proposed mechanisms is capable of accounting in detail for the observed effects.

CHAPTER 1.
PARAMAGNETISM AND PARAMAGNETIC RESONANCE.

The main features of paramagnetism are by now a well understood almost classical subject. The standard work in this field is still that of Van Vleck (Van Vleck 1932) and the related topic of paramagnetic resonance is described in many books and research publications, notably the review articles of Bowers and Owen (1955) and Bleaney and Stevens (1953). A brief outline of the theory will be given here in order to introduce the terminology which will be used later.

Free Paramagnetic ions.

An isolated paramagnetic ion may be described by a Hamiltonian of the following form

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + \lambda \underline{L} \cdot \underline{S} + \beta \underline{H} \cdot (\underline{L} + 2\underline{S}) \qquad (1.1)$$

$\mathcal{H}_1$ represents the Hartree-Fock self consistent field which accounts for the Coulomb interaction between the electrons and nucleus and the central potential part of the electron-electron Coulomb interaction. Solutions of (1.1) for this term alone yield sets of highly degenerate states in which each electron has well defined quantum numbers n,l,m,s. Each set of degenerate states is called a "Configuration". Since $\mathcal{H}_1$ is always the largest terms in the total Hamiltonian these configurations form the starting point for a perturbation treatment of the other terms. These remaining terms in (1.1) differ by orders of magnitude in their relative magnitudes so it is a reasonable approximation to consider them individually by successive perturbation calculations.

$\mathcal{H}_2$ is that part of the electron-electron coulomb interaction which cannot be included in $\mathcal{H}_1$, as a purely central potential field. It is sometimes referred to as the electrostatic or electron-electron correlation energy. In first order theory (i.e. neglecting configuration interactions) its affect is to remove some of the configurational degeneracy producing new states characterised by definite values of total orbital angular momentum $\underline{L}$ and total spin $\underline{S}$. Such states are called "Terms", and for such a treatment to be valid the term energy differences must be much less than corresponding ~~configuration~~ energy differences of the configurations. Since, as far as magnetic effects are concerned, only the lowest energy states are of interest (higher ones not being populated at normal temperatures) we are only interested in the lowest such term which arises from the ground configuration.

Within this lowest term the spin-orbit interaction $\lambda \underline{L}.\underline{S}$ is again treated to first order perturbation theory. Once again some degeneracy is removed and the states thus formed are eigenstates of the total angular momentum $\underline{J}$. These states are given the name of "levels" in atomic spectroscopy and each level still has a degeneracy of $2J+1$. Thus the eigenstates of the ion may be said to consist of a linear combination of states from some definite configuration, constructed in such a way that they have a definite value for the quantum numbers J,L,S.

The magnetic properties of the ion are determined by the behaviour under the influence of the Zeeman interaction $\beta \underline{H}.(\underline{L}+2\underline{S})$, of the degenerate states associated with the ground level. Provided that, as is usually the case, the energy separation between different levels is much greater than the Zeeman energy then once again first order

perturbation theory can be used. This is formally equivalent to the problem of the Zeeman interaction operating on the $2J+1$ degenerate states regarded as a complete set. Thus one may write

$$\mathcal{H}'|\alpha\rangle = \beta\underline{H}\cdot(\underline{L}+2\underline{S})|\alpha\rangle = g_L\beta\,\underline{H}\cdot\underline{J}|\alpha\rangle = E_\alpha|\alpha\rangle$$

(1.2)

where $|\alpha\rangle$ is one of the $2J+1$ states and g_L is the Landé splitting factor

$$g_L = \frac{3J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$

One may therefore refer to $\mathcal{H}'$ as the "magnetic Hamiltonian" which completely describes the magnetic properties of the ion. In contrast to the complexity of (1.1)equation (1.2) is very simple, yielding as immediate solutions $2J+1$ equally spaced levels of separation $g_L\beta H$. The reason for this great simplification is to be found in the fact that (1.2) only applies to the lowest group of degenerate states and in no way describes excited levels nor any interactions between levels which may arise with high magnetic fields.

Paramagnetic ions in crystals.

The treatment of paramagnetic ions in crystals parallels that outlined above for free ions in that it is aimed at deriving some effective Hamiltonian, called the "Spin-Hamiltonian", to describe the lowest group of energy states. Now of course one must include in (1.1) some term to describe the interaction between the paramagnetic ion and its neighbouring diamagnetic ions in the crystal lattice. The simplest way to do this and

one that has been very successful in a qualitative way is to suppose
that the paramagnetic ion experiences an electric field due to its
nearest neighbours. This interaction can then be written in the
form

$$V_c = \sum_{\lambda} e_{\lambda} \sum_{n,m} A_n^m r_{\lambda}^n \, Y_n^m(\theta,\phi) \qquad (1.3)$$

where $Y_n^m(\theta,\phi)$ are spherical harmonics, A_n^m are coefficients and λ
labels the electrons of the paramagnetic ion. It can easily be shown
that selection rules for the matrix elements of V_c within the ground
configuration restrict n to be even and less that or equal to 2ℓ ,
where ℓ is the orbital angulor momentum quantum number of the
electrons in the unfilled shells. Further restrictive selection rules
can be obtained by considering the detailed symmetry of the paramagnetic
ion site. The crystal field interaction must not be interpreted too
naively, for although the symmetry of V_c is adjusted to be consistent
with that at the paramagnetic ion site, the coefficients A_n^m are treated
as disposable parameters. Treated in this semi-empircal way the crystal
field model can give at least a qualitative account of situations in which
considerable covalent banding exists.

The way in which V_c is treated depends to a large extent on the
magnitude of this interaction compared with the other terms in (1.1).
If $V_c < \lambda \underline{L} \cdot \underline{S}$ then the crystal field is said to be a weak field.
This case, exemplifield by the rare earth ions, is not found in the transition
groups and so will not be considered further. In transition group materials
V_c is usually of the same order as $\mathcal{H}_2$. If it is valid to treat

V_c as a perturbation following $\mathcal{H}_2$ $(V_c < \mathcal{H}_2)$ then one has a case of a "medium crystal field". In a "strong crystal fields" $(V_c > \mathcal{H}_2)$ the perturbation treatment of $\mathcal{H}_2$ must follow that of V_c.
In what follows we shall suppose that $\mathcal{H}_2$ and V_c are treated together as a single perturbation on the ground configuration so that the conclusions will be most general, applying to both the strong and medium field cases.

When this perturbation calculation is carried out it is usually found that the symmetry of the crystal field is low enough to leave one non degenerate orbital state lowest. This singlet orbital state has of course associated with it $2S+1$ degenerate spin states. This spin degeneracy must exist at this stage of the calculation since so far no interactions have been considered which depend explicitly on spin variables. The remaining terms in (1.1) do however contain spin variables and it is the splitting induced in the ground spin states by these terms which is of interest in magnetic studies.

Applying perturbation theory without choosing any particular representation for the spin states we obtain the first order contribution to the spin Hamiltonian

$$\langle 0 | \lambda \underline{L} \cdot \underline{S} + \beta \underline{H} \cdot (\underline{L} + 2\underline{S}) | 0 \rangle$$

where $|0\rangle$ is the ground orbital state and $|1\rangle$, $|2\rangle$, etc. label excited orbital states. Since $\langle 0 | \underline{L} | 0 \rangle = 0$ for singlet orbital states the first order contribution becomes simply

$$2\beta \underline{H} \cdot \underline{S}$$

This result is most important, showing that to first order the orbital angular momentum does not contribute to the magnetic properties. This is referred to as the quenching of the orbital angular momentum. In second order however the spin orbit interaction does make a contribution to the spin Hamiltonian of magnitude

$$- \sum_{n \neq o} \frac{\langle o| \lambda \underline{L} \cdot \underline{S} + \beta \underline{H} \cdot (\underline{L} + 2\underline{S}) |n\rangle \langle n| \lambda \underline{L} \cdot \underline{S} + \beta \underline{H} \cdot (\underline{L} + 2\underline{S}) |o\rangle}{(E_n - E_o)}$$

where the summation is over all excited orbital states. Terms not involving orbital variables vanish by orthogonality leaving

$$\sum_{ij} \Lambda_{ij} \left[\beta^2 H_i H_j + 2\beta\lambda H_i S_j + \lambda^2 S_i S_j \right]$$

i, j refer to the cartesian coordinates x, y, z and

$$\Lambda_{ij} = - \sum_n \frac{\langle o| L_i | n \rangle \langle n | L_j |o\rangle}{E_n - E_o}$$

Adding together first and second order terms the spin Hamiltonian is obtained

$$\mathcal{H}_s = \sum_{ij} \left[\beta H_i (2 S_{ij} + 2\lambda \Lambda_{ij}) + \lambda^2 S_i \Lambda_{ij} S_j \right]$$

in which the term quadratic in the magnetic field has been omitted, being merely a constant independent of any spin variables. This term does however lead to a temperature independent paramagnetic susceptibility. The spin Hamiltonian may be written most compactly as

$$\mathcal{H}_s = \beta \underline{H} \cdot \underline{g} \cdot \underline{S} + \underline{S} \cdot \underline{D} \cdot \underline{S} \qquad (1.4)$$

where g and D are second rank real symmetric tensors. To obtain the eigenvalues and eigenfunctions of (1.4) the matrix of $\mathcal{H}_s$ must be evaluated in some chosen representation and then diagonalised in the usual way. When the nucleus of the paramagnetic ion has itself a magnetic moment then hyperfine interactions must be allowed for in (1.1). It can easily be shown that this leads to a tensor coupling in (1.4) between the total spin S and the nuclear spin I. Thus with hyperfine interactions the spin Hamiltonian reads

$$\mathcal{H}_s = \beta \underline{H} \cdot g \cdot \underline{S} + \underline{S} \cdot D \cdot \underline{S} + \underline{I} \cdot A \cdot \underline{S} \qquad (1.5)$$

The spin Hamiltonian is the solid state analogue of the Hamiltonian define by (1.2) for a free ion, g' is now a tensor describing the way the spin energy levels are split by a magnetic field. The D tensor determines the structure of the spin levels in zero applied magnetic field. By the methods of paramagnetic resonance it is possible to stimulate transitions between the various energy levels of the spin system defined by (1.5), and so determine directly the value of the various parameters.

CHAPTER 2

APPARATUS and TECHNIQUES

The energy level structure of the spin systems described in the previous chapter can be investigated by electron paramagnetic resonance (E.P.R.) techniques. By applying R.F. magnetic fields to a paramagnetic material resonant transitions can be stimulated between the various energy levels. These transitions can be detected by observing the power absorbed from the R.F. field. Such techniques also provide a direct method for the investigation of relaxation processes.

The behaviour of a spin system under the influence of an R.F. magnetic field can be described phenomenalogically by a complex susceptibility χ with real and imaginary parts χ' and χ'' respectively. χ'' is related to the power absorbed by the spin system in the following way

$$P = \tfrac{1}{2} \omega H_1^2 \chi'' \tag{2.1}$$

where ω is the angular frequency of the magnetic field of amplitude H_1. χ' determines the refractive index of the material at these R.F. frequencies.

Equation (2.1) can be interpreted in terms of the microscopic properties of the spin system by means of first order perturbation theory. For a simple two level system for instance with energy level splitting $E = h\nu_0$ it can easily be shown that the probability per unit time of a transition being induced between the two levels is

$$W = \frac{1}{\hbar^2} g(0) \, g^2 \beta^2 H_1^2 \tag{2.2}$$

and the corresponding power absorption is

$$P = \frac{1}{\hbar^2} g(\upsilon) \, g^2 \beta^2 H_1^2 \, h\upsilon \,(n_1 - n_2)$$ (2.3)

where υ is the frequency of the R.F. magnetic field of amplitude H_1 and n_1 and n_2 are the populations of the lower and upper levels respectively. $g(\upsilon)$ is a normalised function of frequency describing the resonance line shape. It approximates to a δ function, being large in the region were $\upsilon = \upsilon_o$ and vanishingly small elsewhere. For applied static fields H_o of several thousand gauss this resonance condition

$$h\upsilon = h\upsilon_o = g\beta H_o$$ (2.4)

is satisfied for frequencies lying in the microwave region.

The amount of microwave power necessary to produce observable absorption signals would be quite large if beam transmission methods were used. It is usual in this case to place the sample in a resonant microwave cavity. The increased energy density existing within such a cavity increases H_1 to such an extent that a small klystron microwave source is sufficient for detection purposes. The arrangement however has the disadvantage that the spectrometer must be operated at constant frequency and the E.P.R. transitions found by variation of the magnetic field.

Microwave Spectrometer.

A schematic diagram of the X band $(\sim 9.3 \; KMc/s)$ spectrometer used in this work is shown in figure 1. Apart from the pulsing arrangements it is a conventional superheterodyne spectrometer employing
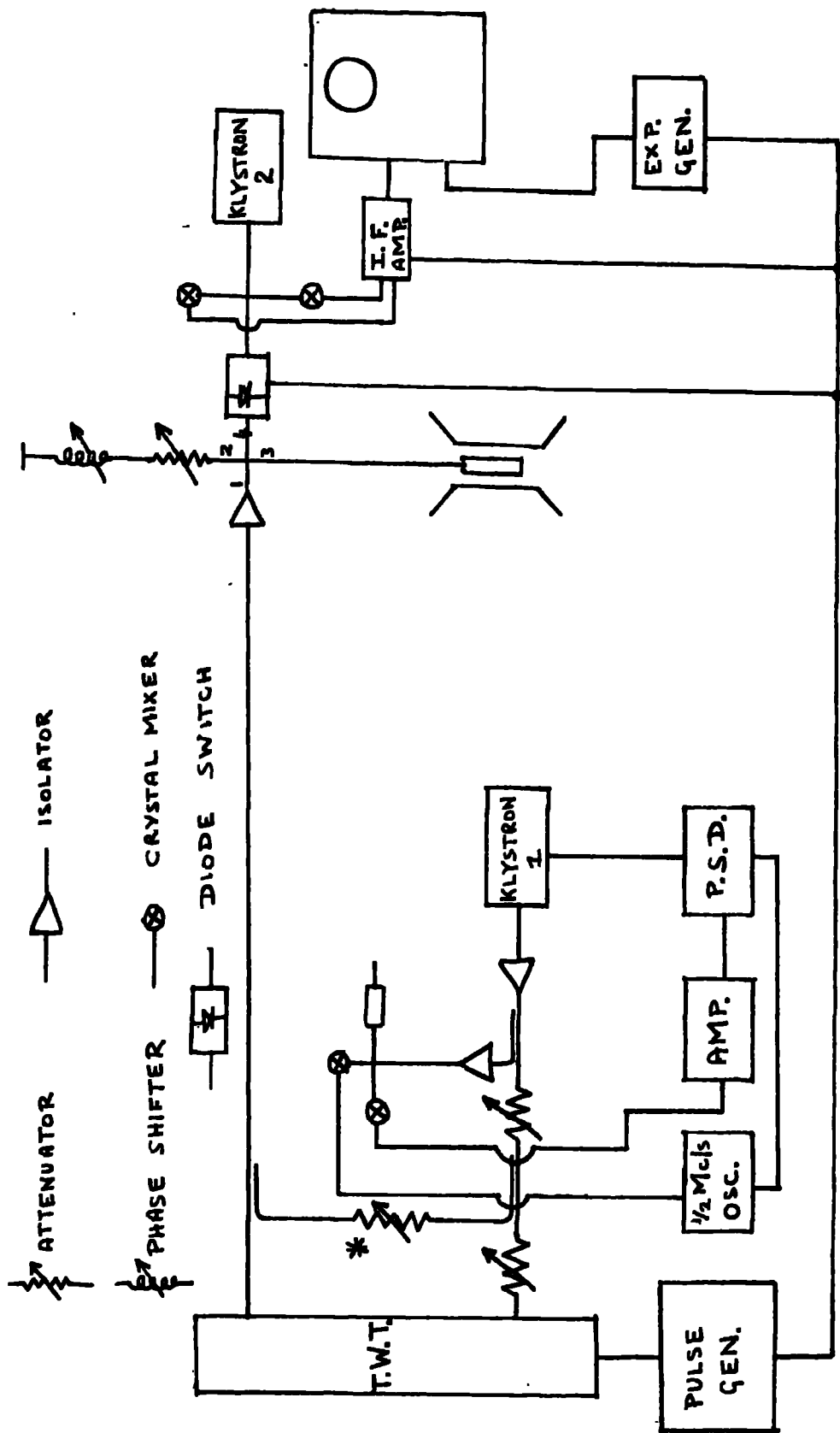
FIGURE 1

MICROWAVE SPECTROMETER

a reflection cavity. The sample cavity consists of a shorted length of X band waveguide (one wavelength long) with iris and screw coupling to the waveguide.

Microwave power from klystron 1 enters the magic-tee bridge through arm 1 and divides equally into arms 2 and 3. Normally the cavity coupling screw is set so that it is a near perfect match to the waveguide; almost all the microwave power incident on the cavity is then absorbed within the cavity. Some microwave power is however reflected back to the magic-tee bridge where it interferes with that reflected from the balance arm 2. By adjustment of the amplitude and phase of the radiation reflected from arm 2 all the reflected power can be arrangedto enter arm 1 where it is absorbed in the isolator. No power enters the detecting arm 4 and under these conditions the bridge is said to be balanced.

Resonant power absorption by the paramagnetic sample changes the reflected signal from the cavity and, by unbalancing the bridge, causes microwave radiation to enter the detecting arm 4 where it mixes with the local oscillator radiation. The resulting I.F. frequency signal, after amplification and rectification, is displayed on an oscilloscope. It can be shown (Faulkner 1964) that the I.F. absorption signal is proportional to χ'' and hence to the population difference between the two levels involved in the observed transition. This proportionality is only true from small signals; sample sizes must be limited so that the paramagnetic power absorption is no more than ten percent of the total power dissipated in the cavity.

Since the magic-tee bridge is a phase sensitive device the microwave power entering the detecting arm 4 will vary with the phase as well as the amplitude of the signal reflected from the cavity. Such phase shifts will occur due to the detuning of the cavity caused by variation of χ' through the E.P.R. line. Signals of this nature are referred to as dispersion signals; they can largely be rejected by unbalancing the bridge in amplitude only. In this work the magic-tee bridge was adjusted in this way so that only absorption signals were detected. Another feature of the bridge and cavity assembly is their sensitivity to the frequency drift and frequency modulation noise of klystron 1. These effects were minimised by locking the frequency of klystron 1 to the resonant frequency of a stable cavity by the Pound frequency stabilisation system shown in figure 1.

Measurement of Relaxation Times.

To measure the relaxation time of paramagnetic transitions it is necessary to produce some disturbance of the populations of the spin energy levels. This was done by applying a large pulse of resonant microwave radiation. If the power level is sufficiently high population is transferred to the higher spin level from the lower level at a rate which overides the relaxation processes. A dynamic equilibrium state will be attained when the populations of the two levels are equalised. This is referred to as the saturation of the transition and corresponds to an effectively infinite spin temperature. The low power "monitoring" signal applied to the cavity, allows the return of the population difference to its equilibrium value

to be observed directly on an oscilloscope. Care must be taken to ensure that the monitoring signal is not in itself sufficient to produce any appreciable saturation, otherwise faster than normal relaxation decay rates will be obtained. Using cavities with Q factors of several thousand (as was the case here) this condition is usually easily satisfied with monitor power levels of several microwatts provided that the relaxation time is not too long. Any great reduction in monitor signal below this level leads to a very poor signal to noise ratio, making it very difficult to measure long relaxation times, such as those encountered in the titanium compounds. Measurements were made in this particular case by use of the novel method of pulsed monitor signal.

Pulsed Monitor Method.

The monitor level setting attenuator, shown marked with an asterisk in figure 1, was replaced by a microwave diode switch (Philco 901A) which gave 30 db attenuation in the off condition. By pulsing this diode switch on at a low repetition rate with a small mark space ratio, up to 30 db reduction in the mean monitor level was obtained without any loss in sensitivity. Using this technique effective monitor power levels of the order of millimicrowatts were obtained, sufficient to permit measurements of relaxation times up to at least 30 seconds.

Auxiliary Pulse Equipment.

The schematic diagram shows the other pulsing arrangements used. Saturating microwave pulses are obtained from a travelling wave tube amplifier (G.E.C. TWX-8) fed from klystron 1. The amplifier is used in pulsed operation giving 30 db gain in the on condition (maximum power output 1 Watt) and 60 db attenuation in the off condition.

This arrangement ensures that the frequency of the pulsed source is the same as that of the monitoring signal and is correspondingly simpler in operation than the more conventional one using a separate pulsed klystron.

To protect the sensitive receiver from serious overload a blanking off pulse was applied to the I.F. amplifier during the power pulse. This blanking pulse was obtained from the same pulse generator that triggered the travelling wave tube, and by a complicated arrangement of monostable and bistable multivibrator circuits it was made to overlap the saturing pulse at each end in time. Thus the I.F. amplifier was switched off before the beginning of the saturating pulse and remained off for a few microseconds after the end of the saturating pulse. This guarded against I.F. amplifier overload at the fast rising edges of the saturating pulse. The pulse circuitry was designed so that the blanking pulse could also switch off a microwave diode switch placed immediately before the microwave mixer crystals, to afford these crystals some protection against possible burn out during the saturating pulse. It was found however that this was not necessary, so this facility was rarely used.

Analysis of Relaxation Traces.

The simplest way of determing the time constant of the observed relaxation traces is by comparing them directly with an electronically generated exponential waveform on a double beam oscilloscope display. Since the observed traces were not in general uniexponential a double exponential generator was built using pulse charged stable RC networks. This instrument gave as an output waveform a sum of two exponential functions each independently variable in amplitude and time constant.

Using this technique the time constants of a double exponential
waveform can be determined to within $\pm$ 10% accuracy. A single
exponential can be analysised more accurately to about $\pm$ 5%.
The internal RC couplings in this instrument restricted its use
to measurement of relaxation times less than 100 milliseconds.
Longer relaxation times were encountered in the titanium compounds
and these were analysised in the more conventional way from polaroid
photographs of the traces displayed on a Techtronix oscilloscope.

Auxiliary Facilities.

The sample cavity and waveguide lead were contained in a glass
double Dewar assembly for measurements at helium temperatures. A
helium pumping line was included in this apparatus to allow measurements
in the range 1.6 K to 4.2 K. Temperatures within this range were
determined from measurements of the helium vapour pressure. To
prevent entry of liquid helium into the cavity a brass sheathing can
was used, forming a screwed joint with the waveguide lead. It was
found that a coating of vacuum grease on the screw threads was
sufficient to prevent even superfluid helium from entering the cavity.

Magnetic fields up to 5 kilogauss were provided by a Newport 4
inch electromagnet with its associated stable power supply. Accurate
magnetic field measurements were made using a Newport N.M.R. magnetometer.

CHAPTER 3.

CRYSTAL GROWTH and ANALYSIS.

Crystallography.

The magnetic materials used in this investigation were the acetylacetonates of transition metal ions. These compounds have the general formula $X(C_5 H_7 O_2)_3$ where X represents a trivalent metal ion. They were chosen as suitable for study for the following reasons.

(1) Most of these materials (e.g. Cr, Ti, Ru, Mo) form an isomorphous series and can be grown as mixed crystals with the corresponding diamagnetic aluminium and cobalt compounds.

(2) Due to their solubility in various organic solvents single crystals can be grown readily at room temperature.

(3) With the exception of the titanium compound they are chemically stable in air.

(4) The strong trigonal fields present in these molecules make possible, for the first time, a detailed study of the very interesting Ti^{3+} ion.

(5) Despite the low crystal symmetry the magnetic ions have a nearly regular octahedron of nearest neighbour oxygen atoms. This allows one to consider the crystal field as predominantly of cubic form and so to compare the results with the relaxation theories of Van Vleck (1940).

The molecular structure of the acetylacetonates is shown in figure 2. It consists of an octahedron of oxygen atoms with the acetylacetonate ligands bridging the oxygen atoms in such a way that the molecule has the point group symmetry D_3 . Such cage like structures enclosing a metal ion are known as "chelates". The crystal structure is monoclinic

FIGURE 2

3 FOLD AXIS

C_5H_7 C_5H_7 C_5H_7

M

$c=16.2A°$

$b=7.5A°$ $a=13.9A°$
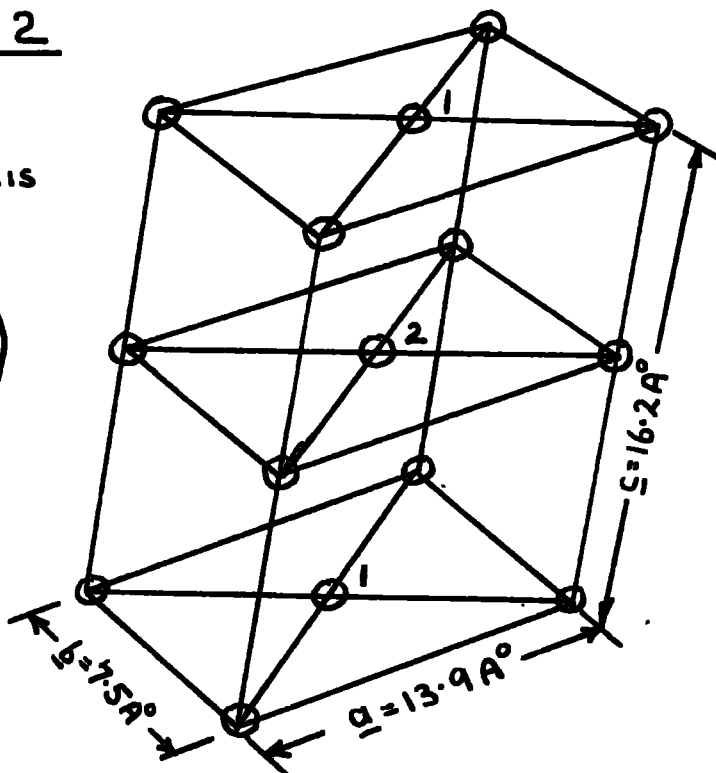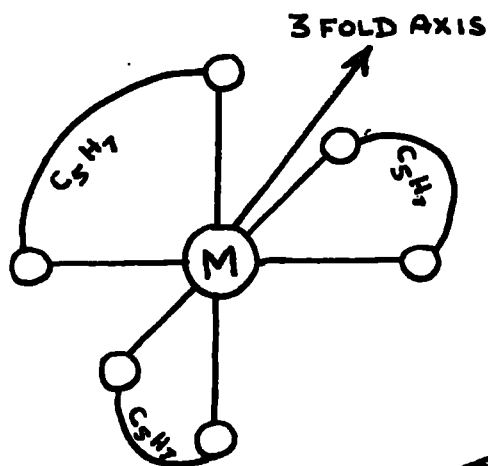
MOLECULAR STRUCTURE   CRYSTAL STRUCTURE

b

31° 31°

α

99°

a

c
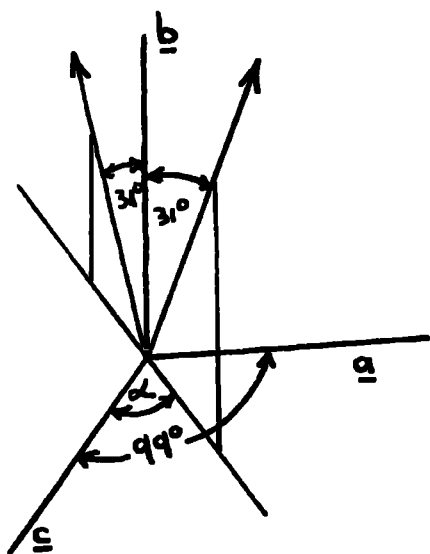
$\alpha = 23°\pm1°$ $Cr:Al(C_5H_7O_2)_3$

$\alpha = 24°\pm2°$ $Cr:Co(C_5H_7O_2)_3$

$\alpha = 24°\pm4°$ $Ti:Al(C_5H_7O_2)_3$

ORIENTATION OF MOLECULAR AXES

(Astbury 1926, Roof 1956) and consists of alternate layers of left
and right handed molecules (optical isomers). The E.S.R. studies
(Singer 1955, Jarrett 1957, McGarvey 1963 and 1964) show that the
optical isomers form two inequivalent magnetic sites related to each
other by a 180° rotation about the **b** axis. The orientation of the
molecular axes to the crystal axes is shown in figure 2.

Crystal Growth.

The acetylacetonates of aluminium, cobalt and chromium were
purchased from Alfa Inorganics Limited, and a small quantity of
ruthenium acetylacetonate was obtained from Johnson Matthey Limited.

The diamagnetic chelates appeared to be quite free of
paramagnetic impurities in that no E.S.R. signals were observed in
undoped crystals. The aluminium chelate, nominally a colourless
material, did however show a brown colouration in solution, presumably
due to some organic impurity. Although this impurity did not appear
to affect the relaxation properties, some efforts were made to remove
it so that paramagnetic concentrations of mixed crystals could be
determined spectrophotometrically. Various separation techniques were
tried. Fractional crystallisation and vacuum sublimation proved partially
successful, but by far the most effective method proved to be chromato-
graphic separation on activated alumina (Brinkman activity No. 1).
A concentrated solution of the aluminium chelate in benzene solution
was passed once through a short separation column. After washing the
column once with benzene a completely colourless solution was obtained,
containing about 90% of the original material. The coloured impurity
was strongly chemisorbed on the surface of the column and did not pass
down through it despite repeated washings in benzene. All the aluminium

acetylacetonate was purified in this way before use in crystal growth.
A similar procedure for the cobalt compound was not attempted since
this chelate is itself strongly green coloured, making spectrophotometric
analysis of mixed crystals impractical.

Of the various solvents tried, acetone was found to be most
convenient for the growth of large single crystals. Using this solvent,
single crystals of the aluminium chelate, doped with chromium or
ruthenium chelates, were grown by evaporation at room temperature. It
was found that the cobalt chelate formed crystals much less readily and
required slow evaporation rates extending over a week or more to form
large single crystals.

Unlike the other chelates the titanium compound is not stable in
air. In fine powder form or in solution it oxydises readily when exposed
to air, to form the diamagnetic oxyacetylacetonate. This chemical
instability is not a peculiarity of the acetylacetonate compounds,
but reflects the general tendency of the Ti^{3+} ion to oxydise to the Ti^{4+}
state. This partially accounts for the scarcity of experimental data
for this ion. The titanium chelate is not commercially available and
so was sythesised from the trichloride by the methods described by
Barnum (1961). After synthesis under nitrogen atmosphere this compound
was purified by vacuum sublimation at $150^{\circ}C$ followed by recrystallisation
from benzene solution. The single crystals obtained in this way were
much more stable than the powder and could be handled in air for short
periods of time without undue oxydation.

The growth procedures for titanium doped crystals were of necessity
somewhat different from those described above. Unsuccessful attempts

were made to grow crystals by evaporation in a dessicator, purged
continuously with a flow of nitrogen gas. The air leaks into such
a system were so great, that complete oxydation occurred before
crystallisation. All glass vacuum sealed systems were then used.
The form of this apparatus finally arrived at is shown in figure 3.
It consists of a long two necked flask with "quickfit" seals and taps,
joined concentrically to another flask with a single neck. The standard
growth procedure adopted was as follows.

(1) A weighed amount of purified aluminium chelate (5 grammes) was
introduced into the lower flask, together with a sufficient quantity
of acetone (100 mls.).

(2) The flask was purged continuously with nitrogen gas as the acetone
was brought to the boil. After cooling to room temperature (with
continuing nitrogen flow) this boiling and purging operation was repeated
once more.

(3) When all the oxygen had been removed from the acetone and flask
the required amount of titanium chelate was introduced to the solution
through a filter funnel, against a counter flow of nitrogen gas.

(4) The flask was held at 50° C in a water bath for an hour to allow
the chelate to fully dissolve. The taps were then closed and the bath
temperature lowered to 40° C quickly and then allowed to cool slowly
(15 - 20 hours) to room temperature. With 5 grammes of chelate dissolved
in about 70 mls. of acetone it was found that crystallisation began below
30° C, precipitating about one gramme of crystal on cooling to 20° C.

This technique was very successful. The extremely air sensitive
solution is at no time exposed to the air and the growth proceeds in
sealed nitrogen atmosphere. No problems due to oxydation during growth
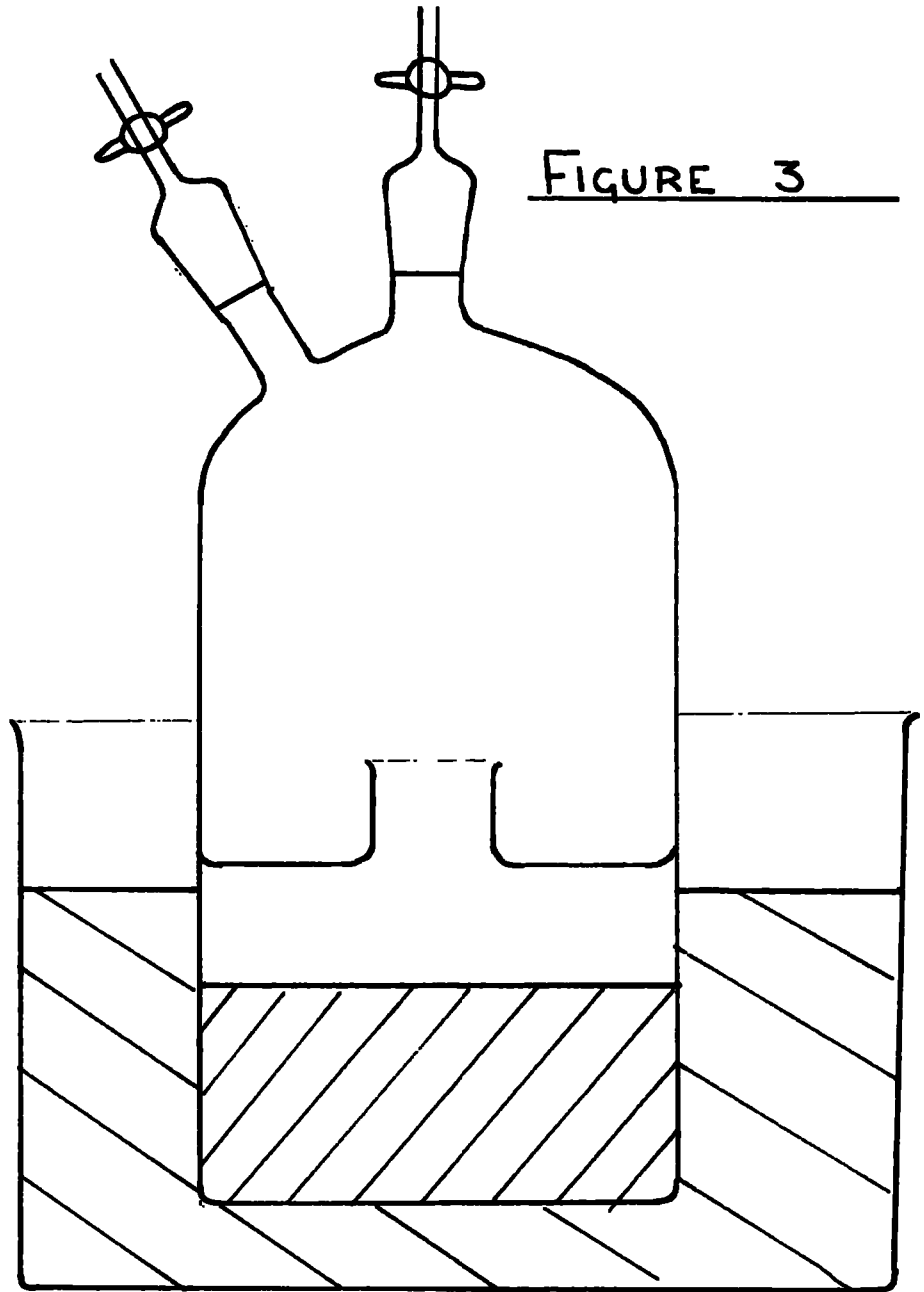
FIGURE 3

were encountered. In fact very dilute solutions could be kept in the flask for days if necessary without any noticeable oxydation occurring. The double flask construction of the growth tube also prevented condensed acetone from washing vacuum grease down from the "quickfit" seals into the growing solution. The mixed single crystals produced were of course quite stable in air over a period of several weeks, the oxydation rate being determined by diffusion of oxygen through the crystal lattice. However, to keep the crystals indefinitely they were stored under paraffin oil in an evacuated dessicator.

Analysis of Crystals.

The paramagnetic chelates are all coloured; chromium and ruthenium chelates are red and the titanium chelate is an intense blue colour. Since the aluminium chelate is colourless the paramagnetic concentration of the mixed crystals can be determined spectrophotometrically.

For the chromium and ruthenium doped crystals a weighed amount of the crystal was made up to 10 mls. of solution in benzene. The absorbance of this solution in the optical region was then determined using a Unicam S.P. 1800 spectrometer, with pure benzene as a reference. Glass cells of 1 cm optical path length were used for these measurements. The relationship between absorbance and concentration was determined using standard solutions made from the pure chelates. These calibration curves are shown in figure 4, where the absorbance of the main visible absorption peak is shown plotted against concentration. It can be seen that, for 1 cm peak lengths, Beer's law is satisfied over the range of concentrations used. It was also found that the presence of large amounts of aluminium acetylacetonate in the solutions made no difference to the absorption

28.

FIGURE 4

Ti(C₅H₇O₂)₃ AT 600 mµ

Ru(C₅H₇O₂)₃ AT 518 mµ

Cr(C₅H₇O₂)₃ AT 356mµ

ANALYSIS CALIBRATION

PATH LENGTH = 1 cm.

CONCENTRATION (MASS PER 100 ml SOL")

1 DIV.≡ 10 MILLIGRAMMES (Cr) ; 4 MILLIGRAMMES (Ru) ; 5 MILLIGRAMMES (Ti)

ABSORBANCE
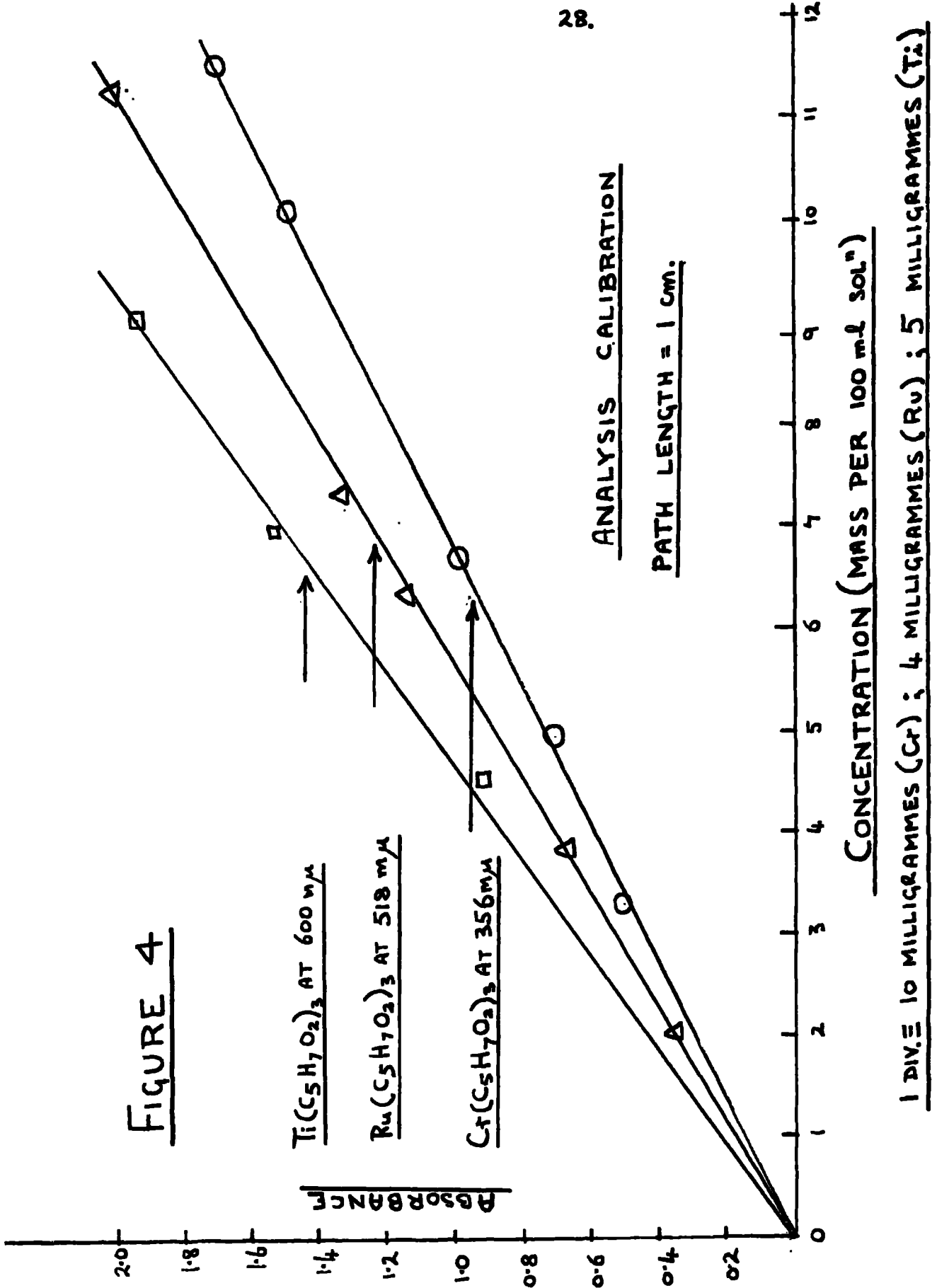
spectra of the paramagnetic chelates. The analysis of the titanium doped chelates was essentially similar. The solutions were however made up and transferred to stoppered glass cells inside a nitrogen glove box.*

* Nitrogen glove box facilities were kindly made available by Dr. Glockling and Mr. Garrick of the Chemistry Department, Durham University.

CHAPTER 4.

RELAXATION THEORIES.

Spin-Spin Relaxation.

The long range dipolar interactions within a spin system give rise to two main effects. Firstly they cause broadening of the Zeeman levels giving a finite width to the E.P.R. transitions. Secondly they cause transitions to occur within the Zeeman levels and within the closely spaced groups of levels that comprise each broadened Zeeman level. By this second process of spin-spin relaxation internal equilibrium within the spin system can be established. The first attempt to calculate a relaxation time for such processes was that of Waller (1936) who considered a simple system of $S = \frac{1}{2}$ ions interacting by dipolar forces.

$$\mathcal{H} = \sum_j g \beta \underline{H} \cdot \underline{S}_j + \sum_{j > k} \frac{g^2 \beta^2}{r_{jk}^3} \left(\underline{S}_j \cdot \underline{S}_k - \frac{3}{r_{jk}^2} (\underline{r}_{jk} \cdot \underline{S}_j)(\underline{r}_{jk} \cdot \underline{S}_k) \right) \quad (4.1)$$

where $\underline{r}_{jk}$ is the vector connectiong ions $j \to k$.

With the assumption of small applied fields ($g\beta H \ll \frac{g^2 \beta^2}{r^3}$) Waller showed that the spin-spin relaxation time, T_{20}, was

$$T_{20} \sim \frac{6 g^2 \beta^2 N^{1/2}}{h r^3}$$

where N is the number of nearest neighbour spins with separation r. For $r \sim 5 \mathring{A}$ this relaxation time is very short being of the order 10^{-9} secs. Since it in no way involves the lattice vibrations this relaxation time is of course independent of temperature. In magnetically dilute crystals the interspin distances are increased but even so the spin-spin relaxation time is short in low applied magnetic fields.

This classic result was later extended by Kronig and Bowkamp (1938)
to include the more usual situation of Zeeman energies greater than the
internal dipolar energies. The relaxation time of the above system is
found to be

$$T_2 = T_{20} \exp\left({}^H/_{H_i} \right)^2 \tag{4.3}$$

H_i is an internal magnetic field and is equal to the average field
experienced by one spin due to all the others. In order of magnitude
it is equal to the width of the Zeeman levels. Such an increase in
relaxation time with applied field is to be expected physically. As
the Zeeman energy level separation increases so the spin system finds
it more difficult to re-arrange its dipolar configuration to provide the
energy involved in a transition between Zeeman levels. Spin-spin
relaxation times of the form (4.3) are indeed found by the Dutch workers
using non resonant field modulation techniques. Under E.P.R. conditions
the magnetic fields and concentrations are such that $H \gg H_i$ and
spin-spin relaxation is entirely insignificant compared with spin-lattice
relaxation.

This conclusion is not necessarily valid however for more complicated
spin systems, such as those consisting of ions with $S > \frac{1}{2}$ or with two
or more species of paramagnetic ions. In these cases the energy
differences between pairs of Zeeman levels may approximately be equal
or harmonically related to each other. Cooperative processes are then
possible involving the similtaneous transitions of two or more ions so
that the total Zeeman energy is almost conserved. Spin-spin relaxation
of this kind is called cross relaxation and can be quite fast even in

dilute spin systems. Like all spin-spin interactions cross relaxation involves the cooperative action of all the spins in the spin system and the calculation of transition probabilities is rather involved. The theoretical development of this subject was initiated by Bloembergen, Shapiro, Pershan and Artman (1959) and has received its most general treatment in the recent papers by Grant (1964). Some detailed measurements of cross relaxation that have been made (Mims & Mc'gee 1960, Pershan 1960) are in reasonable agreement with Grant's theoretical predictions. This agreement between theory and experiment does not extend in general to the field of spin-lattice relaxation.

Spin-Lattice Relaxation.

Waller in his classic paper (1936) also considered spin-lattice relaxation. The mechanism assumed in these calculations involved the modulation of the dipolar forces by the lattice vibrations. Although this work clearly demonstrated the two main relaxation processes (direct and Raman processes), the relaxation times derived were far too long to account for the experimental results subsequently obtained.

It was later realised by Heitler and Teller (1936), Fierz (1938) and Kronig (1939), that the modulation of the crystalline electric field could yield a more potent relaxation mechanism. This process is non-cooperative, each ion relaxing independently to thermal equilibrium with the lattice. These ideas of single ion relaxation were developed into a more exact theory by Van Vleck (1940). The theory was elaborated further by Orbach (1961) for the special case of rare earth ions and by Mattuck and Strandberg (1960), who developed a spin Hamiltonian formulation for transition group ions. To demonstrate in a formal way the essential features of spin-lattice relaxation it is convenient to use a general

formulation of the theory which is applicable in principle to rare earth and transition group ions. In the explicit calculations in later chapters however the spin-Hamiltonian formulation of Mattuck and Strandberg is used, since this is particularly suitable for transition group ions.

Lattice Vibrations.

It is usual in relaxation theory to make great approximations regarding the description of the lattice vibrations. A Debye model is assumed in which all the anisotropic nature of the lattice is lost. A continuum theory of this kind is equivalent to assuming that all the atoms of the crystal have equal mass and therefore equal amplitudes of vibration. Very few attempts have been made to treat the lattice vibrations in any greater detail than this even though Van Vleck considers these approximations to be the weakest link in the theory.

The quantum state of the lattice vibrations, in the Debye model, can be specified by $3N$ quantum numbers $|n_1 - \cdots n_p \cdots n_{3N}\rangle$, where N is the total number of atoms in the crystal; n_p denotes the number of quanta (phonons) associated with the pth vibrational mode. The Hamiltonian of the lattice is

$$\mathcal{H}_L = \sum_p \hbar \omega_p \left(a_p a_p^\dagger + \tfrac{1}{2} \right) \tag{4.4}$$

where ω_p is the frequency of the pth mode and $a_p^\dagger$, a_p are the phonon creation and annihilation operators with the usual non zero off diagonal matrix elements given by

$$a_p^\dagger |n_1 \cdots n_{p} \cdots n_{3N}\rangle = (n_p+1)^{1/2} |n_1 \cdots n_{p+1}, \cdots n_{3N}\rangle$$

$$\tag{4.5}$$

$$a_p |n_1 \cdots n_{p} \cdots n_{3N}\rangle = (n_p)^{1/2} |n_1 \cdots n_{p-1}, \cdots n_{3N}\rangle$$

The thermal average number of phonons in any mode is determined by the Bose-Einstein factor

$$\overline{n}_p = \left(\exp\left(\hbar\omega_p / kT \right) - 1 \right)^{-1} \tag{4.6}$$

The density of modes per unit frequency interval is given by the expression

$$\rho(\omega) = \frac{3 \omega^2 V}{2\pi^2 v^3} \tag{4.7}$$

in which no distinction is made between the velocities of longitudinal and transverse waves. V is the volume of the crystal and v the velocity of sound. In terms of this Debye model the displacement from the equilibrium position of any atom can be written as

$$U_{\ell\alpha} = \left(\frac{2\hbar}{M}\right)^{1/2} \sum_p \frac{1}{\omega_p^{1/2}} \phi_{p\alpha} (a_p^\dagger + a_p) \cos\left(\underline{k}_p \cdot \underline{r}_\ell + \Delta_p \right) \tag{4.8}$$

where $U_{\ell\alpha}$ is the displacement in the α direction ($\alpha = x, y, z$) of the atom at position $\underline{r}_\ell$.

M is the mass of the crystal.

$\phi_{p\alpha}$ is the α component of the unit polarisation vector of the pth mode.

$\underline{k}_p$ is the wave vector of the pth mode ($2\pi/\lambda_p$) and Δ_p is an arbitrary phase factor.

Crystal Electric Field Modulation.

The vibrational waves described above will produce at each paramagnetic ion site a modulation of the local electric field. If only nearest neighbour interactions are considered it is convenient to describe the vibrations of the cluster of nearest neighbours in terms of the normal coordinates of the cluster (Q_f etc.). We shall suppose that, as is usually the case, the nearest neighbours form a sixfold coordinated cubic

cluster. The modulation of the crystal electric potential (dynamic crystal field) can be expressed in terms of these normal coordinates as follows.

$$V = V_0 + \sum_f \frac{\partial V}{\partial Q_f} Q_f + \frac{1}{2} \sum_{f,f'} \frac{\partial^2 V}{\partial Q_f \partial Q_{f'}} Q_f Q_{f'} + \cdots \cdots \tag{4.9}$$

V_0 is the static crystal field considered earlier (Chapter 1). The normal coordinates are a linear combination of the displacements of the atoms of the cluster.

$$Q_f = \sum_{\ell,\alpha} q_{f\ell\alpha} U_{\ell\alpha} \qquad \begin{array}{l} \ell = 1 \cdots 6 \\ \alpha = x, y, z \end{array} \tag{4.10}$$

The interaction between the paramagnetic ion and the lattice vibrations is then

$$\mathcal{H}_{SL} = \sum_{f,p} V^f A^{fp} (a_p^+ + a_p) + \sum_{f,f',p,p'} V^{ff'} A^{fp} A^{f'p'} (a_p^+ + a_p)(a_{p'}^+ + a_{p'}) + \cdots \tag{4.11}$$

where

$$V^f = \frac{\partial V}{\partial Q_f} \qquad ; \qquad V^{ff'} = \frac{1}{2} \frac{\partial^2 V}{\partial Q_f \partial Q_{f'}}$$

and

$$A^{fp} = \left(\frac{2\hbar\omega_p}{Mv^2} p\right)^{1/2} \sin \Delta_p \sum_{\ell,\alpha} \phi_{p\alpha} q_{f\ell\alpha} \underline{K}_p \cdot \underline{R}_\ell = \left(\frac{2\hbar\omega_p}{Mv^2}\right)^{1/2} B^{fp} \tag{4.12}$$

$\underline{K}_p = \frac{\underline{k}_p}{|\underline{k}_p|}$; $\underline{R}_\ell$ is the vector position each nearest neighbour referred to the paramagnetic ion as origin.

In obtaining (4.11) the approximation has been made that the wavelength of the phonons is much larger than the dimensions of the cluster.

The spin-lattice transition probability can now be calculated by forming the matrix elements of (4.11) between simultaneous eigenstates of the paramagnetic system and the lattice. The eigenstates of the lattice are given in (4.5). The eigenstates of the paramagnetic system are the complete

solutions of (1.1) and (1.3) and are not to be confused with the effective spin states of the spin-Hamiltonian. In the following we will denote two typical paramagnetic eigenstates by $|a\rangle$ and $|b\rangle$; these states will of course be rather complicated mixtures of spin and orbital states.

Direct Process.

The largest term in (4.11) is the first, which is linear in the lattice operators. In first order perturbation theory this term gives rise to processes, called direct processes, in which the spin system makes a transition from $|a\rangle$ to $|b\rangle$ with the emission (or absorption) of one phonon. With the energy conservation restraint

$$\left| E_a - E_b \right| = \hbar \omega_p$$

the transition probability for direct processes is

$$U_{ab} = \frac{2\pi}{\hbar^2} \left| \langle a, n_p | H_{SL} | b, n_{p+1} \rangle \right|^2 \varrho(\omega) \tag{4.13}$$

Using (4.5), (4.7) and the high temperature approximation of (4.6) this becomes

$$U_{ab} = \frac{3 \omega_p^2 \, kT}{\pi \hbar^2 \, v^5 \rho} \left| \langle a | \sum_f V_f \, B^{fp} | b \rangle \right|^2 \tag{4.14}$$

where ρ is the density of the crystal.

The observed transition rate is obtained by averaging (4.14) over all directions of propagation and polarisation of the lattice waves (Van Vleck 1940).

It can be seen from (4.14) that the transition probability is directly proportional to the absolute temperature. This linear temperature dependence arises from (4.6) and is independent of any approximations made elsewhere in the theory. To discuss the other significant features of (4.14) it is enlightening to consider separately the two cases of Kramers and non-Kramers ions.

For a non-Kramers ion (i.e. one having an even number of electrons) the matrix element in (4.14) will not in general be vanishingly small. The transition probability will then be proportional to the square of the frequency of the absorbed and emitted phonons (which may be equal to the microwave operating frequency). This is again a general feature of the theory, not critically dependent on any approximations made.

In a Kramers ion (i.e. one having an odd number of electrons) it can be shown (Orbach 1961) that the matrix element in (4.14), between Kramers conjugate states, vanishes in the limit of low applied magnetic field. This zero result is a consequence of the behaviour under time reversal symmetry of Kramers conjugate states and the fact that electric interactions are invariant under this symmetry operation. Cancellations in various terms due to this effect were noted by Van Vleck in his original calculations; they are sometimes referred to as "Van Vleck cancellations". In the formulation of Mattuck and Strandberg (1960) this effect is known as the "quadrupole selection rule".

Thus in a Kramers ion with $S > \frac{1}{2}$, it is expected that the only strongly allowed relaxation transitions will be those connecting states belonging to different Kramers doublets. For an $S = \frac{1}{2}$ ion however there are only two spin states which form a single Kramers doublet; the consequence of time reversal symmetry are now most severe. A non-vanishing matrix element can

only be obtained by explicitly considering the effect of an applied magnetic field in breaking the time reversal symmetry of the system. Matrix elements so obtained are reduced by a factor of the order of $\beta H/\Delta$, where Δ is the energy of the first excited state. Since in this case the microwave frequency is proportional to the applied magnetic field and is equal to the phonon frequency, the net result is a transition probability varying as the fourth power of the microwave frequency. Such a frequency variation has been verified in at least one case (Davids and Wagner 1964).

Raman Process.

Apart from the direct absorption and emission of phonons, a spin transition from $|a\rangle$ to $|b\rangle$ may proceed by the inelastic scattering of phonons. Such a process, by analogy with the optical effect, is called a Raman or two phonon process. It can be visualised as the absorption of one phonon and the simultaneous emission of another, subject to the energy constraint

$$E_a - E_b = \hbar (\omega_j - \omega_i)$$

where ω_i and ω_j are the frequencies of the two phonons involved.

This process arises from the first term of (4.11) in second order theory and from the smaller second term in (4.11) in first order. Higher order processes of this kind can compete with the direct process because of the enormously greater number of phonons which can take part. By the nature of the process all phonons up to the Debye frequency can contribute, rather than just the narrow band of resonant phonons that are effective in the direct process.

It is usually the case that the first term in (4.11) produces the main contribution to the Raman relaxation rate and so for simplicity this term alone will be considered. The Raman transition probability is

$$U_{ab} = \frac{2\pi}{\hbar^2} \int_0^{\omega_D} \left| \sum \frac{\langle a, n_p | H_{sL} | c, n_p{-}1 \rangle \langle c, n_q | H_{sL} | b, n_q{+}1 \rangle}{\hbar \omega_p - \Delta_c} \right|^2 \rho(\omega_p) \rho(\omega_q) d\omega_p$$

(4.15)

$|c\rangle$ is an intermediate excited state of energy Δ_c. ω_D is the Debye frequency of the lattice. Evaluating the matrix elements of lattice operators and simplyfying,

$$U_{ab} = \frac{18}{\pi^3 \rho^2 v^{10}} \int_0^{\omega_D} \omega_p^3 \omega_q^3 \, n_p (n_q{+}1) d\omega_p \left| \sum \frac{\langle a | \sum V^{\epsilon} \beta^{\epsilon p} | c \rangle \langle c | \sum V^{\epsilon} \beta^{\epsilon q} | b \rangle}{\hbar \omega_p - \Delta_c} \right|^2$$

(4.16)

As before the final transition probability must be averaged over all directions of propagation and polarisation of the phonons.

For non-Kramers ions there will not in general be any cancellation of terms in the summation over excited states $|c\rangle$. We can then ignore $\hbar \omega_p$ compared with Δ_c in the denominators of these terms. Also, when $kT \ll \hbar \omega_D$ the main contribution to the integral in (4.16) comes from phonons of energy $\hbar \omega \sim kT$. A good approximation can then be made to the integral (Van Vleck 1940) yielding a final transition probability

$$U_{ab} = \frac{18(6!)}{\pi^3 \rho^2 v^{10}} \left(\frac{kT}{\hbar} \right)^7 \left| \left[\frac{\langle a | \sum V^f \beta^f P | c \rangle \langle c | V^f \beta^f q | b \rangle}{\Delta_c} \right] \right|^2$$

(4.17)

The significant feature of this result is the seventh power dependence on temperature, which arises from the integral in (4.16). Such a rapid temperature dependence is however only to be expected at low temperatures ($kT \ll \hbar \omega_D$). In fact an alternative approximation to the integral, valid at high temperatures ($kT > \hbar \omega_D$) yields a relaxation rate varying as the square of the absolute temperature (Van Vleck 1940). There is no explicit dependence on applied magnetic field, although there may be a small field dependence due to variation of the states $|a\rangle$, $|b\rangle$ etc., with magnetic field.

For a Kramers system the situation is again somewhat different. The excited states $|c\rangle$ will of necessity occur as Kramers conjugate pairs. It can be shown (Orbach 1961) that the two states in each excited doublet will cause destructive interference in (4.16), if the initial and final states are Kramers conjugates. This cancellation is not complete however if allowance is made for the small differences in the energy denominators involved in the summation in (4.16). The net effect is a

reduced relaxation rate of the form

$$U_{ab} = \frac{9! \, 2\hbar^2}{\pi^3 \rho^2 v^{10}} \left(\frac{kT}{\hbar}\right)^9 \left| \sum_c \frac{\langle a | \sum V^t B^{tp} | c \rangle \langle c | \sum V^t B^{tq} | b \rangle}{\Delta_c^2} \right|^2 \quad (4.18)$$

The summation is now understood to be over each excited Kramers doublet.

Thus for an $S = \frac{1}{2}$ ion the Raman relaxation rate is expected to vary as the ninth power of the absolute temperature. Once again multilevel spin systems should have faster relaxation rates ($\propto T^7$) connecting states which belong to different Kramers doublets.

For multilevel spin systems ($S > \frac{1}{2}$) it is possible in principle to observe another type of Raman process in which the intermediate state belongs to the ground spin states rather than the excited orbital states as assumed here. In this case the energy denominators in (4.15) have $\hbar\omega_p \gg \Delta_c$. It can be shown (Orbach and Blume 1962) that this fact leads to a Raman relaxation rate proportional to the fifth power of the absolute temperature.

Orbach Process.

It may happen that the intermediate state $|c\rangle$ is sufficiently near the ground states for the condition $\Delta_c < \hbar\omega_D$ to apply. When this occurs the energy denominators in (4.15) vanish at $\hbar\omega_p = \Delta_c$. Orbach (1961) has shown that a divergence of the integral can be avoided by inserting the finite lifetime of the intermediate state into the energy denominators. This leads to a new two phonon relaxation process, sometimes called the "Orbach process", which has a characteristic exponential temperature dependence. This result may be deduced in a more simple manner when it is realised that the vanishing of the energy denominators implies conservation

of energy in the intermediate state. The transition to the inter-
mediate state. The transition to the intermediate state is then a
real rather than a virtual one and should be equivalent to two
successive direct transitions. Consider then a simple two level
spin system with a single excited state $|c\rangle$ such that $kT < \Delta_c < \hbar\omega_z$.
The rate equations for the populations of states $|a\rangle$, $|b\rangle$ due to
direct transitions to state $|c\rangle$ are

$$\frac{dn_a}{dt} = -n_a U_{ac} + n_c U_{ca}$$

$$\frac{dn_b}{dt} = -n_b U_{bc} + n_c U_{cb} \qquad (4.19)$$

The general solution of (4.19) is a sum of two exponential functions
but, under the assumptions made one will have a short time constant
and small amplitude. The long observable time constant can easily be
seen to have a relaxation time

$$\tau_{ab} = \frac{2(U_{ca} + U_{cb})}{U_{ac} U_{cb} + U_{ca} U_{bc}} \qquad (4.20)$$

which is equivalent to an effective transition probability between
$|a\rangle$, $|b\rangle$ of the form

$$U_{ab} = \frac{U_{ac} U_{cb} + U_{ca} U_{bc}}{U_{ca} + U_{cb}} \qquad (4.21)$$

Expressed explicitly, using (4.13)

$$U_{ab} = \frac{3}{2\pi \rho v^5 \hbar} \left(\frac{\Delta_c}{\hbar}\right)^3 e^{-\Delta_c/kT} \frac{\left|\langle a|\sum v^f B^f P|c\rangle\langle c|\sum v^f B^f P|b\rangle\right|^2}{\left|\langle a|\sum v^f B^f P|c\rangle\right|^2 + \left|\langle c|\sum v^f B^f P|b\rangle\right|^2} \quad (4.22)$$

which is the same expression as that deduced by Orbach in a rather
different manner. The significant difference between direct and Orbach
processes is seen to be that $\Delta_c > kT$ in the Orbach process and so the
exponential cannot be expanded to yield a linear temperature dependence
as in (4.14).

Phonon Bottlenecks.

Throughout this chapter it has been assumed that the lattice
vibrations serve as a thermostat for the relaxation of the paramagnetic
ions. This assumption allows the occupation number of the various phonon
modes n_p, n_q etc., to be replaced by their thermal average values. At
low temperatures this assumption not entirely well founded, since the
specific heat of the lattice becomes small. If the energy flow from the
spin system to the lattice is too great, the lattice temperature must rise
above the ambient temperature. This is most likely to occur in the direct
and Orbach relaxation processes, which involve resonant phonon modes only.
Energy communicated to these resonant modes can only be dissipated by
direct escape through the crystal surface or by inelastic phonon-phonon
scattering into other modes. Under certain circumstances (i.e. fast spin-
lattice relaxation in concentrated materials) the observed relaxation
behaviour can be dominated by these phonon relaxation times. One speaks

then of a "phonon bottleneck" in the relaxation process caused by selectively heated phonon modes ("hot phonons"). Effects due to phonon heating have only been observed here in the concentrated Ti samples and a discussion of these results and hot phonon theories will be given in the relevant later chapter.

Rate Equations.

The experimental relaxation times are related to the calculated transition probabilities by means of rate equations. The problem for a general multilevel system can be stated as follows

$$\frac{dn_i}{dt} = -n_i \sum_{j \neq i} U_{ij} + \sum_{j \neq i} n_j U_{ji} \tag{4.23}$$

where n_i is the population of spin state $|i\rangle$. If the lattice is in equilibrium at temperature T then the conjugate relaxation transition probabilities are related by

$$U_{ij} = U_{ji} e^{\hbar \omega_{ij}/kT} ; \quad \hbar \omega_{ij} = E_i - E_j \tag{4.24}$$

The general solution of (4.23) cosists of a sum of exponential functions

$$n_i = n_{i_0} + \sum_k A_{ki} e^{-\lambda_k t} \tag{4.25}$$

For a spin system with spin quantum number S there will be 2S values of k in (4.25). Only those terms with a large amplitude, $A_{k\lambda}$ will be observed. The relaxation times ($1/\lambda_k$) are constants of the paramagnetic material, but the amplitudes of the various terms will depend to some extent on the initial conditions imposed on (4.25) by the nature of the measurement (i.e. length and intensity of the saturating pulses).

Explicit solutions for the relaxation times are not in general possible. Numerical methods must be used to solve (4.23) for multilevel systems. For a two level system however there is only one exponential in (4.25) and its time constant is simply related to the transition probabilites by

$$ \tau = \left(U_{ab} + U_{ba} \right)^{-1} $$

(4.26)

Cross relaxation between various pairs of levels can complicate (4.23) even further. To show how these processes can be incorporated into the rate equations consider a material with two spin species A and B each consisting of $S = 1/2$ ions. This simple situation is relevant to some of the results described in later Chapters. Let N_A and N_B denote the number of ions of type A and B respectively.

A _____ 2   B _____ 4

_____ 1   _____ 3

$$ \frac{dn_1}{dt} = -n_1 U_{12} + (N_A - n_1) U_{21} - \frac{X}{N_B} (n_1 n_4 - n_2 n_3) $$

$$ \frac{dn_3}{dt} = -n_3 U_{34} + (N_B - n_3) U_{43} + \frac{X}{N_B} (n_1 n_4 - n_2 n_3) $$

(4.27)

Here X represents the cross relaxation transition probability for a simultaneous transition of an ion A from $1 \rightarrow 2$ and an ion B from $4 \rightarrow 3$. The two relaxation rates are given by

$$
2\lambda = \left[U_{12} + U_{21} + U_{34} + U_{43} + X\left(1 + \frac{N_A}{N_B}\right) \right]
$$
$$
\pm \left[\left(U_{12} + U_{21} + U_{34} + U_{43} + X\left(1 + \frac{N_A}{N_B}\right) \right)^2 \right.
$$
$$
\left. - 4(U_{12} + U_{21})\left(U_{34} + U_{43} + X\frac{N_A}{N_B}\right) - 4X(U_{34} + U_{43}) \right]^{1/2}
$$

$$(4.28)$$

The longest time constant will have a large amplitude and would under normal conditions be the only one observed. Under the conditions that species B is less abundant than species A but much faster relaxing we can approximate this expression to

$$
2\lambda = \left(U_{34} + U_{43} + X\frac{N_A}{N_B} \right)\left(1 \pm \left(1 - \frac{2X(U_{34} + U_{43})}{\left(U_{34} + U_{43} + X\frac{N_A}{N_B} \right)^2} \right) \right)
$$

and the longer relaxation time is

$$
\tau = \frac{1}{X} \quad ; \quad \left(U_{34} + U_{43} \gg X\frac{N_A}{N_B} \right)
$$

$$
\tau = \frac{N_B}{N_A(U_{34} + U_{43})} = \frac{N_B \tau_B}{N_A} \quad ; \quad \left(X\frac{N_A}{N_B} \gg U_{34} + U_{43} \right)
$$

$$(4.29)$$

From these results it can be seen that the presence of a small amount
of a second paramagnetic species can drastically affect the relaxation
of a more abundant but slower relaxing species.

Cooperative Relaxation Processes.

The single ion theories do not predict any concentration dependence
of the relaxation times. Their range of validity extends up to one or
two molar percent paramagnetic concentration. For the remaining 90% - 98%
of the paramagnetic range there are as yet no detailed theories to account
for the observed concentration dependent relaxation times. Two suggestions
have been made which may explain these effects.

(1) Van Vleck (1960) suggested the possibility of cross relaxation to fast
relaxing impurities or exchange coupled clusters of ions. The exchange
interaction between neighbouring ions is thought to be very sensitive to
the interspin distances and so modulated strongly by the lattice vibrations.
Energy can then be communicated from the single ions to those clusters by
cross relaxation processes of the type discussed above. This mechanism
clearly provides a relaxation route in parallel to that of the single ions
themselves. It will also be a concentration dependent process since, on
purely statistical grounds the number of such clusters will be strongly
dependent on the paramagnetic concentration.

(2) An alternative suggestion (Kochelaev 1960) is concerned with the effect
of the paramagnetic ion on the lattice vibrations. If the paramagnetic ion
site has a mass and force constant much different from the rest of the
lattice then it should be considered as a point defect. Such a point defect
can have purely localised vibrational modes that may be quite different from
the travelling waves characteristic of the lattice as a whole. It is further

supposed that at a sufficiently high concentration the localised modes at different sites may interact, causing concentration dependent relaxation. If this mechanism is effective it should manifest itself in deviations of the purely single ion relaxation from the predictions of the theories discussed above. Indeed, in materials with a rather gross defect structure, effects of this kind have been observed (Klemens 1965, Murphy 1966).

These mechanisms will be discussed in more detail in following Chapters concerned with the experimental results. It may be helpful however to summarise all the known and postulated relaxation processes. This has been done in Figure 5, which shows the way energy can flow from the spin system to the lattice.
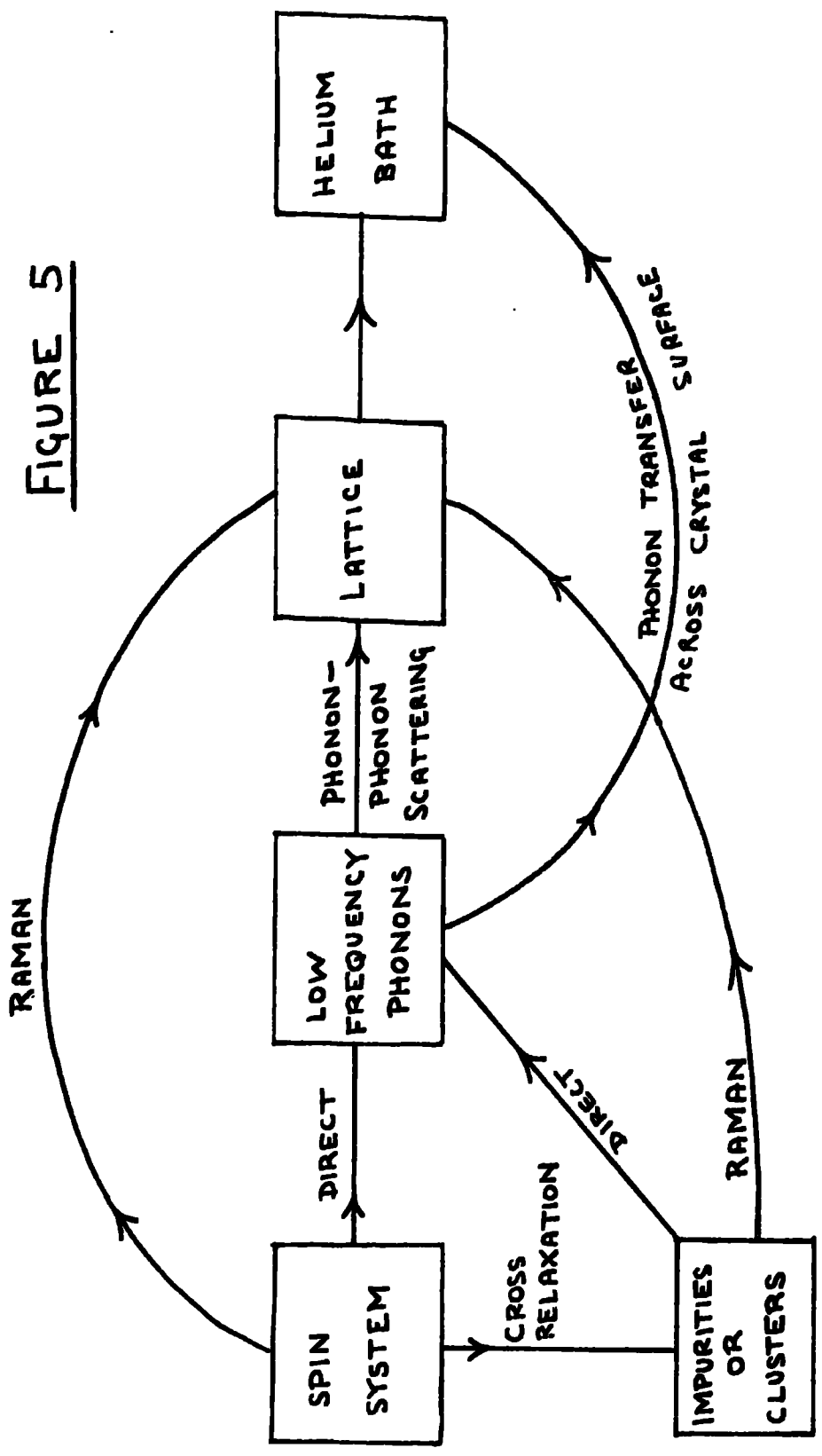
Figure 5

ENERGY FLOW FROM SPIN SYSTEM TO BATH

CHAPTER 5.

TITANIUM ACETYLACETONATE.

Of all the paramagnetic ions in the first transition group, that of Ti^{3+} is the most interesting from the point of view of relaxation theory. It has only one $3d$ electron and therefore the simplest possible spin system, namely a two level system with $S = 1/2$. Furthermore the abundant isotope has no nuclear spin and so there are no complications due to hyperfine interactions. A simple spin system such as this is particularly desirable when attempting to study complicated phenomena such as concentration dependent relaxation. Despite these obvious advantages this ion has received little attention. The reason for this is to be found partly in the chemical instability of this ion and partly in the nature of the crystals used in previous studies.

As was pointed out in Chapter 3, the trivalent titanium ion tends to oxydise readily to the diamagnetic fourvalent state. The greatest difficulty encountered by the author in preparing these samples was not that of oxydation however, but lack of chemical expertise in preparing the original starting material. The chemical synthesis described in Chapter 3 uses the trichloride as a starting material in the preparation of the acetylacetonate. This compound is very reactive, hydrolising readily in moist air to form an acidic solution. In the material available to the author this acidity was sufficient to prevent chemical reaction and resulted initially in very low yields of the chelate. After some experimentation it was found that the ph of the reaction solution could be adjusted to its correct value by the addition of excess ammonia. A better method however, which was developed later, involved purging the trichloride powder with nitrogen gas at an

elevated temperature, to thoroughly expel all the adsorbed hydrochloric acid. The sythesis then proceeded readily and gave abundant yields. Once a consistent oxygen excluding growth procedure had been developed no further difficulties were encountered in growing mixed single crystals; once grown these mixed crystals were quite stable in air over long periods of time, and could be stored indefinitely under paraffin oil.

Previously the Ti^{3+} ion has been studied in the form of Cesium Titanium Alum and in doped samples of Al_2O_3 . In both cases measurements were very difficult because of the nature of the crystal field splittings in these materials. A purely cubic crystal field splits the ^2D term of the titanium ion but does not completely remove the degeneracy
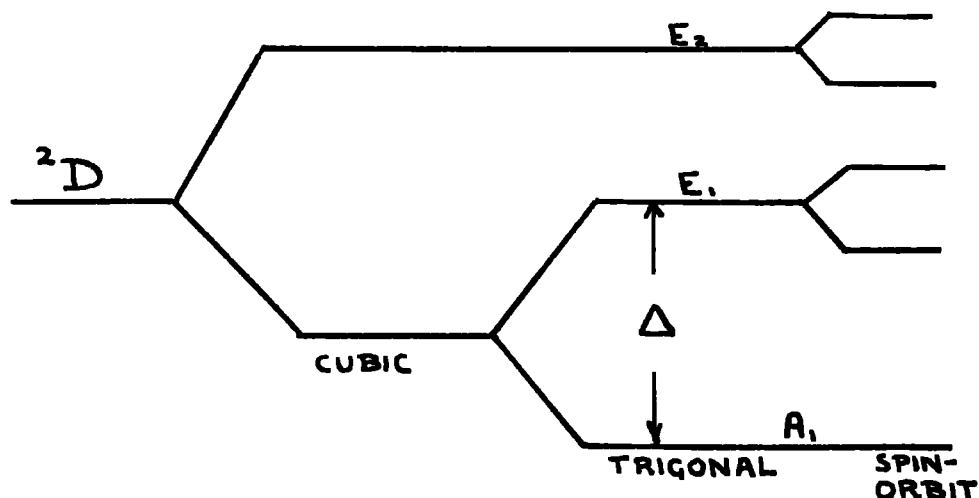
A combination of spin-orbit interaction and lower symmetry crystal field terms can remove the degeneracy from the ground state. Thus the energy level structure of the ground states is critically dependent on the nature of the low symmetry crystal field terms, such as those of trigonal form. In the alum and in Al_2O_3 the trigonal field splittings of the ground triplet are not very large. From the E.P.R. measurements of

Bijl (1950) on powders and Bleaney et al (1956) on single crystals, the trigonal splittings in the alum are seen to be of the order of 100 cm^{-1}. Similar measurements by Kornienko and Prokhorov (1960) on Al_2O_3 samples suggest that the energy interval between the ground and first excited states is 30 cm^{-1}.

The single ion relaxation rate depends critically on the position of these excited orbital states. In general low lying levels give rise to rapid relaxation in the ground state. In the alum the relaxation is so rapid that the E.P.R. absorption line cannot be observed at temperature much above $8^{\circ}K$. From the linewidth at this temperature Bijl (1950) estimates that the spin-lattice relaxation time is of the order of 10^{-11} secs. Even at $1^{\circ}K$ the relaxation time is 10^{-5} secs. (Benzie and Cooke 1951). Relaxation times as short as this are very difficult to measure and in concentrated crystals could well be affected by phonon heating effects. Such low lying orbital states may also allow Orbach relaxation processes to occur. Relaxation behaviour of this kind was observed in Al_2O_3 by Kask et al (1964). Once again the relaxation time at $4.2^{\circ}K$ and above was so short that it could only be estimated from linewidth measurements. Pulse saturation measurements could only be made at temperatures below $3.5^{\circ}K$ and the relaxation time only became long in the lower part of the helium range. Measurements in Al_2O_3 are further complicated by the fact that the trigonal splitting in these crystals is of opposite sign to that in the alums and acetylacetonates (i.e. the states E_1 and A_1 in the above Figure are interchanged). This inversion of the orbital states makes the E.P.R. spectrum very anisotropic with a $g_\perp \sim 0$. A near vanishing $g_\perp$ value leads to a very small E.P.R. transition probability. In the crystals investigated by Kask et al (1964)

the anisotropy in the E.P.R. spectrum also caused large inhomogeneous broadening of the resonance lines.

Van Vleck's calculations for Cesuim Titanium Alum (Van Vleck 1940) suggested that the relaxation time should be very long at low temperatures, in startling contrast to the experimental results obtained by the Dutch workers of the time (De Haas and Du Pre 1938), Gorter, Tuenissen and Dijkstra 1938) and by others since (Bijl 1950, Benzie and Cook 1956). Van Vleck's calculations assumed that the trigonal field splitting Δ was $10^3 \, cm^{-1}$. Now this parameter is involved to the fourth power in the direct process and the sixth power in the Raman process. The miserable agreement between theory and experiment found by Van Vleck can be ~~corrected~~ improved if the more accurate value of $10^2 \, cm^{-1}$ obtained from E.P.R. data is used.

The interesting feature of the acetylacetonate crystals is that they appear to have trigonal splittings of the order assumed by Van Vleck for the alums. The E.P.R. data (McGarvey 1963) shows that the g value has axial symmetry with principal values.

$$g_{\shortparallel} = 2.00 \quad ; \quad g_{\perp} = 1.92$$

The fact that the g tensor is nearly isotropic suggests that there are no excited orbital states close to the ground state. The value of $g_{\perp}$ indicates a trigonal splitting of the order of $3 \times 10^3 \, cm^{-1}$, which is consistent with the optical absorption measurements of Piper and Carlin (1963), who estimated that the trigonal splitting lies in the region 2×10^3 to $5 \times 10^3 \, cm^{-1}$. Some efforts were made by the author to directly detect this transition by infra-red absorption measurements. No transition was detected however, apart from those due to the vibrational modes of the acetylacetonate molecule. This is not too surprising, since such d to d

transitions should have low transition probabilities.

Dilute Samples.

Because of the nearly isotropic nature of the E.P.R. spectrum the resonances from the two inequivalent sites are never very far apart in field values. To eliminate complications due to cross-relaxation between the two sites it was decided to make measurements with the magnetic field along the crystal **b** axis, where the two resonance lines coincide. Several samples of the aluminium acetylacetonate were grown by the techniques described in Chapter 3, having paramagnetic concentrations less than 1%. It was found by analysis that in these crystals, as in the more concentrated ones, the concentration of the crystals was within experimental error the same as that of the growth solutions. The concentrations in the two most dilute samples (0.2% and 0.04%) were not directly determined, but were taken to be the same as that of the growth solution.

The temperature dependence of the relaxation times obtained for these samples is shown in Figure 6. It is gratifying to find that the relaxation times are very long, in agreement with Van Vleck's original calculations. This shows that the "anomalous" results previously obtained are a result of a small trigonal field splitting and not, as is sometimes supposed, due to the chemical instability of this ion (Manenkov and Orbach 1966). The length of these relaxation times initially caused some measurement difficulties, which were overcome by the use of the pulsed monitor technique described in Chapter 2. Using this pulsed measurement system the effect of the monitor signal on the resonance line was investigated in the most dilute sample (0.04%), at the lowest temperatures where the relaxation time is 53 Secs. This was done by sweeping quickly once through the resonance, to determine the unsaturated line intensity. The magnetic

FIGURE 6

TEMPERATURE DEPENDANCE
OF DILUTE SAMPLES
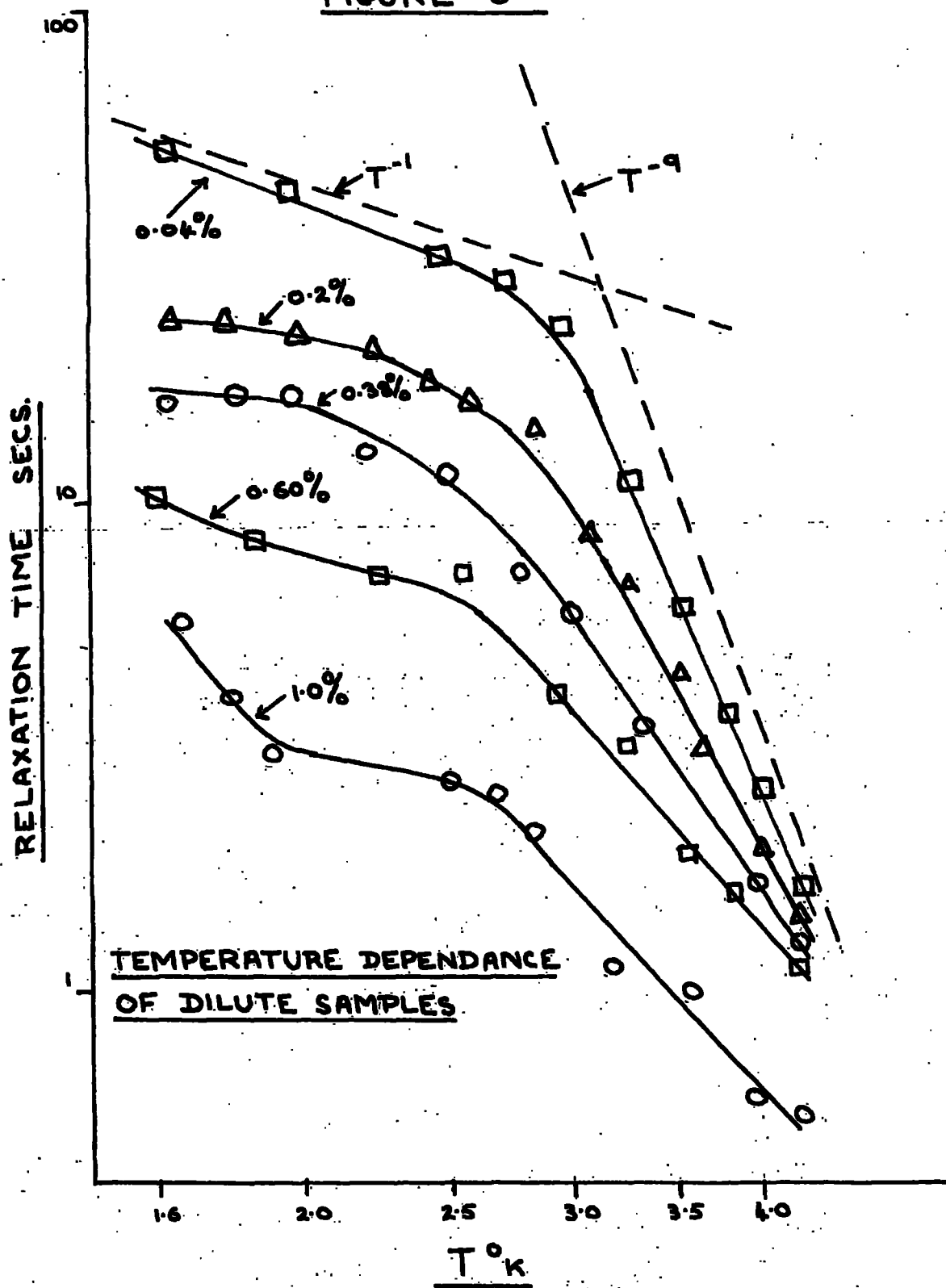
field was then set on resonance to see if any reduction in line intensity occurred due to saturation effects; since no such reduction was observed over a period of several minutes, it was concluded that monitor power saturation was insignificant.

From the results shown in Figure 6 it can be seen that the relaxation time at 4·2°K is tending to a concentration independent limit of about 1·5 secs. The concentration dependence which is evident at this temperature becomes more pronounced at lower temperatures. Here the relaxation time tends to a temperature independent limit in all but the most dilute sample. This most dilute sample shows the temperature dependence expected from the single ion theory and can be fitted by a sum of direct and Raman terms of the following form

$$\frac{1}{T_1} = 1.2 \quad 10^{-2} T + 1.5 \quad 10^{-6} T^9 \quad \text{secs}^{-1} \tag{5.1}$$

Because of the concentration dependence found even in these dilute samples, it is not entirely certain that (5.1) represents the true concentration independent relaxation at low temperatures. Ideally one would like to observe several samples covering a range of concentration in which the relaxation time is unchanged. Because of signal to noise considerations it was not possible however to investigate samples with concentrations below 0·04%, and indeed considerable difficulty was experienced in obtaining sufficiently large samples to permit measurements at this concentration.

Equation (5.1) not only has the form expected from the single ion theory, but the magnitudes of the two terms are in fair agreement with

Van Vleck's theory for the corresponding alum. Van Vleck's expression for the alum at the frequency of 9·3 KMc/s is

$$\frac{1}{T_1} = 5\cdot9 \;\; 10^{-1} \; T \;\; + \;\; 1\cdot0 \;\; 10^{-3} \; T^9 \;\; \text{secs}^{-1} \tag{5.2}$$

The numerical coefficients in (5.2) involve many parameters such as crystal density, velocity of sound, trigonal field splitting etc. The relaxation rates are particularly sensitive to the trigonal splitting, Δ , being proportional to the fourth and sixth powers of this parameter for direct and Raman processes respectively. In fact an expression nearly identical with (5.1) can be obtained from Van Vleck's results by using a value of Δ in the range 2·6 to 2·9 $10^{-3} \; cm^{-1}$ rather than the value of $10^3 \, cm^{-1}$ taken by Van Vleck. Such a value of Δ is in excellent agreement with the E.P.R. and optical data for the acetylacetonate.

Attempts to determine the frequency dependence of the direct process by measurements at Q band frequencies were frustrated by saturation problems. It was found that the resonance could only be observed transiently. When the magnetic field was set on resonance the line was saturated sufficiently to make it unobservable. Similar difficulties were encountered at X-band frequencies before the pulsed monitor method was developed. On the basis of the single ion theory and equation (5.1) one expects that at 35·5 KMc/s the direct process will be dominant throughout the helium range, with a relaxation time of about 100 m Secs. at 4·2°K. The fact that the resonance was easily saturated suggests that the relaxation time is longer than this. This throws doubt on the accuracy of (5.1) in representing the time single ion direct process; possibly even longer relaxation times would be obtained in more dilute samples.

<u>Concentrated Samples.</u>

Other samples were grown to cover the range of concentration up to 10%. During the preparation of these samples some single crystals of the undiluted titanium chelate were also obtained. The results for the samples of medium concentration will be discussed first and the peculiar behaviour observed in undiluted specimens will be discussed separately.

Medium Concentrations.

The concentration dependence, already noted in dilute samples, now becomes most pronounced. The relaxation time continues to decrease monotonically with concentration, up to the highest concentration studied (10%); above 1% concentration the relaxation behaviour is dominated by the concentration dependent process. The magnitude of the variation in relaxation time is remarkable. In the range 0-10% concentration there is three orders of magnitude variation at $4 \cdot 2^O$K and four orders variation at $1 \cdot 6^O$K. In these samples the relaxation recovery was not uni-exponential, but had a secondary component with a time constant which was typically three or four times shorter than that of the dominant component. In all but the most concentrated samples the amplitude of this component was small, so that in what follows the relaxation times quoted refer to this longer dominent relaxation component.

The temperature dependence found in these crystals is shown in Figure 7. From this figure and from Figure 6, it can be seen that the temperature dependence associated with these concentration effects is of a peculiar form. There are regions of rapid variation, of the form T^{-2} up to T^{-3} with regions of temperature independence. The range over which this temperature independence is observed appears to have a systematic

FIGURE 7

Relaxation time secs. (vertical axis)

CONCENTRATED

SAMPLES

2·07%
2·45%
2·48%
3·30%
3·80%
4·4%
5·9%
9·5%
9·3%

T °K

relationship to the concentration. In the more dilute samples, shown
in Figure 6, it covers the lower part of the helium range. As the
concentration increases so the range over which temperature independ-
ence is observed decreases, until at about 2.5% concentration it appears
to vanish altogether. At higher concentrations the temperature independ-
ence reappears at the lower end of the helium range. In the two most
concentrated samples the range of temperature independence is rather
small and appears to be tending to vanish once more. The point at which
this temperature plateau is seen to disappear corresponds approximately
to the point at which the form of the concentration dependence undergoes
a change. This is shown in Figure 8, where the relaxation time observed
is plotted against sample concentration. Below 3% concentration the
functional dependence of the relaxation time on the paramagnetic concentra-
tion, C , is of the form C^{-2} and above this concentration it is of the
form $C^{-3.5}$.

These measurements were repeatable with different samples taken from
the same growth run. Also the presence of some oxydation products in the
growth solution did not appear to affect the relaxation time of the
resulting crystals. This was noticed in two samples as a result of
accidentally allowing oxygen into the growing flask during the transfer
of the titanium chelate. The first such solution, nominally 1% concentra-
tion, produced samples of about 0.2% concentration. Although the growth
solution was green, due to the presence of the yellow oxydation products,
the crystals produced were the usual intense blue colour and had relaxa-
tion times similar to those of crystals produced under oxygen free
conditions. The other sample grown under these conditions was nominally
of 5% concentration, but on analysis was seen to have a concentration of

FIGURE 8

CONCENTRATION DEPENDENCE
AT 9·3 KM·c/s

RELAXATION TIME SECS.

CONCENTRATION C (MOLAR %)

C^{-2}

O   4·2°K
△   2·0°K
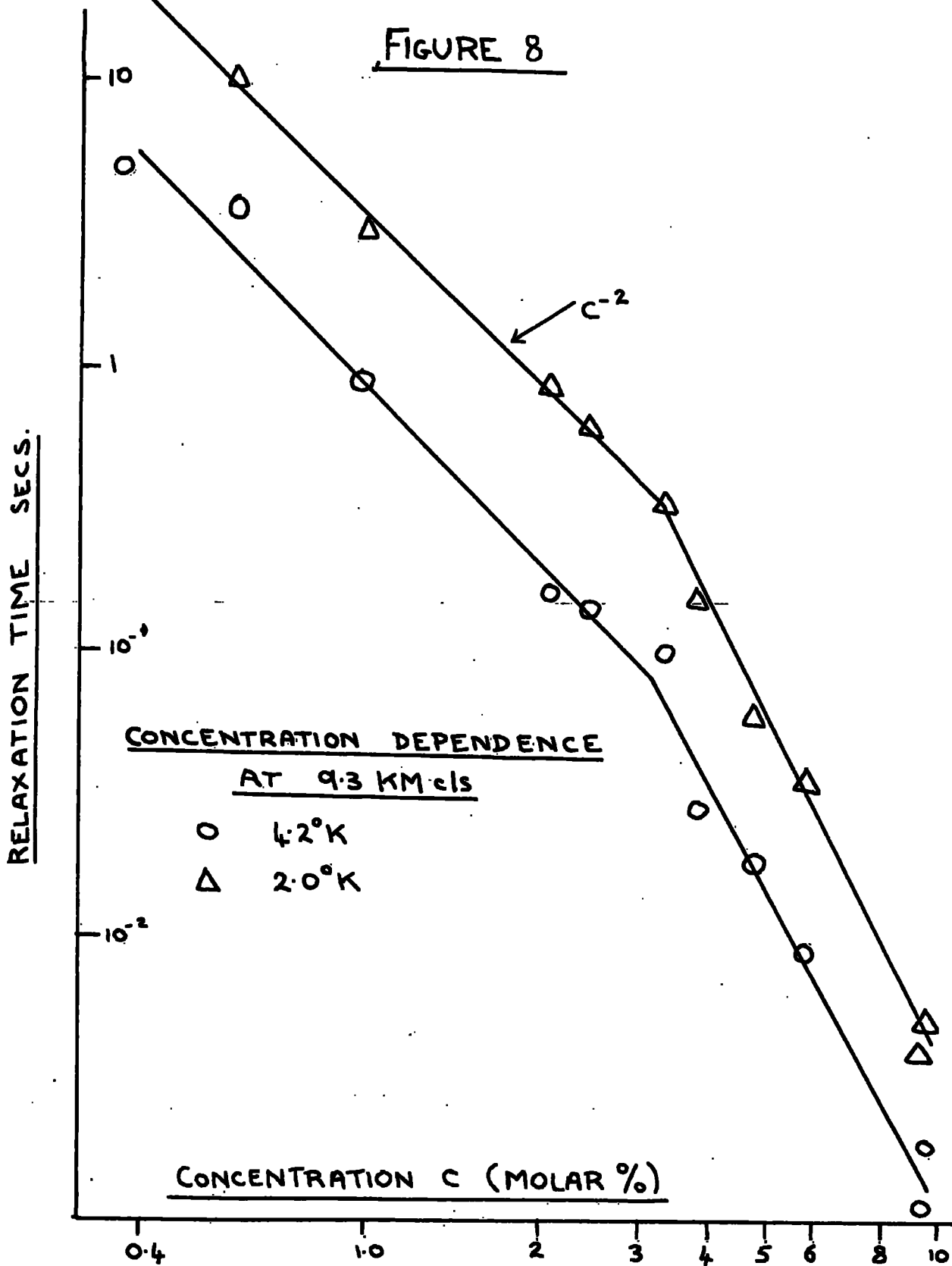
2·48%. Fortuitously this was almost the same concentration as that of another sample grown under normal conditions. It can be seen from Figure 7, that there is no significant difference in the relaxation times of these two samples.

All the above measurements were made with the magnetic field oriented along the crystal $\underline{b}$ axis. Some measurements were made at other angles to see if any angular dependence was associated with the concentration dependence. To eliminate complications due to cross-relaxation between the two inequivalent sites the angular dependence was determined in the two crystal planes in which the spectra of the two sites coincide. One such equivalence plane is the $\underline{a}\,\underline{c}$ crystal plane and the other includes the $\underline{b}$ axis and is perpendicular to the plane containing the two molecular trigonal axes (Figure 2). Measurements were made at 4·2°K and 2°K using 3·3% and 1% samples. In neither case could any angular dependence be detected in the two equivalence planes.

Some measurements were made at Q band frequencies (35·5 KMc/s) on the two most concentrated samples. The analysis figures show that these two samples have almost the same concentration, but slightly different relaxation times were observed at X-band frequencies, with correspondingly different forms for the temperature dependence. Of these two samples the 9·5% sample appears to be somewhat exceptional in that the temperature plateau region occurs between 3.5° and 4°K. In all other samples studied the corresponding plateau region occurs at lower temperatures, below 2·5°K. The Q-band temperature dependence found for these samples is shown in Figure 9a, together with the corresponding X-band results. In both cases

FIGURE 9ₐ

FREQUENCY DEPENDENCE

O SAMPLE 1   9.3%

△ SAMPLE 2   9.5%

35.5 KMc/s

9.3 KMc/s

RELAXATION TIME SECS.

$T°K$
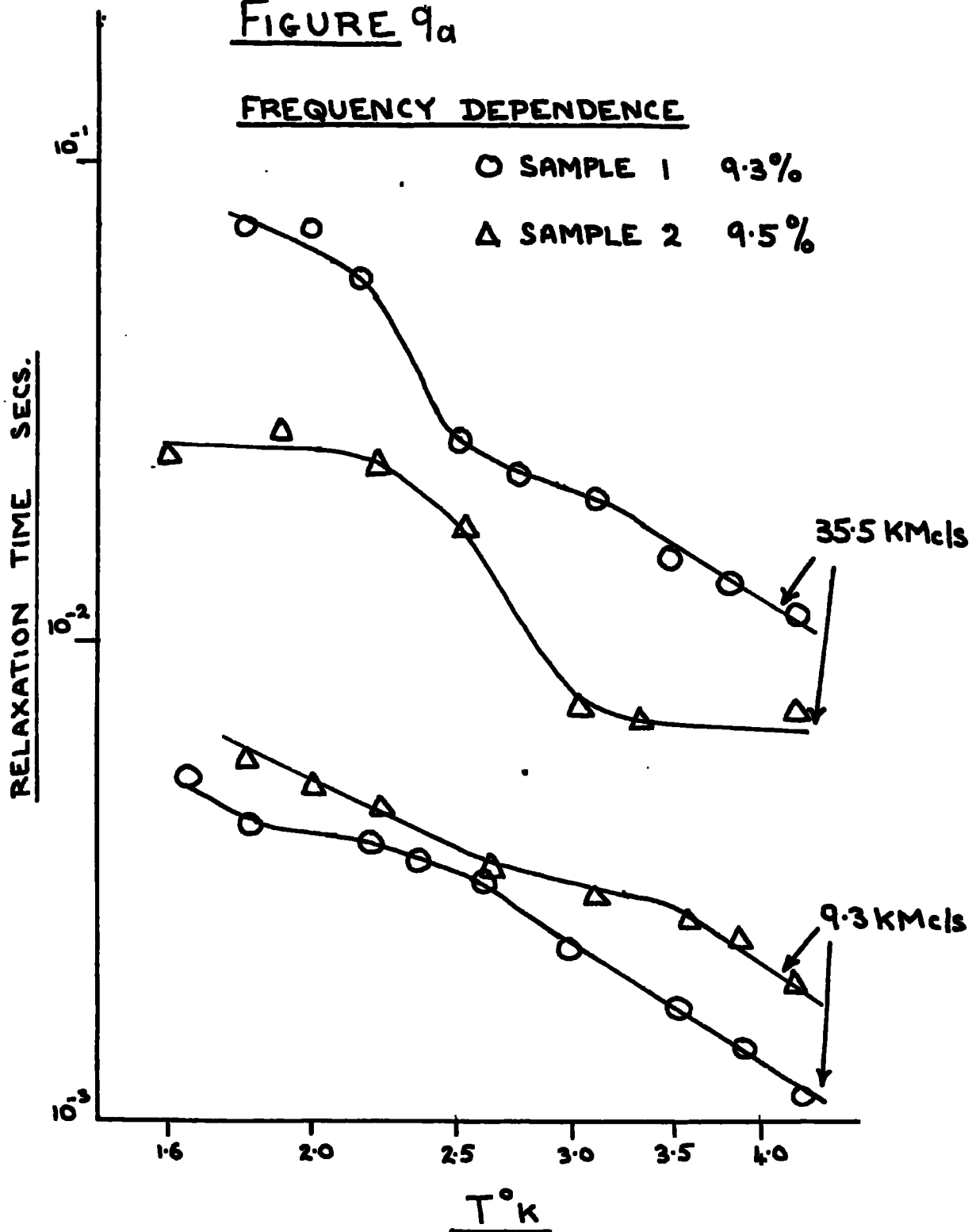
the form of the temperature dependence at the two operating frequencies
is similar, although at the higher Q band frequency a second temperature
independent region is evident at the lowest temperatures. Perhaps the
most significant feature of these results however is the fact that
longer relaxation times are found at the higher operating frequency.
This, it should be noted, is a frequency dependence of the opposite sign
to that predicted by the single ion theories. The fact that the ratio of
the Q to X-band relaxation times is not the same for the two samples is
doubtless connected with the different temperature dependencies found.
Undiluted Samples.

Some undiluted samples of the titanium chelate were also studied at
low temperatures. These crystals were prepared to obtain some information
concerning the exchange interactions in these materials. Because of the
isotropic nature of both the exchange interactions and the g tensor, the
satellite lines arising from clusters of interacting ions will coincide
with the more intense single ion lines. A detailed study of the exchange
interactions, such as that carried out for the corresponding chromium
samples, is not therefore possible. Nevertheless some information can be
obtained from the linewidth of the resonance. From the interionic distances
in these crystals and the theory of Van Vleck (1948), the linewidth due to
dipolar interaction alone is expected to be of the order of 150 to 200
gauss (full linewidth of half intensity) in undiluted crystals. It was
found that in these samples a single sharp resonance line was observable
at X-band frequencies. The angular dependence in the plane which contains
the two molecular trigonal axes shows that this resonance occurs at the
mean position of the two resonances expected from the inequivalent sites.
The observed linewidth of 14 gauss is independent of orientation in this

plane. The lineshape was seen to be approximately of the Lorentzian form characteristic of exchange narrowed resonance lines. The fact that only one resonance could be observed despite the presence of two inequivalent sites shows that the exchange interactions between inequivalent ions is considerably larger than the magnitude of the anisotropic terms in the single ion spin-Hamiltonian. This is consistent with the direct observation of inequivalent ion interactions in the chromium samples (Chapter 6). From the theory of exchange narrowing presented by Anderson and Weiss (1953) the exchange interactions in these samples can be described by an average isotropic exchange parameter J approximately one order of magnitude greater than the dipolar linewidth. Such an exchange constant, of the order of 4 KMc/s, is comparable with those directly observed in the chromium samples (Chapter 6).

Because of the intensity of the E.P.R. absorption at this concentration only very small samples could be investigated at helium temperatures. The relaxation properties of such samples were quite different to those observed previously. Using short saturating pulses (100 μ Secs.) very little saturation of the resonance line could be achieved. With long saturating pulses (5 m Secs.) only about 50% to 60% saturation could be achieved, even though the relaxation rates observed were quite long. The resonances in more dilute crystals with similar relaxation rates could be saturated easily with either long or short pulses. This behaviour alone suggests that there is some thermal capacity involved in the saturation of the resonance, such as could arise from the heating of the crystal lattice. Phonon heating effects are also suggested by the form of the relaxation traces observed, which are not of an exponential nature. Figure 9b shows the relaxation traces obtained from a sample of approximate

FIGURE 9b.

RELAXATION RECOVERIES IN UNDILUTED

$Ti(C_5H_7O_2)_3$

PULSE WIDTH 5 m SECS

$T = 4.2°K$

$T = 2.2°K$

TIME m SECS
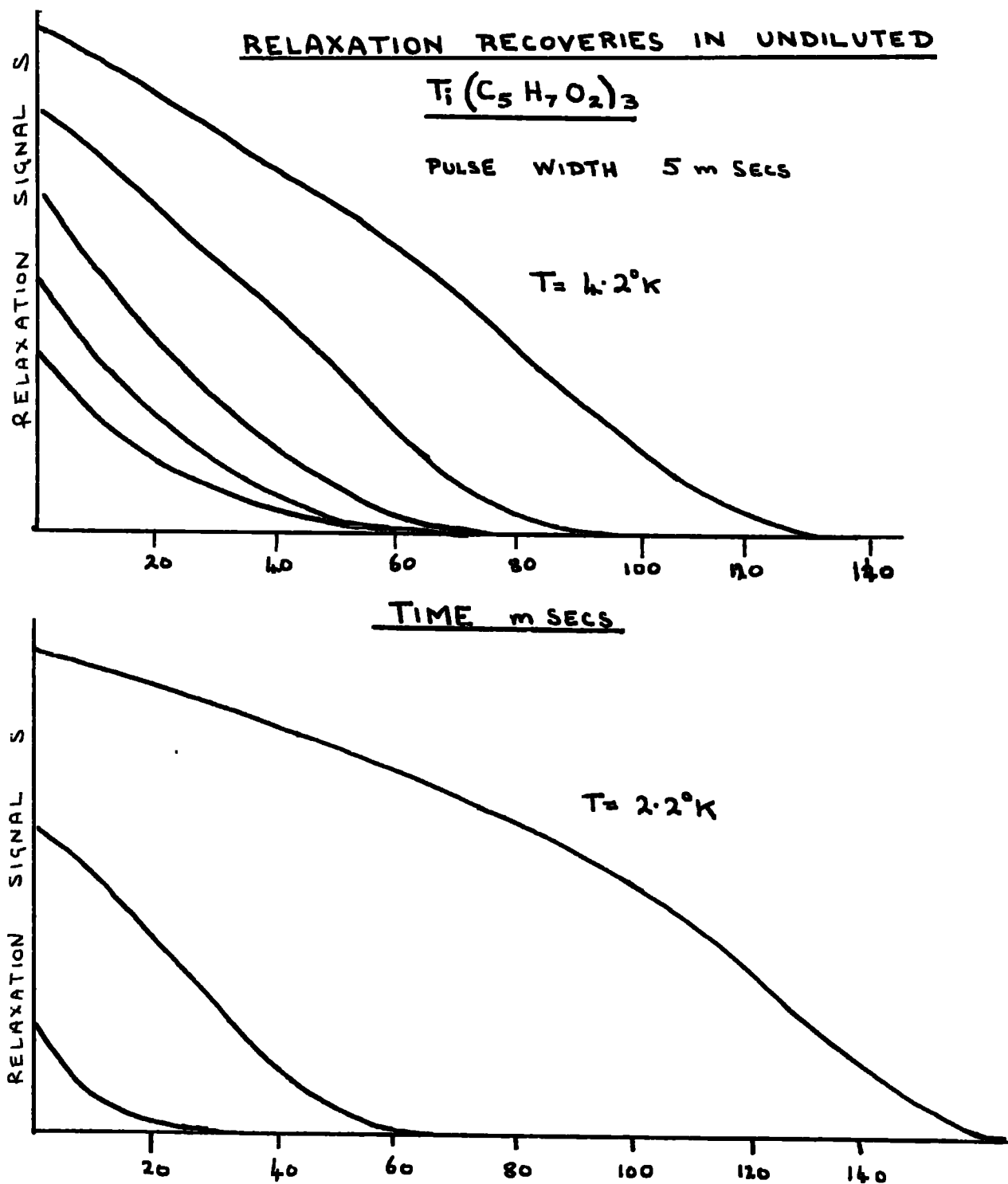
dimensions 1 x 1 x$\frac{1}{2}$ m.m. at two temperatures, for a variety of saturating pulse power levels. The maximum power corresponds to a pulse of approximately $\frac{1}{2}$ Watt incident on the microwave cavity, and in all cases the pulse width is 5 m Secs.

It can be seen from these figures that for the largest saturation value ($\sim$ 50%) the relaxation rate immediately following the saturating pulse is low and of non-exponential form. This rather flat initial recovery is most pronounced at low temperatures. The non-exponential behaviour does not appear to be due to instrumental effects since the same results were observed by directly monitoring the resonance line with a 50 c/s field sweep. An exponential relaxation recovery could only be obtained using low power saturating pulses. The time constant of this exponential actually decreased with decreasing temperature, from 25 m Secs. at 4.2^{o}K to approximately 8 m Secs. at 2°K. These measurements were made with the crystal fixed to the cavity wall with vacuum grease. Similar measurements made with the same crystal held freely in polystyrene foam, or immersed in liquid helium, showed similar relaxation behaviour.

These effects can only be understood in terms of phonon heating. The theory of such relaxation phenomena, in the case of direct process relaxation involving a narrow frequency band of phonons, has been described by Faughnan and Strandberg (1961). The relaxation recovery predicted by this theory does not however describe the present results. This suggests that the spin-lattice relaxation is so rapid and involves so many phonon modes, that the entire crystal lattice and spin system are held at the same temperature. This explanation accounts for the observed thermal capacity which is apparently involved in the saturation

of the resonance line and goes some way towards accounting for the initially flat relaxation recoveries observed. If T represents the common temperature of the lattice and spin system, then the relaxation signal S is

$$S = 1 - \frac{\Delta n}{\Delta n_0} = 1 - \frac{T_0}{T}$$

(5.3)

where Δn is the population difference of the two levels involved in the transition and the subscript 0 refers to ambient temperature conditions. Following a saturating pulse one might expect that T will relax back to the ambient temperature T_0 in an exponential manner

$$T = T_0 + A \, exp(-\alpha t)$$

(5.4)

Clearly when $T \gg T_0$, S is more or less constant over a wide range, demonstrating the kind of relaxation behaviour observed. In the present case however it is clear that at most $T = 2.5 T_0$, so that the flattening of the initial part of the relaxation recovery is not expected to be very pronounced. Nevertheless such a simple interpretation does demonstrate all the observed features and no doubt more quantitative agreement could be obtained by considering the temperature distribution through the crystal and a different form for the temperature reocvery (5.4). The significance of these results in the present context lies in the fact that the spin-lattice relaxation time, although not directly determined, is undoubtedly very short, showing that the concentration dependence extends up to the highest concentrations.

Concentration Dependent Relaxation.

The interpretation of the concentration dependent relaxation described in the previous section will be considered in terms of the two existing theories relating to such effects. Some of the observed effects appear to be quite a general feature of concentration dependent relaxation. Temperature dependencies greater than the linear form expected for direct process relaxation have been observed before (e.g. Gorter 1947, Bowers and Mims 1959), although the temperature plateaus found in the present case are quite a new feature. From the results of the early Dutch workers it is also known that an anomalous frequency dependence is also a typical feature (Van Der Marel, Van Den Broek and Gorter (1957), Du Pre (1940)). The fact that concentration dependent processes are inhibited by large applied magnetic field is also apparent from the results obtained for Fe^{3+} in cobalticyanide. The results of Paxman (1961) and Bray, Brown and Kiel (1962) show that at X-band frequencies there is little if any concentration dependence in material up to 6% concentration. At lower frequencies however the concentration dependent relaxation rate increases remarkably (Prokhorov and Fedorov 1964), and dominates the relaxation behaviour in relatively dilute samples. To see how these effects may be understood the two proposed mechanisms will be discussed, with particular reference to the present results.
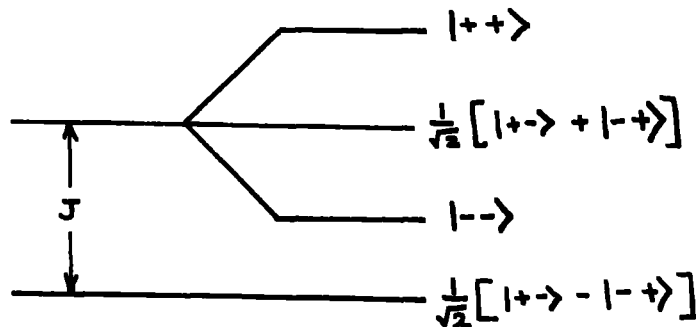
Exchange coupled Clusters.

Van Vleck (1960) proposed a mechanism involving pairs or clusters of neighbouring ions coupled together by exchange interactions. It is assumed that these exchange interactions are strongly dependent on the

interspin distances within the cluster and so very susceptible to modulation by the lattice vibrations. Such clusters may therefore have a very short spin-lattice relaxation time. If a mechanism exists to transfer energy from the abundant single ions to these clusters then clearly a reduction in the relaxation time of the single ions will be observed. The known mechanisms of energy transfer are those of cross-relaxation and cross-spin-lattice relaxation (Bloembergen et al (1961)). The rate equations relevant to the cross-relaxation process were discussed in Chapter 4. From (4.29) two limiting cases can be distinguished. The first occurs when the relaxation rate is limited by the cross-relaxation process. In this case the cross-relaxation rate will be observed, with a characteristic temperature dependence (temperature independent if only ground spin states are involved). Such a process appears to occur in the relaxation of the chromium doped samples discussed in Chapter 6. When the relaxation rate is very fast the relaxation rate of the clusters will be the limiting process. The observed relaxation rate in this case will be proportional to the ratio of the number of such clusters to the number of single ions. On statistical grounds the density of clusters at low concentrations can easily be shown to be related to the total paramagnetic concentration C, by a simple power law (i.e. proportional to c^2 for pairs and c^3 for triads).

The simplest cluster, relevant to the present case, consists of a pair of interacting $S = 1/2$ ions with isotropic g values. The spin-Hamiltonian for such a pair is

$$\mathcal{H}_p = g\beta \underline{H} \cdot (\underline{S}_1 + \underline{S}_2) + J \underline{S}_1 \cdot \underline{S}_2 \qquad (5.5)$$

The eigenfunctions of (5.5) consist of a triplet and singlet state shown below

$$
\begin{aligned}
&|++\rangle \\
&\tfrac{1}{\sqrt{2}}\left[\,|+-\rangle + |-+\rangle\,\right] \\
&|--\rangle \\
&\tfrac{1}{\sqrt{2}}\left[\,|+-\rangle - |-+\rangle\,\right]
\end{aligned}
$$

where a ket such as $|+-\rangle$ denotes $\left|S_{1z}=+\tfrac{1}{2},\ S_{2z}=-\tfrac{1}{2}\right\rangle$.
The fact that the Zeeman and exchange terms in (5.5) commute with one another leads to some difficulties. The only allowed E.P.R. transitions are those within the triplet state which coincide with the single ion transition. Thus the exchange interactions between pairs of this type cannot be determined directly by E.P.R. methods. A more serious difficulty in the present context arises from the fact that the exchange term has no off-diagonal matrix elements within the pair system. Thus, no matter how strongly modulated by the lattice vibrations, this term is incapable of inducing relaxation transitions within the pair system. This negative result can only be overcome by adding further terms to (5.5) to spoil the perfect commutation. Such terms arise naturally in multilevel systems with zero field splittings, but in the present case they can only arise through dipolar interaction or anisotropic exchange, both of which are quite small.

As was pointed out by Van Vleck (1961) clusters of three or more ions offer a more promising model for $S=\tfrac{1}{2}$ ions. Assuming exchange interactions between nearest neighbours only the spin-Hamiltonian for such a triad is

$$\mathcal{H}_T = g\beta\underline{H}\cdot(\underline{S}_1 + \underline{S}_2 + \underline{S}_3) + J_A\,\underline{S}_1\cdot\underline{S}_2 + J_B\,\underline{S}_2\cdot\underline{S}_3$$

$$(5.6)$$

With $J_A = J_B$ the eigenfunctions of (5.6) are as shown below

$$|+++\rangle$$

$$\tfrac{1}{\sqrt{3}}\big[\,|+-+\rangle + |-++\rangle + |++-\rangle\,\big]$$

$$\tfrac{1}{\sqrt{3}}\big[\,|+--\rangle + |-+-\rangle + |--+\rangle\,\big]$$

$$|---\rangle$$

$$\tfrac{1}{\sqrt{2}}\big[\,|-++\rangle - |++-\rangle\,\big]$$

$$\tfrac{1}{\sqrt{2}}\big[\,|+--\rangle - |--+\rangle\,\big]$$

$$\tfrac{1}{\sqrt{6}}\big[\,2|+-+\rangle - |-++\rangle - |++-\rangle\,\big]$$

$$\tfrac{1}{\sqrt{6}}\big[\,2|-+-\rangle - |+--\rangle - |--+\rangle\,\big]$$

$J/2$

J
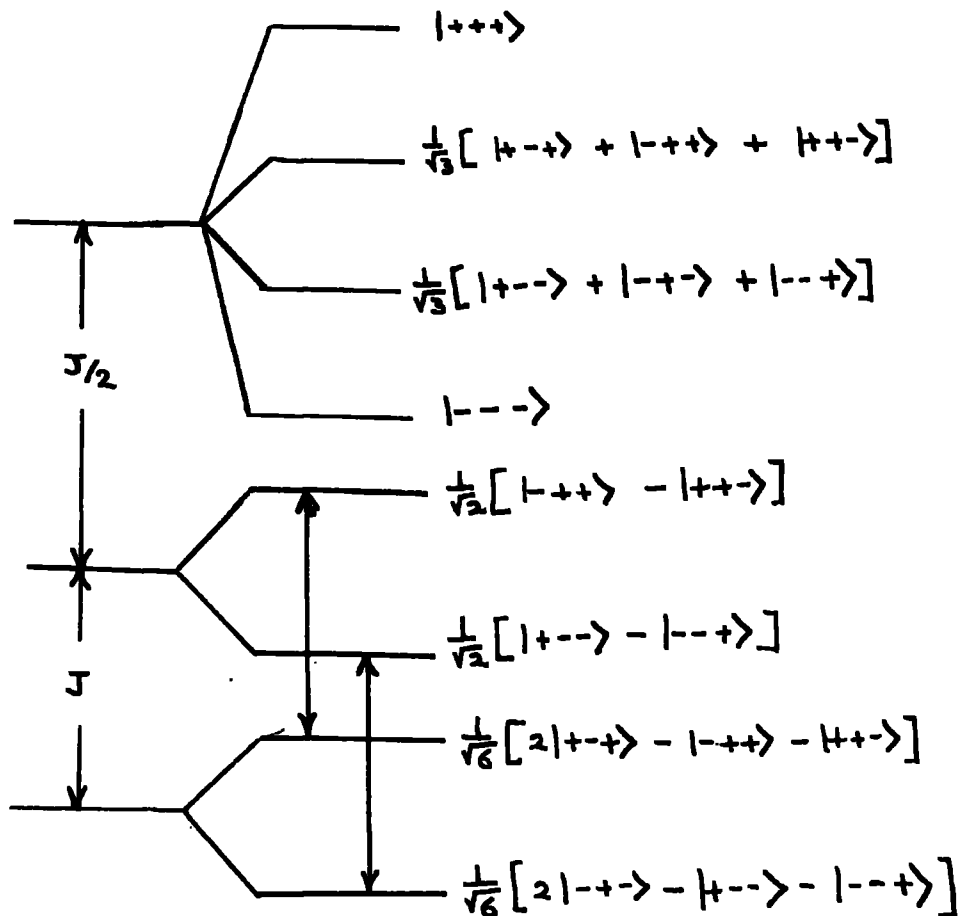
Once again the only allowed E.P.R. transitions coincide with those of the single ions. However, if the two exchange interactions are modulated differently, there will be allowed relaxation transitions between the doublet states, as indicated in the figure.

To obtain an order of magnitude estimate of the relaxation time due to direct process transitions between these states the functional

dependence of J_A and J_B on the interspin distances will be taken to be of the form

$$J = A e^{-\alpha |R_1 - R_2|} = A e^{-\alpha R} \qquad (5.7)$$

The effectiveness of the lattice vibrations in modulating the exchange terms depends to some extent on the geometry of the triad. A linear array is rather unfavourable since J_A and J_B will be modulated similarly by all lattice waves. It will be assumed for simplicity that a given lattice mode only modulates one of the exchange terms, such as might be the case in a non linear array. Expanding (5.7) about the equilibrium position $(R_1 - R_2)_0$

$$J = J_0 \left(1 + \alpha(S_1 - S_2) + \frac{\alpha^2}{2}(S_1 - S_2)^2 + \cdots \right) \qquad (5.8)$$

where S_1 and S_2 are the displacements of ions 1 and 2 along the axis joining these two ions. From (4.8)

$$S_1 - S_2 = \left(\frac{2\hbar\omega_p}{M v^2} \right)^{1/2} (a_p + a_p^+) \left[\phi_p \, \underline{K}_p \cdot \underline{R}_0 \sin \Delta_p \right] \qquad (5.9)$$

In order of magnitude the direct process transition probability is

$$U_{ab} \simeq \frac{1}{\hbar^2} \left(\frac{2\hbar\omega_p}{M v^2} \right) (\alpha J_0)^2 \left(\begin{matrix} n_p \\ \text{or} \\ n_p+1 \end{matrix} \right) \frac{R^2}{v^3} 12\pi \sigma^3 V \left| \langle a | \underline{S}_1 \cdot \underline{S}_2 | b \rangle \right|^2$$

$$(5.10)$$

In (5.10) we can take the matrix element to be unity for the allowed transitions and ignore the averaging over phonon phases etc. These approximations will tend to over estimate the transition probability somewhat which now reduces to

$$U_{ab} \sim 6 \omega_p^3 n_p (\alpha R_0 J_0)^2 / \pi \hbar \rho v^5$$

(5.11)

In the present case we are interested in triads with exchange constants J_0 of the order of 4 KMc/s. Using such a value of J_0 and taking αR_0 to be 20 as is indicated by the work of Statz et al (1961) on Cr^{3+} pairs in Ruby, the numerical value of the direct process transition probability is

$$U_{ab} \sim 200 \text{ sec}^{-1} @ 4^\circ K$$

This corresponds to a relaxation time of 5 milliseconds. The temperature dependence of the exchange interactions found in the chromium doped samples suggests that αR_0 may be of the order of 100 in these materials, in which case the relaxation time becomes approximately $1/5$ of a millisecond.

Such relaxation times would be short enough to account for the observed relaxation behaviour were it not for the fact that the allowed transitions only connect similar Zeeman states of the two doublets. One would expect fast cross-relaxation only between the Zeeman levels of the triads and single ions, where the corresponding transitions are coincident. This is not however sufficient to produce concentration dependence since the two Zeeman levels of the triad involved in any such transition are not connected, directly or indirectly, by allowed relaxation processes. It might be argued that cross-relaxation occurs in such a way that the allowed

relaxation transitions are involved directly. Such a process could only occur if by an accident $J \sim g \beta H$.   . It might also be thought that the observed temperature independent relaxation could be accounted for in this way, in terms of such weakly allowed cross-relaxation. The range over which such temperature independence is observed is however not great enough to support such an explanation. The temperature plateau regions should, in this explanation, extend upwards in temperature until the point is reached where the single ion relaxation rate begins to dominate. Also the fact that limited regions of temperature independence are observed at Q-band frequencies is not consistent with such an explanation. It is hardly conceivable that accidental degeneracies between the triad and single ion transitions should occur at two completely different frequencies. Cross-spin-lattice relaxation, involving simultaneous triad and single ion transitions, may also be considered. At very low concentrations the dipolar interaction between such triads and distant single ions is rather small, and so such a process can hardly account for the observed concentration dependence below 1%.

Mixing of Zeeman Levels.

It appears therefore that one must conisder dipolar interactions within the triads themselves, in order to mix the various Zeeman states. Such mixing will occur in general when the dipolar interactions contain terms such as $S_{1z} S_{2+}$, $S_{1z} S_{2-}$ etc. The mixing of states will be of the order of the ratio of dipolar to Zeeman energies, which at X-band frequencies is of the order 10^{-2} in the acetylacetonates. Relaxation between different Zeeman levels will then become weakly allowed with transition probabilities about 10^{-4} times smaller than those estimated above. An interpretation along these lines is attractive in that it does

predict an anomalous field dependence. As the field increases so the mixing of states decreases as H^{-2}, thus cancelling the increase in transition probability due to the enhanced density of phonon modes, which varies as H^{+2}. The resulting field independent relaxation rate does therefore go some way towards explaining the general tendency of the observed relaxation times to increase with increasing field.

A similar scheme to this has been proposed by Harris (private communication) to account for the relaxation properties of Ir^{4+} in some platinum compounds (Harris and Yngvesson 1966). Ir^{4+} is an $S = \frac{1}{2}$ ion and, as in the present case, the concentration dependence of the observed relaxation time was of the form c^{-2} at low concentrations, suggesting relaxation through exchange coupled triads. The exchange interactions in these materials were found to be very large, of the order of 3 cm^{-1} so that, even allowing for the reduced matrix elements which arise through the mixing of Zeeman states, sufficiently large transition rates can be obtained to account for the results.

In the present case of weak exchange interactions however, one can only obtain sufficiently large relaxation rates by assuming that the exchange modulation is very much greater than that previously supposed, corresponding to values of αR_0 of about 10^3. With such a tremendous exchange modulation the second order Raman process becomes competitive with the direct process even at liquid helium temperatures. The Raman process can operate in such a triad by using one of the ground triad states as an intermediate level. The temperature dependence of the relaxation time in such a Raman process is expected to be proportional to T^{-5} (Orbach and Blume 1962). One can also envisage a Raman process with a T^{-7} dependence, which uses excited states as intermediate levels.

In such a process one of the virtual transitions to the intermediate level will involve exchange modulation and the other crystal electric field modulation. This avoids the "Van Vleck cancellation" of terms which occurs in the single ion Raman process, where both virtual transitions involve crystal field modulation.

The observed temperature dependence of the relaxation time does in fact suggest that Raman processes are involved. Temperature dependencies greater than the linear form are very difficult to explain in terms of any kind of single phonon direct process, unless one assumes that excited states are involved. Single phonon Orbach processes can then occur, giving exponential temperature dependencies. Such an explanation accounts for the $\mathcal{I}_+^{4+}$ results mentioned previously, but cannot be valid in the present case because of the relatively weak exchange interactions. If indeed Raman processes dominate the relaxation of triads at low temperature, then an explanation of the peculiar temperature dependence observed may be ~~accounted for~~ given in terms of defect vibrations within the cluster.

Defect Relaxation.

The completely different mechanism of concentration dependent relaxation proposed by Kochelaev (1960), is concerned with point defects associated with each paramagnetic ion site. In mixed crystals it may be that the paramagnetic impurities act as point defects in the vibrations of the diamagnetic lattice. This will be the case if the mass and force constants of the paramagnetic impurities are very different from those of the host lattice. Localised vibrational modes may then exist at each paramagnetic ion site and so affect the relaxation properties. Interactions between neighbouring local modes then provides a mechanism for

concentration dependent relaxation. For various reasons this proposal does not appear to be compatible with the experimental evidence.

(1) When measurements are made up to 100% concentration (Benzie 1951, Bowers and Mims 1959), it is found that there is a monotonic relationship between relaxation time and paramagnetic concentration. This counts against the defect theory, since the density of paramagnetic point defects should have a maximum around 50% concentration and fall to zero at 100% concentration.

(2) A defect structure at each ion site should have an effect even on the single ion relaxation. It is generally found, as in the present case, that the single ion theories of Chapter 4 describe quite well the relaxation in the concentration independent region.

(3) Generally concentration effects are most noticeable in materials with long relaxation times (e.g. compare T_1^{3+} and R_u^{3+} in the present work). This suggests that the concentration dependence is due to processes acting in parallel with that of the single ion process. Exchange coupled clusters constitude such a parallel process, but the defect theory is so to speak a series process and should be equally effective in fast and slow relaxing materials.

One can however envisage a modification of this theory which may have some relevance to the present case. Although the vibrations at single ion impurity sites do not appear to have a significant defect character, this may not be so within a cluster of two or more impurity ions. Castle et al (1965) have shown that if such defect vibrations occur, then they can have a significant effect on the temperature dependence of the Raman process. These authors considered the case of radiation induced defects in silica. The model taken assumed that each paramagnetic defect site

has one or more characteristic modes of vibration which are driven into forced oscillations by the surrounding diamagnetic lattice. Incident phonons, with a frequency close to that of one of the natural resonances of the defect, can induce large amplitudes of vibration at the defect site. The amplitude of the resonances so induced will be determined by the nature of the damping terms. Assuming velocity damping these authors showed that the strain at the paramagnetic site due to a natural mode of frequency ω_λ, driven into forced oscillations by incident phonons of frequency ω is

$$\varepsilon = R e^{i\omega t} \tag{5.12}$$

where

$$R = \frac{\left[\left(1 - f^2 - (1-f^2)^2 - \lambda^2 f^2 \right)^2 + \lambda^2 f^2 \right]^{1/2}}{(1-f^2)^2 + \lambda^2 f^2}$$

λ is the damping parameter and $f = \omega/\omega_\lambda$. In the absence of any defect vibrations the temperature dependence of the Raman relaxation rate is determined by the value of the integral

$$\int_0^{\omega_D} \omega^n e^{-\hbar\omega/kT} \, d\omega$$

which, in the low temperature limit, gives a functional dependence of the form T^{n+1} (Chapter 4). In this integral a factor ω^4 arises from the strain induced by the two participating phonons. If this factor is replaced by (5.12) it is seen that the temperature dependence of the
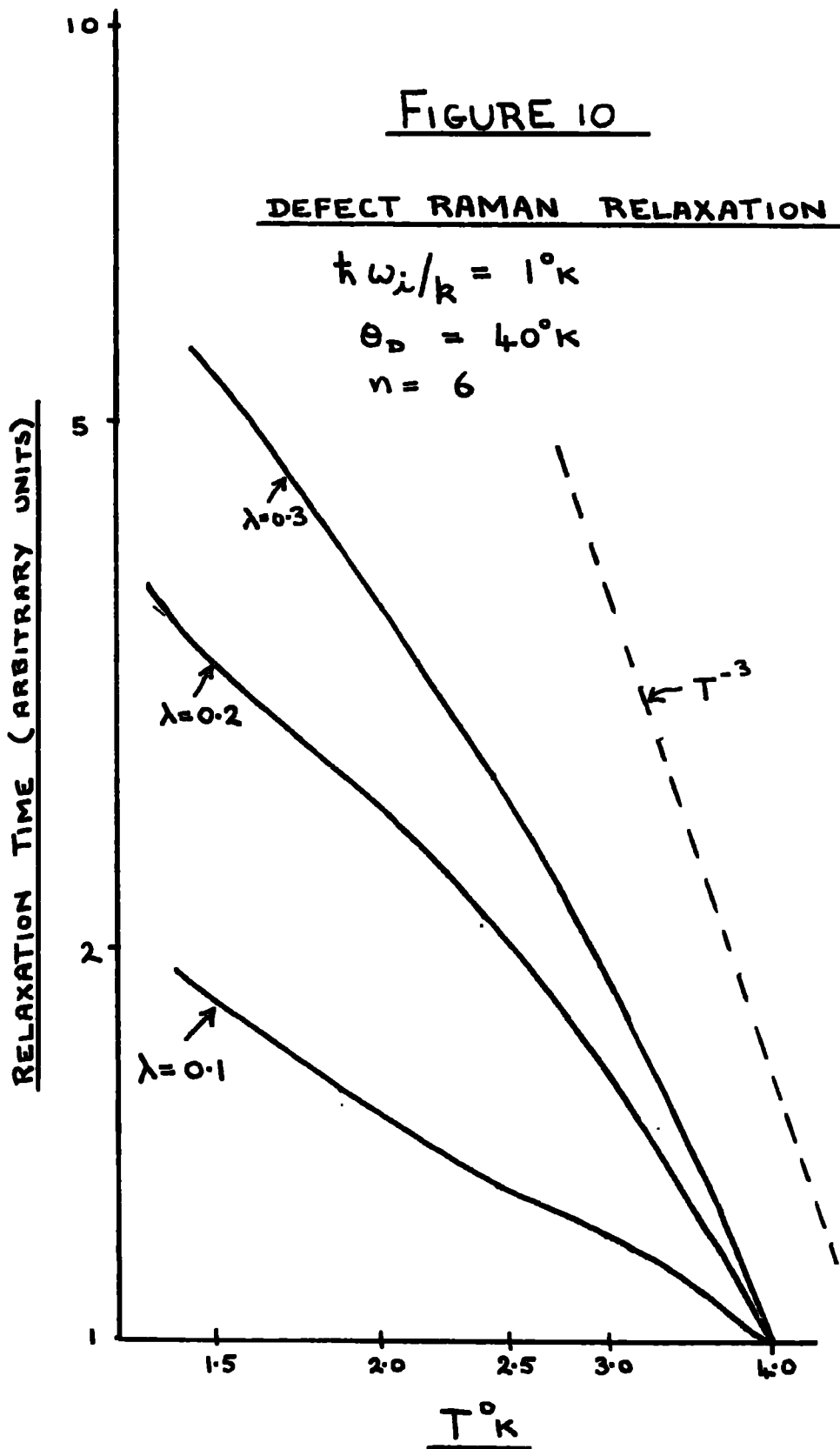
defect Raman process is

$$\int_0^{\omega_D} \omega^{n-4} R^4 e^{-\hbar\omega/kT} d\omega \qquad (5.13)$$

Castle et al made an approximation which is equivalent to assuming heavily damped vibrations (large λ). The parameter R is then constant throughout most of the region of integration so that (5.13) is readily evaluated to yield a temperature dependence of the form T^3, in agreement with the results obtained for radiation induced defects in silica.

Such a temperature dependence is also observed in the present case over a limited region. This model was therefore investigated further to see if it could also yield limited regions of weak temperature dependences. Various values of the damping parameter λ were considered in the range 0.1 to 1.0, which according to Castle et al are not physically unreasonable. The value of n appropriate to the present case is uncertain in that the nature of the assumed Raman process is also uncertain. Also the neglect of the strain of the participating phonons is likely to be incorrect in the present case of an extended cluster of impurities. Various values of n were therefore considered namely 4, 6, and 8. A computer programme was written to evaluate numerically the integral (5.13), for these various values of n and λ. It was found that for $n = 6$ the relaxation times so obtained did indeed show some features similar to those observed. The temperature dependencies are shown in Figure 10, for an assumed local mode frequency corresponding to $1^\circ K$ and a Debye temperature of $40^\circ K$.

The temperature dependencies found show that the T^3 form is obtained at high temperatures but that this gives way to a weaker dependence at the lower part of the helium range. The weakening of the temperature dependence becomes more pronounced as the damping parameter λ is reduced.

FIGURE 10

DEFECT RAMAN RELAXATION

$\hbar\omega_i/k = 1°K$

$\Theta_D = 40°K$

$n = 6$

$\lambda = 0.3$

$\lambda = 0.2$

$\lambda = 0.1$

T^{-3}

RELAXATION TIME (ARBITRARY UNITS)

$T°K$

For a value of λ of 0.1 an inflexion in the curves is obtained at about 2.5°K, which is suggestive of the limited temperature independent regions actually observed. The form of the temperature dependence is quite sensitive to the choice of λ. This feature could account for the observed variation in temperature dependence from sample to sample. A more elaborate theory of defect vibrations within clusters could therefore conceivably account for the peculiar temperature dependencies observed. In the present case it hardly seems possible to account for these effects in any other way. In view of the anomalous temperature dependencies found in other materials by other workers, a theory of this type may have quite a general application.

An interpretation of the temperature dependence in this way fits in quite well with the idea of exchange modulation within clusters of ions. The exchange interactions are sensitive to intramolecular motions, rather than just the intermolecular ones which are considered in the single ion theory. It is known that in these materials a phase change occurs at about 77°K, which appears to be connected with molecular rotations about the trigonal axes (Chapter 6). It may be that paramagnetic molecules within clusters experience different molecular rotations and so constitute vibrational defects by virtue of their misalignment in the surrounding lattice. Enhanced amplitudes of rotational vibrations within such clusters could strongly modulate the exchange interactions between molecules without producing any comparable modulation of the crystal electric fields within each molecule. In this way one could account for the observed lack of defect relaxation in the single ion process.

CHAPTER 6.

CHROMIUM ACETYLACETONATE.

The E.P.R. spectrum of mixed single crystals of chromium and aluminium acetylacetonate shows that the crystal field has trigonal symmetry (Singer 1955). The spectrum can be fitted by a spin-Hamiltonian of the form

$$\mathcal{H}_s = g\beta \underline{H} \cdot \underline{S} \; + \; D\left(S_z^2 - \tfrac{1}{3}S(S+1)\right) \qquad (6.1)$$

with $g = 1.983$; $2D = -1.18 \text{ cm}^{-1}$ (35.5 Kmc/s).
The value of 2D for Cr^{3+} in the cobalt chelate is slightly larger in magnitude (-1.2 cm^{-1}). In both cases the zero field splitting is so large that at X band frequencies only one spin transition is observable. In weak field notation this is the $+\tfrac{1}{2} \rightarrow -\tfrac{1}{2}$ transition. There is also evidence for a small rhombic term in (6.1) (McGarvey 1964), but since this is so small it has been neglected in the following discussion. To include such a term would complicate numerical computations considerably and would not be warranted in view of the approximations which have to be made later. The orientation of the trigonal axes of the two inequivalent sites is shown in Figure 2. The spectra of the two sites became equivalent when the magnetic field lies in the ac plane.

The predictions of the single ion theories for the relaxation properties of this ion will be considered first and compared with the results obtained in dilute crystals. Since the measurements were all made at low temperatures where the direct process is dominant, this process alone will be considered. At each Cr^{3+} site the nearest neighbour oxygen atoms form an almost regular octahedron. Thus the crystal field is predominantly of cubic form and the

description of the single ion relaxation follows closely that given by Van Vleck for the alums. However Van Vleck's calculations were concerned with the interpretation of non-resonant data obtained from powder samples. Such calculations involve the assumption of a definite spin temperature and averages over angles etc., to obtain a single relaxation time, and are not applicable here. The individual transition probabilities between the various spin states are required, so as to allow explicit calculation of the temperature and angular dependencies.

Crystal Field.

The dominant term in the static crystal field will be of the cubic form

$$V_c = c\left(x^4 + y^4 + z^4 - \tfrac{3}{5}r^4\right) \tag{6.2}$$

In terms of medium crystal field theory the effect of (6.2) is to cause splittings of the ground ^4F term of Cr^{3+}. It can be shown that the splittings are such that a singlet orbital ground state is produced as shown below
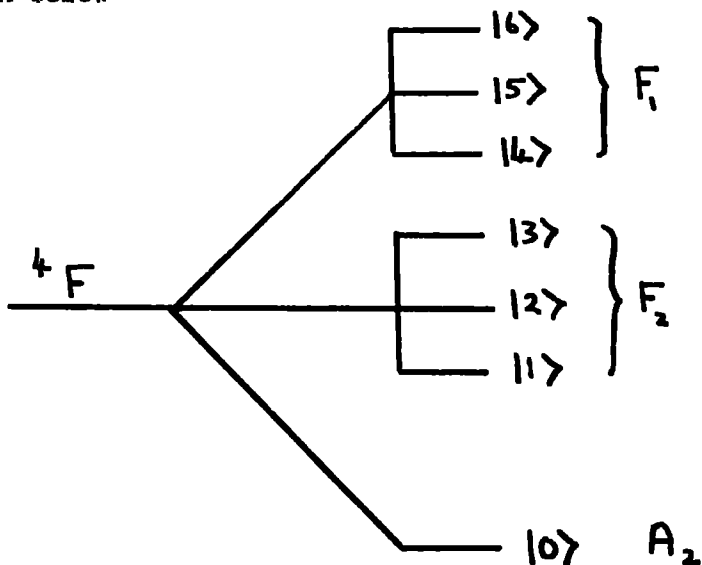
The wavefunctions and energy levels of these crystal field states are

$$|6\rangle = \frac{i}{\sqrt{2}}\left[\sqrt{3/8}(\psi_1 + \psi_{-1}) + \sqrt{5/8}(\psi_3 + \psi_{-3})\right]$$

$$|5\rangle = \frac{1}{\sqrt{2}}\left[\sqrt{3/8}(\psi_1 - \psi_{-1}) - \sqrt{5/8}(\psi_3 - \psi_{-3})\right] \Bigg\} \quad E_2 = \frac{36}{105}C\bar{r}^4$$

$$|4\rangle = \psi_0$$

$$|3\rangle = \frac{i}{\sqrt{2}}\left[\sqrt{5/8}(\psi_1 + \psi_{-1}) - \sqrt{3/8}(\psi_3 + \psi_{-3})\right]$$

$$|2\rangle = \frac{1}{\sqrt{2}}\left[\sqrt{5/8}(\psi_1 - \psi_{-1}) + \sqrt{3/8}(\psi_3 + \psi_{-3})\right] \Bigg\} \quad E_1 = \frac{20}{105}C\bar{r}^4$$

$$|1\rangle = \frac{1}{\sqrt{2}}\left[\psi_2 + \psi_{-2}\right]$$

$$|0\rangle = \frac{i}{\sqrt{2}}\left[\psi_2 - \psi_{-2}\right] \qquad\qquad E_0 = 0$$

$$(6.3)$$

ψ_λ denotes an orbital state of the ^4F term with $L_z = \lambda$.
The linear combination of states in (6.3) is chosen so that each eigen-
function is real.

By making some assumptions concerning the distribution of electric charge
over the octahedral structure it is possible to give the constant C some
quantitative significance. It is assumed that a point charge, Ze ,
resides on each oxygen atom, which is at a distance R from the Cr^{3+} ion,
then

$$C = 35Ze^2/4R^5$$

The addition of trigonal or low symmetry components to the crystal field would cause further splittings of the states (6.3). However, for the purposes of relaxation theory, these splittings are not significant, being much smaller than those due to the cubic term. It is of course essential to include such terms when attempting to account for such things as the zero field splitting parameter D. Also such terms must be considered in the case of the T_i^{3+} ion, where a purely cubic crystal field leaves an orbitally degenerate ground state.

Direct Process.

For explicit calculations involving transition group ions the most convenient formulation of the theory is that of Mattuck and Strandberg (1960). Here the spin-lattice interaction is expressed in spin-Hamiltonian form, thus enabling matrix elements to be evaluated readily. In this notation the general expression for the direct process spin-lattice relaxation is

$$
\mathcal{H}_{SL} = \sum_{P,f} A^{fP}(a_P^+ + a_P)\left[\sum_{i>j}\left\{ \beta H\lambda \mathcal{L}_i^f (g_{kk'}S_i + S_i\varepsilon - \varepsilon S_i) \right.\right.
$$
$$
\left. + 2\beta\lambda \mathcal{L}_{ij}^f(S_iH_j + S_jH_i) + \lambda^2 \mathcal{L}_{ij}^f(S_iS_j + S_jS_i)\right\}
$$
$$
\left. + \sum_i \mathcal{L}_{ii}^f(\lambda^2 S_i^2 + 2\lambda\beta S_iH_i)\right]
$$

$$(6.4)$$

where
$$
\mathcal{L}_i^f = \sum_n \frac{\langle o|V^f|n\rangle\langle n|L_i|o\rangle}{(E_n - E_o)^2}
$$

$$
\mathcal{L}_{ij}^f = \sum_{nn'} \frac{\langle o|L_i|n\rangle\langle n|L_j|n'\rangle\langle n'|V^f|o\rangle + \langle o|L_iV^fL_j|o\rangle + \langle o|V^fL_iL_j|o\rangle}{(E_n - E_o)(E_{n'} - E_o)}
$$

and

$$
\langle s|\varepsilon|s'\rangle = E_s S_{ss'}/\beta H
$$
$$
g_{kk'} = (E_k - E_{k'})/\beta H
$$

a_P^+, a_P, V^f, A^{fp}, are defined by (4.5) and (4.11). It should be noted that (6.4) is not identical with Mattuck and Strandberg's published expression, which contains numerous misprints. Similar misprints are present in the expressions given by these authors for the Raman process (A.M. Stoneham, private communication). The transition probability for spin-lattice relaxation between two spin states $|k\rangle$ and $|k'\rangle$ of (6.1) is

$$U_{kk'} = \frac{2\pi}{\hbar^2} \langle k| \mathcal{H}_{SL} |k'\rangle \, \rho(\omega) \tag{6.5}$$

It is important to note that at low fields the main term in (6.4) is quadratic in the spin operators. It is easily shown that this term has vanishing matrix elements between Kramers' conjugate states. Only the terms linear in the spin operators are non vanishing in this case and so an explicit dependence on applied magnetic field is introduced. This effect is known in the present context as the "quadrupole selection rule". It is a consequence of time reversal symmetry in Kramers' systems and was discussed in these terms in Chapter 4. In the case of multilevel spin systems, such as Cr^{3+}, this rule shows that the quadratic spin operators will cause rapid relaxation between states belonging to different Kramers' doublets. Since these relaxation transitions are sufficient in themselves to bring the spin system to equilibrium with the lattice, there is no need to consider the smaller linear terms in (6.4). In the following therefore only the quadratic spin operator terms of (6.4) will be retained.

To evaluate (6.4) in any particular case it is necessary to calculate the various tensor components d_{ij}^f. From their definition it can be seen that they involve the matrix elements of the dynamic crystal field and orbital angular momentum between the various eigenstates (6.3). Of the

fifteen purely vibrational modes of the octahedral complex it is possible to show that only the five symmetric modes are effective in causing spin-lattice relaxation (Van Vleck 1939). Using Van Vleck's numbering for these modes the dynamic crystal field potential takes the form

$$V = \sum_{f=2}^{6} V^f Q_f \qquad (6.6)$$

The matrix elements of these five potential functions, V^f are given by Van Vleck as are the matrix elements of the orbital angular momentum. Using these results the various non zero components of the $\mathcal{L}_{ij}^f$ tensor are

$$\mathcal{L}_{yy}^2 = -\mathcal{L}_{xx}^2 = a/E_1^2$$

$$\mathcal{L}_{xx}^3 = \mathcal{L}_{yy}^3 = -\frac{a}{\sqrt{3}E_1^2} \; ; \; \mathcal{L}_{zz}^3 = \frac{2a}{\sqrt{3}E_1^2}$$

$$\mathcal{L}_{xy}^4 = \mathcal{L}_{xz}^5 = \mathcal{L}_{yz}^6 = b/E_1^2$$

$$a = \frac{25}{3}\left(\frac{Ze^2\overline{r^4}}{R^6}\right)$$

$$b = -\frac{76}{21}\left(\frac{Ze^2\overline{r^2}}{R^4}\right) + \frac{10}{63}\left(\frac{Ze^2\overline{r^4}}{R^6}\right)$$

$$(6.7)$$

Using the values of the tensor components (6.7) the matrix elements of (6.4) can now be evaluated, squared and then averaged over all polarisations, phases and directions of propagation of the phonons. When this averaging is done it is found (Van Vleck 1940) that cross products between terms arising from different normal modes of the octahedral complex vanish. Using Van Vleck's results for these averages and evaluating the matrix

element of the lattice variables the following spin-lattice transition probability is obtained.

$$U_{kk'} = \frac{2\lambda^4 a^2 R^2 \omega_P^3}{3\rho\pi \hbar v^5 E_1^4} \left\{ \begin{array}{c} n_P \\ \text{or} \\ n_{P+1} \end{array} \right\} \left[S_2^2 + S_3^2 + \eta(S_4^2 + S_5^2 + S_6^2) \right]$$

(6.8)

where

$$S_2 = \langle k| S_y^2 - S_x^2 | k' \rangle$$
$$S_3 = \langle k| \sqrt{3} S_z^2 - \tfrac{1}{\sqrt{3}} S(S+1) | k' \rangle$$
$$S_4 = \langle k| S_x S_y + S_y S_x | k' \rangle$$
$$S_5 = \langle k| S_x S_z + S_z S_x | k' \rangle \qquad\qquad (6.9)$$
$$S_6 = \langle k| S_y S_z + S_z S_y | k' \rangle$$
$$\eta = (b/a)^2$$

So far in this calculation the x,y,z axes have referred to the fourfold axes of the octahedral structure. It must be noted however that the spin-Hamiltonian (6.1) refers to the threefold axis as Z axis. So, before the matrix elements (6.9) can be evaluated between the eigenstates of (6.1), the spin operators must be transformed so that they too refer to the threefold axis as Z axis. Transformed in this way the spin operators (6.9) become

$$S_2 = \tfrac{1}{\sqrt{3}} \langle k| S_x S_y + S_y S_x + \sqrt{2}(S_x S_z + S_z S_x) | k' \rangle$$
$$S_3 = \tfrac{1}{\sqrt{3}} \langle k| S_y^2 - S_x^2 - \sqrt{2}(S_y S_z + S_z S_y) | k' \rangle$$
$$S_4 = \tfrac{1}{\sqrt{3}} \langle k| 3 S_z^2 - S(S+1) | k' \rangle$$
$$S_5 = \tfrac{1}{\sqrt{3}} \langle k| \sqrt{2}(S_x S_y + S_y S_x) - (S_x S_z + S_z S_x) | k' \rangle$$
$$S_6 = \tfrac{1}{\sqrt{3}} \langle k| \sqrt{2}(S_y^2 - S_x^2) + (S_y S_z + S_z S_y) | k' \rangle$$

(6.10)

For simplicity a slightly different combination of spin operators has been employed in (6.10) for S_4, S_5 and S_6. This corresponds to the use of Van Vleck's normal modes Q_4', Q_5' and Q_6' rather than Q_4, Q_5, Q_6 as in (6.9).

Calculation of Relaxation Times.

The matrix elements of (6.10) can now be evaluated between the various spin eigenstates of (6.1). These spin states will be numbered 1, 2, 3, 4, in order of decreasing energy. The transition $1 \rightarrow 2$ corresponds to the one observed at X band frequencies. The general solution for a spin eigenstate is of the form

$$|1\rangle = a_1|+3/2\rangle + b_1 e^{i\phi}|+1/2\rangle + c_1 e^{2i\phi}|-1/2\rangle + d_1 e^{3i\phi}|-3/2\rangle$$

The value of the real coefficients a,b,c,d depend on the polar angle, θ, between the trigonal axis and the magnetic field. ϕ is the azimuthal angle of the applied field. Computer solutions of (6.1) were obtained for θ varying in $10°$ steps from $0°$ to $90°$, such that in each case the energy difference between states 1 and 2 corresponded with the operating frequency of 9.3 KMc/s.

Of the various transitions within the four spin states the most important will be those connecting states 1 and 2 with states 3 and 4, i.e. transitions across the zero field splitting. The transition rates for these processes will be large because of the relatively large frequencies involved. Also the transition rates from 1 to 2 say will be small because of the quadrupole selection rule. (In fact such transitions are completely forbidden at $\theta = 0°$).

With these approximations the rate equations are

$$\frac{dn_1}{dt} = -n_1(U_{13} + U_{14} + U_{41}) + n_3(U_{31} - U_{41}) - n_2 U_{41}$$
$$+ N U_{41}$$

$$\frac{dn_2}{dt} = -n_2(U_{23} + U_{24} + U_{42}) + n_3(U_{32} - U_{42}) - n_1 U_{42}$$
$$+ N U_{42} \qquad (6.11)$$

$$\frac{dn_3}{dt} = -n_3(U_{31} + U_{32}) + n_1 U_{13} + n_2 U_{23}$$

The general solution of (6.11) for the recovery of the populations
($n_2 - n_1$) contains three time constants

$$(n_2 - n_1) = (n_2 - n_1)\left(1 - A e^{-\lambda_1 t} - B e^{-\lambda_2 t} - C e^{-\lambda_3 t}\right) \qquad (6.12)$$

From the computed eigenfunctions and eigenvalues of (6.1) the matrix

elements (6.10) were calculated and inserted into (6.8) to obtain the

various transition probabilities. A computer programme was written to

solve (6.11) for the three time constants and amplitudes occurring in

(6.12). Although the time constants are fixed parameters the amplitudes

depend to some extent on the nature of the initial population disturbance.

Two limiting cases were considered, consisting of saturating pulses that

were very short or very long compared with the relaxation times of (6.12).

The results of these computer calculations show that of the three time constants in (6.12), the one of intermediate value has the largest amplitude under all conditions. The shortest time constant has a small amplitude for both short and long saturating pulses and would not be observed experimentally. The amplitude associated with the longest time constant however is not negligible. Using long saturating pulses the amplitude of this term is predicted to be of the order of 20%, except in the vicinity of $\theta = 90°$ where it is extremely small. An exponential term with an amplitude of this order should be detectable experimentally, although the accuracy of the determination of its time constant would not be very high.

Dilute Samples.

The crystals were in the form of psuedo-hexagonal plates with well developed faces. Using silicone vacuum grease they were bonded to a perspex wedge fixed to the side of the microwave cavity. The wedge was cut and oriented so that the two molecular trigonal axes and the crystal **b** axis were in the horizontal plane. The magnetic field could then be rotated to allow measurements at all value of θ from $0°$ to $90°$.

During the course of these measurements it was observed that there was a phase change in these crystals. For the aluminium chelates this phase change occurs at about $100°K$. The corresponding temperature for the cobalt chelates was not determined accurately but lies between $70°K$ and $4.2°K$. The room temperature E.P.R. spectrum consists of two overlapping spectra, characteristic of a pair of inequivalent sites related to each other by $180°$ rotations about the **b** axis (Figure 2). At temperatures below the phase change point there are three such pairs of inequivalent

sites. This phase change causes each room temperature resonance line to split into three components. The splitting however is not very great, being of the order of the resonance line width and in fact in the more concentrated crystals the three components of the line could barely be distinguished. Since no such line splittings were observed in the titanium chelates even in the most dilute crystals which have narrow resonance lines, this phase change may be associated with molecular rotations about the threefold molecular axes. Each of the three sites associated with one split line will then have the same trigonal Z axis but slightly different rhombic axes x,y. The spectrum of the titanium chelate is not sensitive to the rhombic components of the crystal field whereas it is known from room temperature measurements that the spectrum of the chromium chelate does have a small dependence on these rhombic terms(McGarvey 1964).

Relaxation time measurements were made on various crystals and the results show that there is little if any concentration dependence up to about 2%. To test the predictions of the single ion theories the most dilute sample was chosen ($0 \cdot 1$ molar percent) so as to eliminate as far as possible any complications due to cross relaxation between the various levels of the spin system. The angular dependence of the relaxation time was determined at $4.2^{\circ}K$, and the temperature dependence in the helium range at the angle $\theta = 0^{\circ}$.

Angular dependence.

Using short saturating pulses (100μ secs) the relaxation traces were found to be unexponential with a time constant of 0.5 msecs. at $\theta = 0^{\circ}$ and $T = 4.2^{\circ}K$. It was found that the relaxation time increased by about 50% as the magnet was rotated to the $\theta = 90^{\circ}$ orientation. The variation

over this angular range is shown in Figure 11. Also shown in this

Figure are the theoretical predictions for the dominant time constant

of (6.12), for various values of the parameter η. It can be seen

that the fit between theory and experiment is quite good for $\eta = 0$.

The fit is not very good if a value of η of 5 or 50 is used. From the

definition of η in (6.7) it can be seen that this parameter depends on

various averages over 3d radial wavefunctions (i.e. $\overline{r^2}$, $\overline{r^4}$) which

would be difficult to predict from first principles. However Van Vleck

(1940) gives some semiempirical estimates of the various terms in (6.7).

These estimates yield a value of η of 0·3, which is not in conflict

with the relaxation results. Such a low value of η shows that the

direct process relaxation is caused mainly by the normal modes Q_2 and Q_3.

Computer solutions were also obtained for (6.11) using the spin-

Hamiltonian (6.1) with a zero field splitting parameter D of opposite

sign (i.e. $+ve\ D$). The effect of a change in the sign of D is to

interchange the transition probabilities U_{ij}, U_{ji} in (6.11). In

this case it was found that the dominant time constant is the longest.

The predicted angular dependence for this dominant time constant is shown

in Figure 12, where it can be seen that the variation has the opposite sign

to that of Figure 11 , tending to a shorter time constant as θ tends to

90°. These predictions were tested using a dilute Cr^{3+} doped $Mg Al_2 O_4$

spinel ($0.011\%\ Cr$). Previous measurements by the author (Dugdale 1965)

of the temperature dependence in a series of doped spinels had shown that,

in this crystal, the relaxation was dominated by the single ion process.

The Cr^{3+} site in these crystals consists of a nearly regular octahedron of

oxygen atoms with the spin–Hamiltonian Z axis oriented along the threefold

FIGURE 11

ANGULAR DEPENDENCE FOR NEGATIVE D

ⴲ EXPERIMENTAL POINTS FOR $Cr^{3+}:Al(C_5H_7O_2)_3$, (0·1%)

At 9·3 KMc/s ; 4·2°K
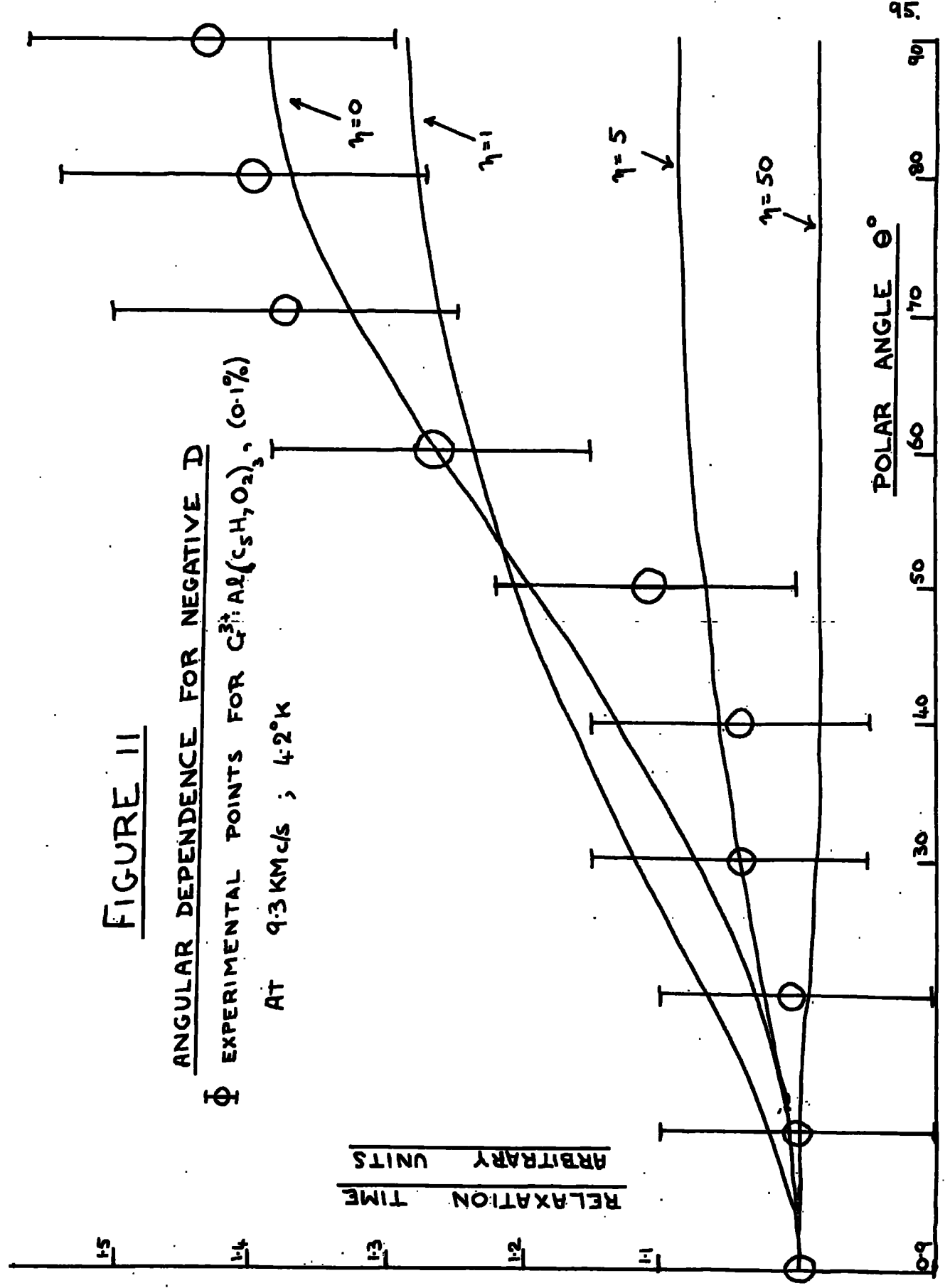
axis of this cubic array. The zero field splitting parameter 2D of
+55.5 KMc/s is of opposite sign and somewhat greater magnitude than
that found in the acetylacetonates. Thus the previous theoretical
expressions developed for the acetylacetonates should be applicable
here.

The experimental results for this sample are shown in Figure 12.
In this case the predicted angular dependence is not very sensitive to
the choice of the parameter η , and the data is not sufficiently accurate
to clearly distinguish between the various curves. Possibly a low value
of η gives the best fit, the other curves having too rapid a variation
around $\Theta = 0^\circ$. The most important feature of these results however lies
in the opposite sign of the angular variation compared to that of the
acetylacetonate crystals. This not only provides evidence that the
parameter D is of negative sign in the acetylacetonates, but also gives
confirmation of the essential correctness of the single ion theory and the
rate equations (6.11).

Temperature Dependence.

In the direct process the observed $+\frac{1}{2} \rightarrow -\frac{1}{2}$ transition relaxes to
equilibrium through transitions via the $\pm\frac{3}{2}$ spin states. This is in
effect an example of the Orbach process discussed in Chapter 4. The only
difference between the present situation and that usually considered in
Orbach processes is the fact that the intermediate $\pm\frac{3}{2}$ states are not
very far removed in energy. Nevertheless the energy difference is
sufficiently large compared with kT to make the high temperature approxi-
mation of the Bose-Einstein factors (n_p and n_p+1 in (6.8)) inadmissible.
Thus one expects deviations from the linear temperature dependence normally
considered characteristic of the direct process. For a positive D the $\pm\frac{3}{2}$

FIGURE 12

ANGULAR DEPENDENCE FOR POSITIVE D

Φ EXPERIMENTAL POINTS FOR $Cr^{3+} : MgAl_2O_4$ (0·011%)

AT 9·3 KMc/s ; 4·2°K

$\eta = 0$
$\eta = 1$
$\eta = 5$
$\eta = 50$

RELAXATION TIME
ARBITRARY UNITS

POLAR ANGLE θ

97.
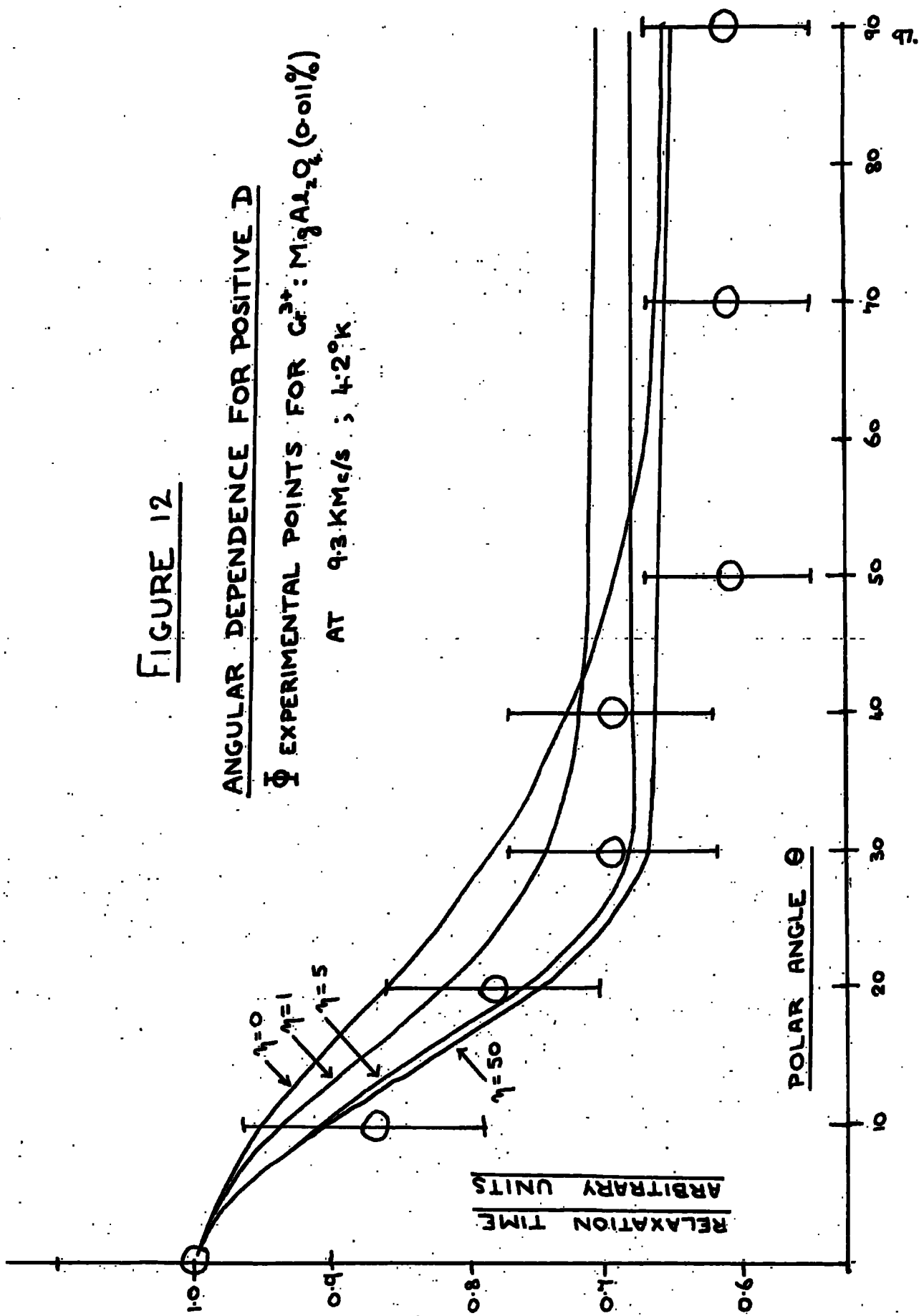
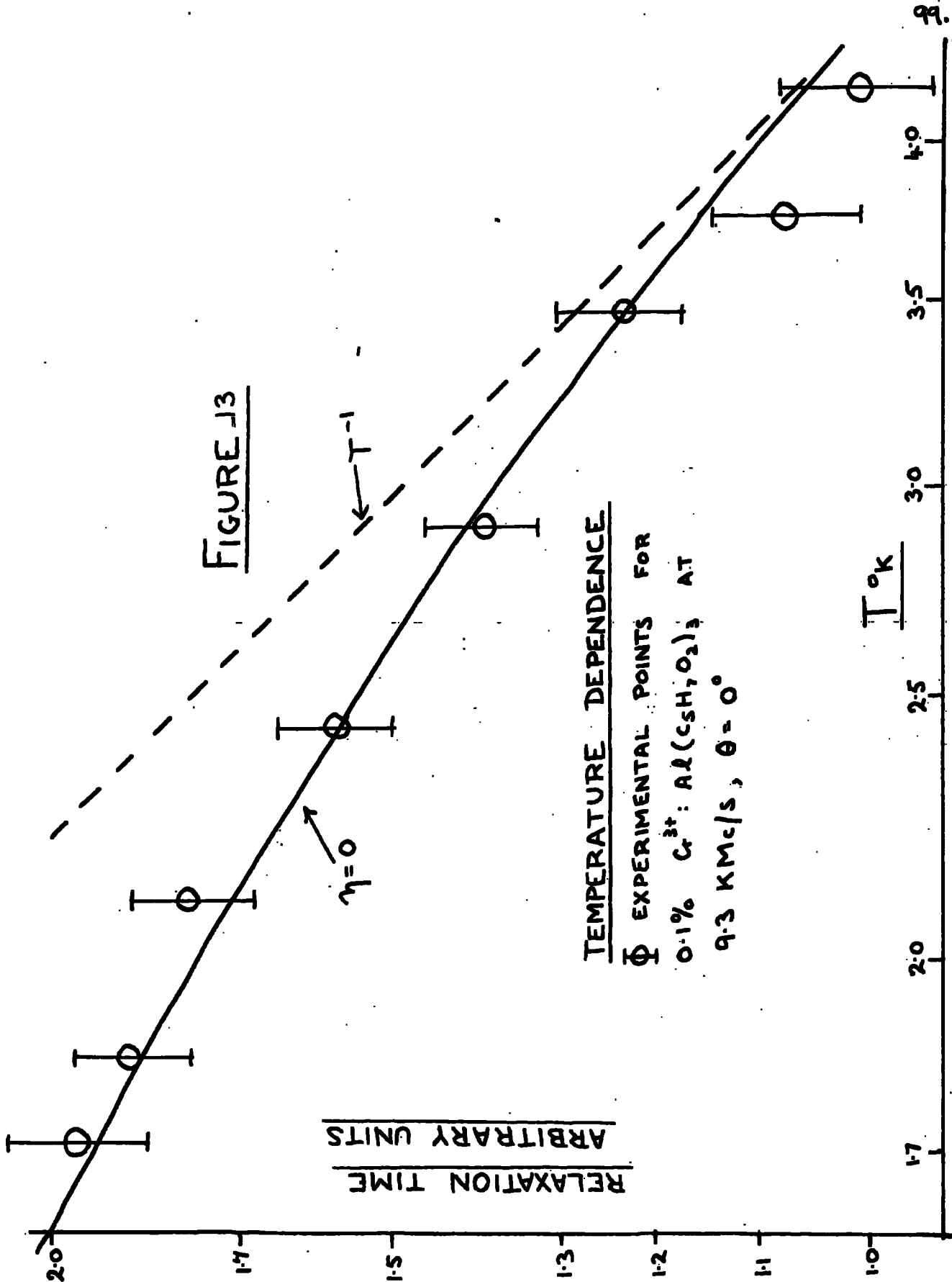states have higher energies than the $\pm \frac{1}{2}$ states. One expects in this case an enhanced temperature dependence, tending in the limit $D \gg kT$ to the exponential form characteristic of the Orbach process. Such temperature dependencies have been found previously for the spinels (Dugdale 1965) and in other materials (Emel'yanova et al 1963). For the present case of the acetylacetonates the $\pm \frac{3}{2}$ states lie below the $\pm \frac{1}{2}$ states in energy. This is so to speak an inverted Orbach process which can be shown leads quite generally to a reduced temperature dependence, becoming temperature independent in the limit $D \gg kT$.

The experimental results shown in Figure 13 do indeed show this reduced temperature dependence and agree quite well with the theoretically predicted temperature dependence (also shown in the figure). This gives added confirmation of the negative sign of the zero field splitting parameter D in the acetylacetonates.

Some efforts were made to detect the longer time constant component of the relaxation traces predicted by the rate equation analysis. It was predicted that this longest time constant would be about 3.5 times longer than that of the dominant term and, under long saturating pulse conditions, have an amplitude of the order of 20% at $\Theta = 0°$, $T = 4.2°K$. There was some evidence that such a relaxation component was present in the 0.1% sample, in that the measured relaxation times tended to be about 20% longer under long saturating pulse conditions (5 msecs.). It was found that in more concentrated crystals, of the order of 1%, a longer relaxation component was clearly detectable at $\Theta = 0°$ but not at $\Theta = 90°$. Due to the small amplitude of this component, the time constant could not be determined accurately but lay in the region of 1 msecs. This is somewhat smaller than the expected value of 1.8 msecs., suggesting that the rate equations

FIGURE 13

TEMPERATURE DEPENDENCE.

$\oint$ EXPERIMENTAL POINTS FOR

0·1% $Cr^{3+} : A\ell(C_5H_7O_2)_3$, AT

9·3 KMc/s, $\theta = 0°$

T^{-1}

$\eta = 0$

RELAXATION TIME
ARBITRARY UNITS

$T°_K$

(6.11) do not predict the ratios of the various time constants accurately.

The failure to unambiguously detect this longer time constant in the most dilute samples is probably connected with the poor signal to noise ratio inherent in these measurements. Its observation in the 1% samples does not appear to be connected with any concentration dependence since the dominant time constant was unchanged up to 2% concentration. More accurate determinations of the longer time constant could only be made by improving the signal to noise ratio. This could be achieved by the use of a Computer of Average Transients. An accurate determination of the ratios of the time constants would be of some interest since this quantity, like the angular and temperature dependencies, is connected with the fundamental structure of the theory and is independent of most of the approximations and unknown parameters which are involved in the scaling factor of (6.8). Such techniques would also improve the accuracy of the determination of the angular dependence and allow an accurate assignment of the parameter η .

Absolute value of the Relaxation Times.

The occurance of so many unknown parameters in the scaling factor of (6.8) makes it very difficult to give any accurate estimate of the absolute value of the relaxation times, quite apart from the uncertainties involved in the crystal field description of the relaxation process. However, the fact that $\eta = 0$ may be taken in (6.8) simplifies somewhat the numerical estimate in that it allows a purely semi-empirical estimate of the constant a. This constant involves fourth order crystal field terms in the same way as the splitting of the orbital states by the cubic crystal field. The latter quantity can then be obtained from the optical absorption data of Piper and Carlin (1963). Using the value of $10Dq$ given by these authors

(E_1 in the present notation) of 18,000 cm^{-1} and the following values for
the other parameters

$$\lambda = 90 \ cm^{-1}$$
$$r = 2.3 \ 10^5 \ cm/sec$$
$$\rho = 1.3 \ gm/cc$$

equation (6.8) becomes

$$U_{k k'} = \frac{1}{70} \upsilon^3 \left\{ \begin{matrix} n_p \\ or \\ (n_p+1) \end{matrix} \right\} \left[S_2^2 + S_3^2 \right] \tag{6.13}$$

with υ in KMc/s.

From this result and the computed value of the matrix elements
the dominant time constant is predicted to be 70 μ Secs. compared with the
experimentally observed value of 500 μ Secs. The fact that this estimate
is shorter than that given by Van Vleck for the alum is due almost entirely
to the larger zero field splitting in the acetylacetonates. The order of
magnitude of the predicted relaxation is in agreement with the experimental
results; no better agreement than this could be expected in view of the
many approximations inherent in the theory. Probably the greatest error
arises from the treatment of the lattice vibrations. The treatment given
supposes that all atoms within the crystal have equal amplitudes of vibration
in the acoustic spectrum. In fact the intermolecular forces are much stronger
than the intramolecular ones. The amplitudes of vibration within the
molecular complex will therefore be overestimated by such a model, leading
to an overestimate of the relaxation rate.

Exchange Interactions.

Since the exchange interactions between paramagnetic ions are thought to be connected with concentration dependent relaxation, some efforts were made to determine the nature of these interactions in the acetylacetonates. Exchange interactions are a purely quantum mechanical phenomenon, arising through the combined action of Coulomb interaction and the exclusion principle. Since these interactions depend on the spatial overlap of adjacent electron orbitals they are typically of short range, and are usually only significant between near neighbour ions within a cluster. In dilute crystals by far the most numerous type of cluster corresponds to a pair of interacting ions. The presence of an exchange interaction term in the spin-Hamiltonian of such a pair may modify considerably the E.P.R. spectrum. This will manifest itself in the E.P.R. spectrum of dilute crystals by the appearance of satellite lines close to those of the single ions. In the simple spin system of the titanium chelate these satellite lines unfortunately coincide with those of the single ions, and so in this case the exchange interactions cannot be studied directly by E.P.R. methods. For this reason the more complicated chromium doped crystals were chosen for detailed study. Here the presence of the zero field splitting ensures that, in general, the satellite lines do not coincide with those of the single ions.

Several chromium doped chelate crystals in the concentration range 2-6% were studied. In all samples a multitude of satellite lines was observed. The intensity of these lines was rather low, so that measurements were more easily made at liquid nitrogen temperature rather than room temperature. Not only was the intensity of the resonance lines increased at these temperatures but there appeared to be also some reduction in line width,

suggesting that the relaxation time of the satellite lines was shorter than that of the single ions. Because of the low temperatures used the chromium doped cobdlt acetylacetonate crystals were used, so as to avoid excessive complications due to the low temperature phase change mentioned earlier. In view of the isomorphous nature of these materials one would expect the exchange interactions to be essentially similar in the cobolt and aluminium doped crystals, and indeed the room temperature E.P.R. spectra of the satellite lines in these two materials were not noticeably different. The intensity of these satellite lines was strongly dependent on the sample concentration; below 2% concentration the satellite lines were difficult to detect but were very easily observed in 6% samples. The angular variation of the satellite spectrum was very complex with much crossing of resonance lines. To distinguish between the various resonance lines it was necessary to use 2% samples; the narrower lines found in these samples more than compensated for the greater intensities associated with the more concentrated samples.

From the crystal structure (Figure 2) it can be seen that there are several different types of near neighbour sites in the acetylacetonates. These can be classified into two main types, namely pairs of equivalent ion sites and pairs of inequivalent ion sites. Of the pairs composed of equivalent ions at least three types can be distinguished. One such pair has its axis along the crystal $\underline{b}$ axis and has the smallest interionic distance of all namely 7.5 $\overset{o}{A}$. The other two types of equivalent pairs have axes lying in the $\underline{a}\underline{b}$ plane with slightly larger interionic distances. Of the various inequivalent ion pairs that can be distinguished only the one with its axis along the crystal $\underline{c}$ axis has an interionic distance comparable with those
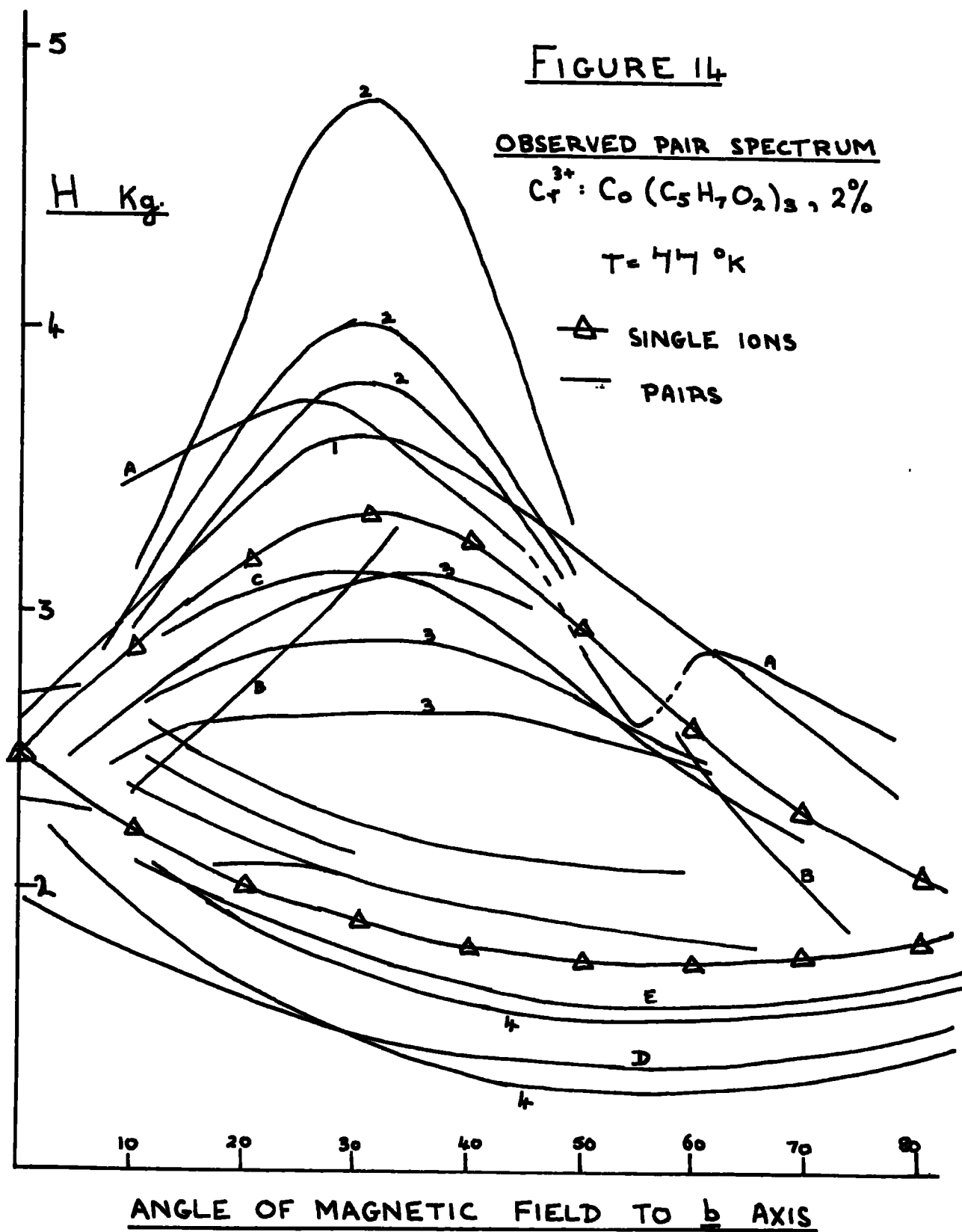
of the equivalent pairs. Thus the crystal structure suggests that there may be several types of pairs in the acetylacetonates each with a different exchange constant. Since each pair produces many satellite lines the complete spectrum is expected to be very complex, as indeed is the case. To verify that the satellite lines observed are due to exchange interactions between ion pairs and if possible to distinguish between the various pair types, a careful plot of the angular variation of the E.P.R. spectrum was made at $77^{\circ}K$, using a 2% sample. The crystal was oriented so that the magnetic field swept through the plane which contains the crystal $\underline{b}$ axis and the trigonal axes of the two inequivalent ions (Figure 2).

This plane includes the $\theta = 0^{\circ}$ and 90° orientations for each inequivalent ion and so the spectrum exhibits the greatest angular variation. Angular plots were made over a 90° range, from the crystal $\underline{b}$ axis through one of the trigonal axes to the $\underline{a}\underline{c}$ plane. The E.P.R. spectrum over this range is shown in Figure 14. Not all the satellite lines observed could be followed throughout the entire angular range. Where such a line is shown in Figure 14 ending abruptly, either the intensity became too low for detection or the resonance was lost among other satellite lines or disappeared into the wings of the main lines. The assignment of these various lines to the relevant ion pairs within the crystal will be discussed separately for the two cases of equivalent and inequivalent pairs.

Equivalent Pairs.

Since the orbital angular momentum of the Cr^{3+} ion is well quenched in the acetylacetonates, one expects that the exchange interactions will be of the isotropic form (Erdos 1966). A pair of such interacting ions has a spin-Hamiltonian of the form

$$\mathcal{H} = g\beta \underline{H} \cdot (\underline{S}_1 + \underline{S}_2) + D\left(S_{1z}^2 + S_{2z}^2 - \frac{2}{3}s(s+1)\right) + J\,\underline{S}_1 \cdot \underline{S}_2$$

$$(6.14)$$

FIGURE 14

OBSERVED PAIR SPECTRUM

$Cr^{3+} : Co\,(C_5 H_7 O_2)_3$, 2%

$T = 44\ °K$

△ SINGLE IONS

—— PAIRS

ANGLE OF MAGNETIC FIELD TO b AXIS

where the Z axis refers to the common trigonal axis. The complete

solution of (6.14) is rather formidable, involving the diagonalisation

of many 16 x 16 matrices. However, in view of the rather large interionic

distances involved, it is expected that $J < g\beta H < D$, so that a

perturbation treatment of the exchange interaction term will not be too

bad an approximation. Accordingly the computer solutions of (6.1) previously

evaluated for relaxation time calculations were used as a starting point in

a perturbation calculation. Labelling the single ion states $|1\rangle, |2\rangle, |3\rangle, |4\rangle$

as before the corresponding zeroth order pair states are $|1,1\rangle$, $|1,2\rangle$

$\frac{1}{\sqrt{2}}\left[|1,2\rangle \pm |2,1\rangle\right]$ etc. A computer programme was written to evaluate the first

order perturbation shifts of these pair states. The fact that the measure-

ments are made as a function of applied field at a fixed frequency complicates

the theoretical position somewhat. The perturbation calculation yields the

frequency shifts of transitions at constant field. To translate these

results into an experimentally significant form it is necessary to use a

scaling factor which depends on the nature of the field-frequency relation-

ship of the relevant transition. Fortunately at X band frequencies, the

field-frequency relationship is almost linear so that the translation from

frequency shifts to field shifts is not too difficult in this case. After

considerable machine and hand calculation the predicted satellite spectrum

shown in Figure 15   was obtained. In this Figure a J value of $+1$ KMc/s

was assumed, corresponding to a weak antiferromagnetic interaction. To

within the approximations inherent in a perturbation calculation the spectrum

for other J values can be obtained from Figure 15 by suitably scaling the

splittings of the satellite lines from the main single ion lines. In

particular the spectrum to be expected from a ferromagnetic interaction of

the same magnitude can be obtained from Figure 15 by reflecting each

FIGURE 15

PAIR SPECTRUM OF EQUIVALENT IONS

△ SINGLE IONS

—— PAIRS

J = +1 KMc/s

H Kg.

ANGLE OF MAGNETIC FIELD TO b AXIS
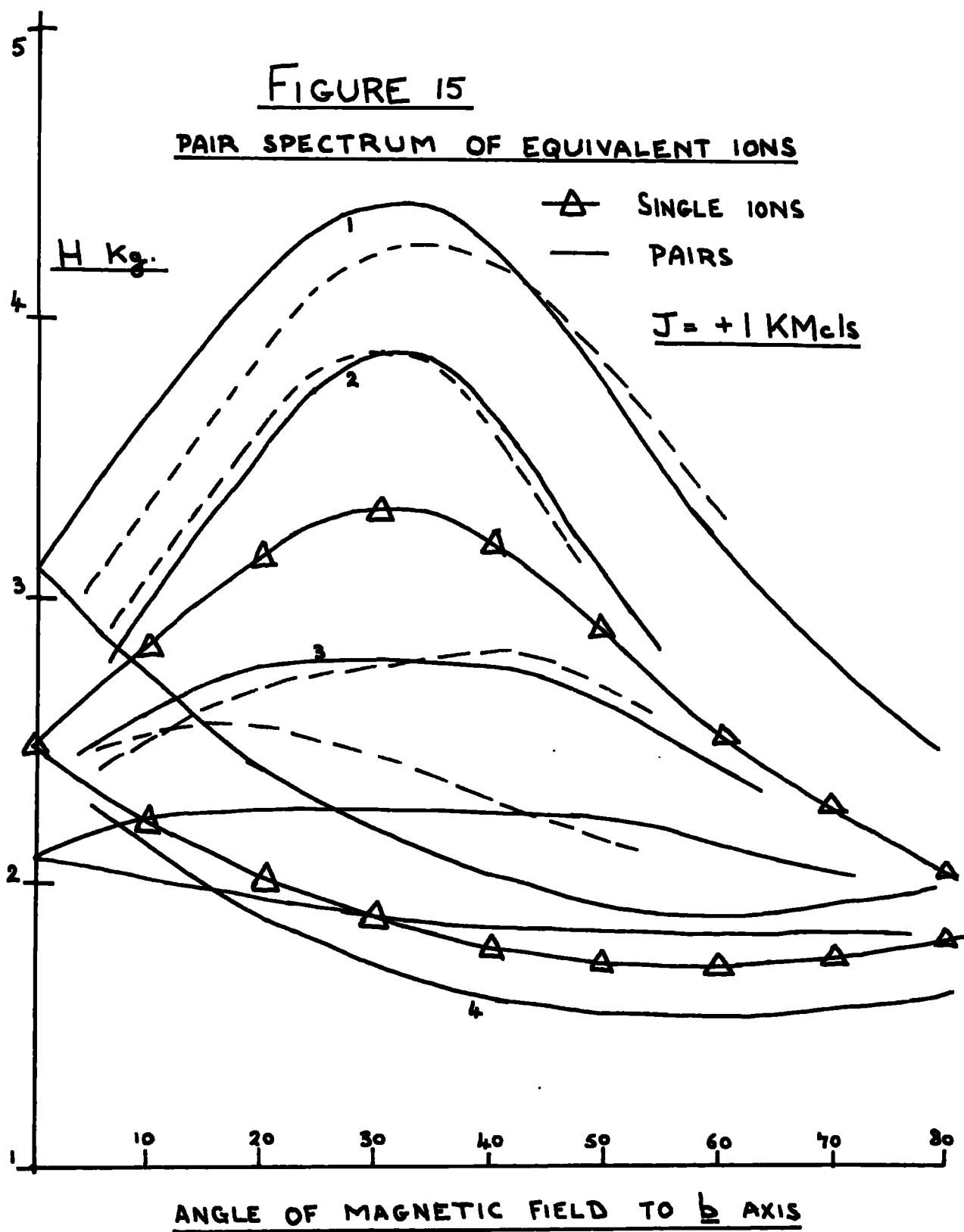
satellite line through the main single ion line. When this is done a
slightly different satellite spectrum is obtained, thus allowing assignment
of the sign as well as the magnitude of the exchange interaction.

For small exchange interactions of the order of 1 KMc/s ($3.3 \, 10^{-2} \, cm^{-1}$)
the influence of dipolar interactions may be significant. This was invest-
igated for the case of a pair whose axis lies along the **b** axis, with an
interionic distance of 7.5A^0 . The dipolar interaction is of the form

$$\mathcal{H}_D = g^2 \beta^2 / r_{12}^3 \left[\underline{S}_1 \cdot \underline{S}_2 - 3 (\underline{b} \cdot \underline{S}_i)(\underline{b} \cdot \underline{S}_2) \right] \qquad (6.15)$$

With $r_{12} = 7.5 \, Å$ the magnitude of the dipolar term $g^2 \beta^2 / r_{12}^3$ is $4.1 \, 10^{-3} \, cm^{-1}$.
A computer programme was written, similar to the previous one, to evaluate
the field splittings of the satellite lines produced by such a dipolar
interaction. The corrections that this term imposes on the spectrum
previously obtained is shown in Figure 15 by broken lines. The dipolar
corrections for such a pair are not insignificant for some of the satellite
lines and their effect is to produce a characteristic asymmetry in the
spectrum about the trigonal axis (angle of 31° in the diagram). This
asymmetry is of some help in identifying the various resonance lines.

The experimental results contained in Figure 14 show many lines,
some of which are more or less symmetrical about the trigonal axis and one
or two lines which are not. The symmetrical spectrum can be assigned to
pairs of equivalent ions. The satellite lines which are displaced most
from the main lines are quite symmetrical about the trigonal axis. This
shows that they are due to pairs which do not lie along the **b** axis. Most
probably therefore they correspond to pairs whose axes lie in the **a b** plane.

Some estimates were made of the dipolar corrections to be expected from
pairs of this type and the results show that the corrections are quite
small and do not involve significant asymmetry. The lines that are
observed fit quite well the theoretical predictions without dipolar
corrections. Three types of such pairs can be distinguished with exchange
constants of

$$+ 0.85 \; , \; + 1.21, \quad + 2.40 \quad KMc/s$$

Not all the satellite lines of each pair can be distinguished. The most
highly displaced pair lines are not in fact evident in Figure 14   .
Resonance lines were observed however at both high and low applied magnetic
field which are not shown in the Figure since they were rather broad and
extremely difficult to follow as a function of angle. In fact from the
pairs with the largest exchange interaction these lines would lie so far
from the main lines that they would be outside the range of available
magnetic field in the region around the trigonal axis.

Other lines can be distinguished which correspond with a further type
of equivalent pair. In this case the asymmetric dipolar correction is quite
marked and is of the form expected from pairs oriented along the crystal $\underline{b}$
axis. After correcting for the dipolar interaction the exchange constant J
is found to be + 0.4 KMc/s. It is rather surprising that the exchange
constant should be so small since the interionic distance for these pairs
is smaller than that of the other types. Also the fact that three sets of
pairs in the $\underline{ab}$ plane were distinguished rather than just two suggests that
the simple crystal structure shown in Figure 2 is not quite correct. Instead
of being a simple layered structure as indicated in the Figure it may be that
ions such as 1 and 2 of Figure 2 are displaced to positions between layers in

the manner suggested by Astbury (1926). In this case one would expect
four types of pairs in addition to the one oriented along the $\underline{b}$ axis.
As was stated earlier numerous resonance lines were observed which for
various reasons could not be clearly distinguished and are not recorded
in Figure 14 . It may be therefore that there is a further type of
equivalent ion pair which has not been detected.

Inequivalent Pairs.

Apart from the exchange interactions between equivalent ions it is
possible for such interactions to couple ions at inequivalent sites. A
pair compared of such ions connot be described by the spin-Hamiltonian
(6.14) since the Z axes of the two interacting ions are differently
oriented in space. To deal with such a case a common system of axes
must be chosen. It is convenient to choose the magnetic field as Z
axis, in which case the relevant spin-Hamiltonian is

$$\mathcal{H} = g\beta \underline{H} \cdot (\underline{S}_1 + \underline{S}_2) + J \underline{S}_1 \cdot \underline{S}_2$$
$$+ D\Big[\cos^2(31^\circ + \theta) S_{1z}^2 + \sin^2(31^\circ + \theta) S_{1x}^2 - \cos(31^\circ + \theta)\sin(31^\circ + \theta)(S_{1z}S_{1x} + S_{1x}S_{1z})$$
$$+ \cos^2(31^\circ - \theta) S_{2z}^2 + \sin^2(31^\circ - \theta) S_{2x}^2 + \cos(31^\circ - \theta)\sin(31^\circ - \theta)(S_{2z}S_{2x} + S_{2x}S_{2z})$$
$$- \tfrac{2}{3} S(S+1) \Big] \tag{6.16}$$

where θ is the angle between the magnetic field and the crystal $\underline{b}$ axis.
As before exact solutions of the single ion Hamiltonian were obtained by
computer calculation and the exchange term treated by perturbation theory.
Although these eigenstates appear different to those obtained previously,
because of the different choice of Z axis, they can be labelled as before
$|1\rangle, |2\rangle, |3\rangle, |4\rangle$. The zeroth order pair states are now $|1,1\rangle$, $|1,2\rangle$
etc. Pair states such as $|1,2\rangle$ and $|2,1\rangle$ are not now degenerate, except at
special degeneracy points such as $\theta = 0^\circ$ and 90 . For equivalent ion
pairs such states are of course always degenerate and so the linear

combinations $\frac{1}{\sqrt{2}}\left[\,|1,2\rangle + |2,1\rangle\,\right]$ and $\frac{1}{\sqrt{2}}\left[\,|1,2\rangle - |2,1\rangle\,\right]$ must be

taken as zeroth order pair states. In equivalent pairs, transitions

between states corresponding to the antisymmetric combination are little

removed from the main single ion transitions at all angles and so cannot

be detected. One feature therefore of the inequivalent pair spectrum is

the fact that more satellite lines should be observed. The most significant

feature of inequivalent ion pairs however is the expected asymmetry of the

spectrum compared with that of the single ions. The asymmetry arises in

the following way. When forming matrix elements, the exchange term is most

conveniently expressed in the form

$$ J\,\underline{S}_1 \cdot \underline{S}_2 \;=\; J\left[\, S_{1z}\,S_{2z} + \tfrac{1}{2}\left(S_{1+}S_{2-} + S_{1-}S_{2+} \right) \right] $$

Consider the form of the matrix element of such a term in the neighbourhood

of $\theta = 31^{\circ}$ (i.e. when the magnetic field passes through a trigonal axis).

The eigenstates of ion 2 in (6.16) will be of the form

$$ |\lambda\rangle \;=\; a_\lambda\,|+\tfrac{3}{2}\rangle \;+\; b_\lambda\,|+\tfrac{1}{2}\rangle \;+\; c_\lambda\,|-\tfrac{1}{2}\rangle \;+\; d_\lambda\,|-\tfrac{3}{2}\rangle $$

Because $\sin(31^{\circ}-\theta)$ changes sign at $\theta = 31^{\circ}$ the coefficients b_λ and d_λ also

change sign at this angle, causing a corresponding change of sign in the

matrix elements of S_{2+} and S_{2-}. Thus at this orientation an asymmetry

in the pair spectrum is expected for those satellite lines whose splitting

from the main line depend strongly on the magnitude of these matrix elements.

This rather subtle effect of the relative phases of the various states

forming a spin eigenstate is only observed in the spectrum of inequivalent

ion pairs. It can be shown that these relative phases have no effect on

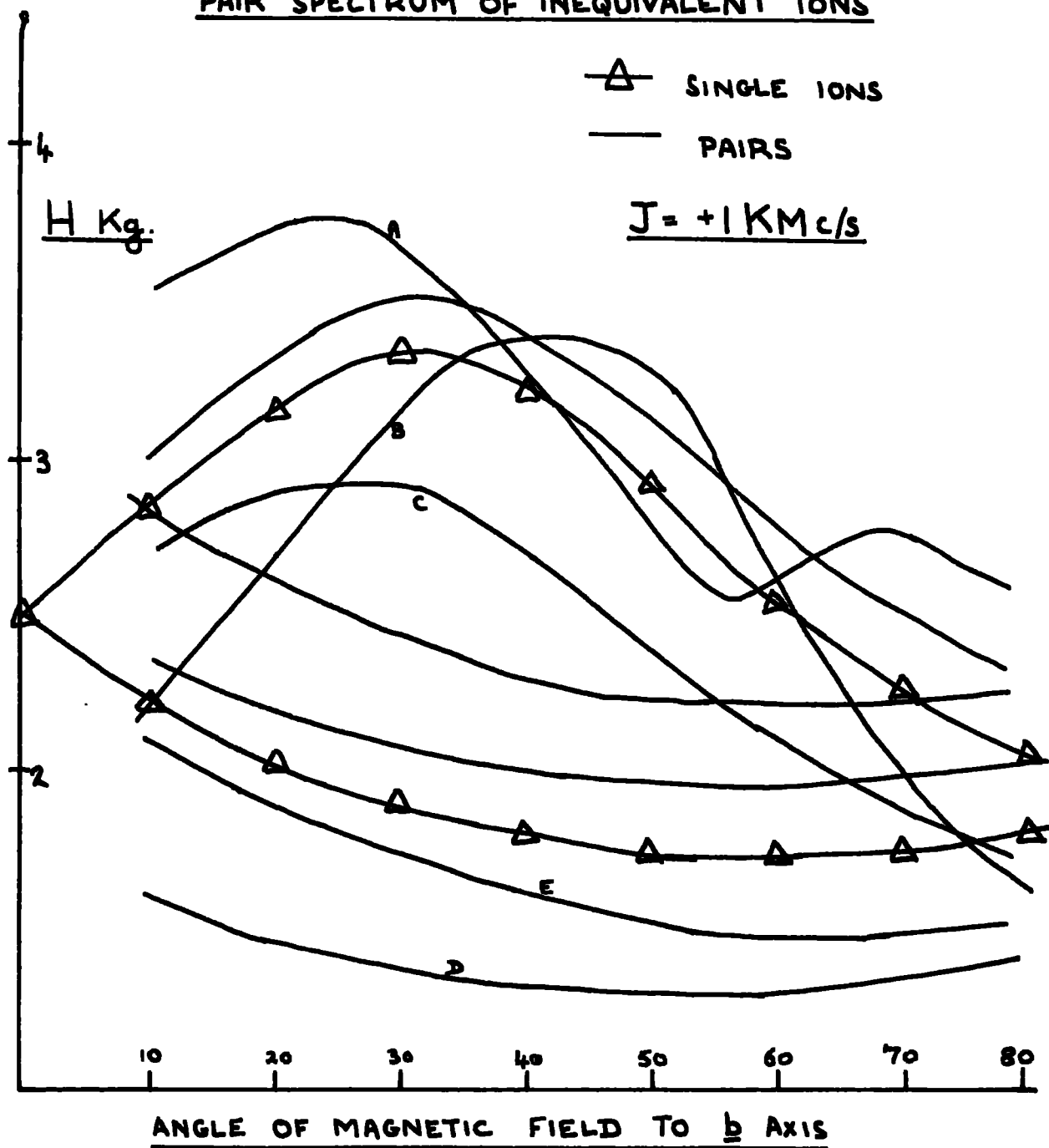the energies or transition probabilities in the single ion spectrum, nor

any effect on the relaxation properties. To produce similar effects in the spectrum of the equivalent pairs it is necessary to introduce some term which destroys the axial symmetry of the spin-Hamiltonian. Such a term can arise from dipolar interactions, directed along an axis which does not coincide with the trigonal axis. The small asymmetries which arise in this way were discussed previously.

When the full perturbation calculation is carried out it is found that there are several resonance lines in the pair spectrum which show marked asymmetry. These lines can clearly be seen in Figure 16 which shows the complete spectrum expected from an inequivalent ion pair with J = +1 KMc/s. The observed spectrum in Figure 14 shows some lines which can be identified as arising from pairs of this type. The agreement between the predicted and observed spectrum is quite good without considering any dipolar correction. For one particular angle ($\theta = 31°$) the dipolar correction was calculated and found to be small. The observed exchange constant is + 0·91 KMc/s. Presumably this figure corresponds to an ion pair oriented along the crystal $\underline{c}$ axis; this orientation gives the shortest interionic distance for an inequivalent pair.

All the observed exchange interactions are of the antiferromagnetic type (positive J). The interactions are therefore of the superexchange type, operating through the intervening diamagnetic oxygen atoms. In the $\underline{a} \underline{b}$ crystal plane the interactions are quite extensive since four different types of equivalent pairs can be distinguished. Only one type of inequivalent ion pair could be detected, which is consistent with a crystal structure consisting of alternate layers of inequivalent ions.

FIGURE 16

PAIR SPECTRUM OF INEQUIVALENT IONS

—△— SINGLE IONS

——— PAIRS

$J = +1 \, KMc/s$

ANGLE OF MAGNETIC FIELD TO b AXIS

Temperature Dependence of The Pair Spectrum

Using a 6% sample the satellite spectrum could be observed at
room temperature. At this temperature the spectrum appeared to be
similar to that found at 77°K but was compressed closer to the single
ion lines. From this it follows that the exchange interactions are
temperature dependent. Such a temperature dependence arises naturally
from the expansion of the lattice if, as is often assumed, the exchange
constants, J, are strongly dependent on the interspin distances. Although
the spectrum was too indistinct to allow a detailed analysis it is clear
that the J values are reduced at room temperature by amounts of the order
of 20%. No data exists concerning the expansion coefficients of the
acetylacetonates but a figure of 0·1% change in lattice dimensions between
liquid nitrogen and room temperature is not an unreasonable estimate. If
the functional dependence of the exchange constants on interspin distance
is of the assumed exponential form

$$J = A e^{-\alpha |r|}$$

then from the estimated values

$$\alpha \sim 200/r_0 \sim 25 \text{ A}^{-1}$$

Such temperature dependent exchange interactions have been observed in at
least one other case. Statz et al (1961) have shown that the exchange
constants in Ruby change by 10% for a 0·1% change in lattice dimensions.
This strong dependence on interspin distances makes the exchange interactions
very susceptible to modulation by the lattice vibrations. It is for this
reason that exchange coupled pairs and higher clusters are considered as
possible sources of the concentration dependent relaxation which is often
observed.

<u>Concentrated Samples.</u>

Samples of chromium doped aluminium acetylacetonate were grown with concentrations up to 10%. For samples with a concentration in excess of 2% a reduction in spin-lattice relaxation time was observed, together with a weaker temperature dependence. This tendency continued up to the highest concentration studied, where the relaxation time was very short and appeared to be quite independent of temperature in the range $1 \cdot 6^{O}K$ to $4.2^{O}K$.

Measurements were made with the magnetic field along a trigonal axis. Using short saturating pulses the relaxation traces were predominantly composed of a single exponential component. The time constant of this dominant component is shown in Figure 17 plotted against sample concentration. It can be seen that the variation of relaxation time with concentration, C, is quite rapid, involving a functional dependence of the form C^{-3} or C^{-4}. For the lowest concentration samples in Figure 17 , two relaxation times are shown. The shortest of these corresponds to the one observed and the longest corresponds to the relaxation time due to the concentration dependent process alone, calculated on the assumption that this process acts in parallel with that of the single ion process.

In the most concentrated samples a small amplitude component with a time constant longer than that of the dominant component could be detected, using long saturating pulses. The time constant of this component appeared to be the same in the 7%, 8% and 10% samples, and was in the 100 μ Sec. to 200 μ Sec. range. This component, like the dominant one, was independent of temperature in the range $1 \cdot 6^{O}K$ to $4 \cdot 2^{O}K$. This behaviour is very similar to that observed previously by the author in Cr^{3+} doped spinels (Hayward and Dugdale 1964). Here an extra long component in the relaxation traces was

FIGURE 17

CONCENTRATION DEPENDENCE

OF $Cr : Al (C_5 H_7 O_2)_3$

$T = 4.2°K$

$\theta = 0°$

$\Im = 9.3$ KMc/s

RELAXATION TIME μ SECS.

MOLAR PERCENT. CONCENTRATION
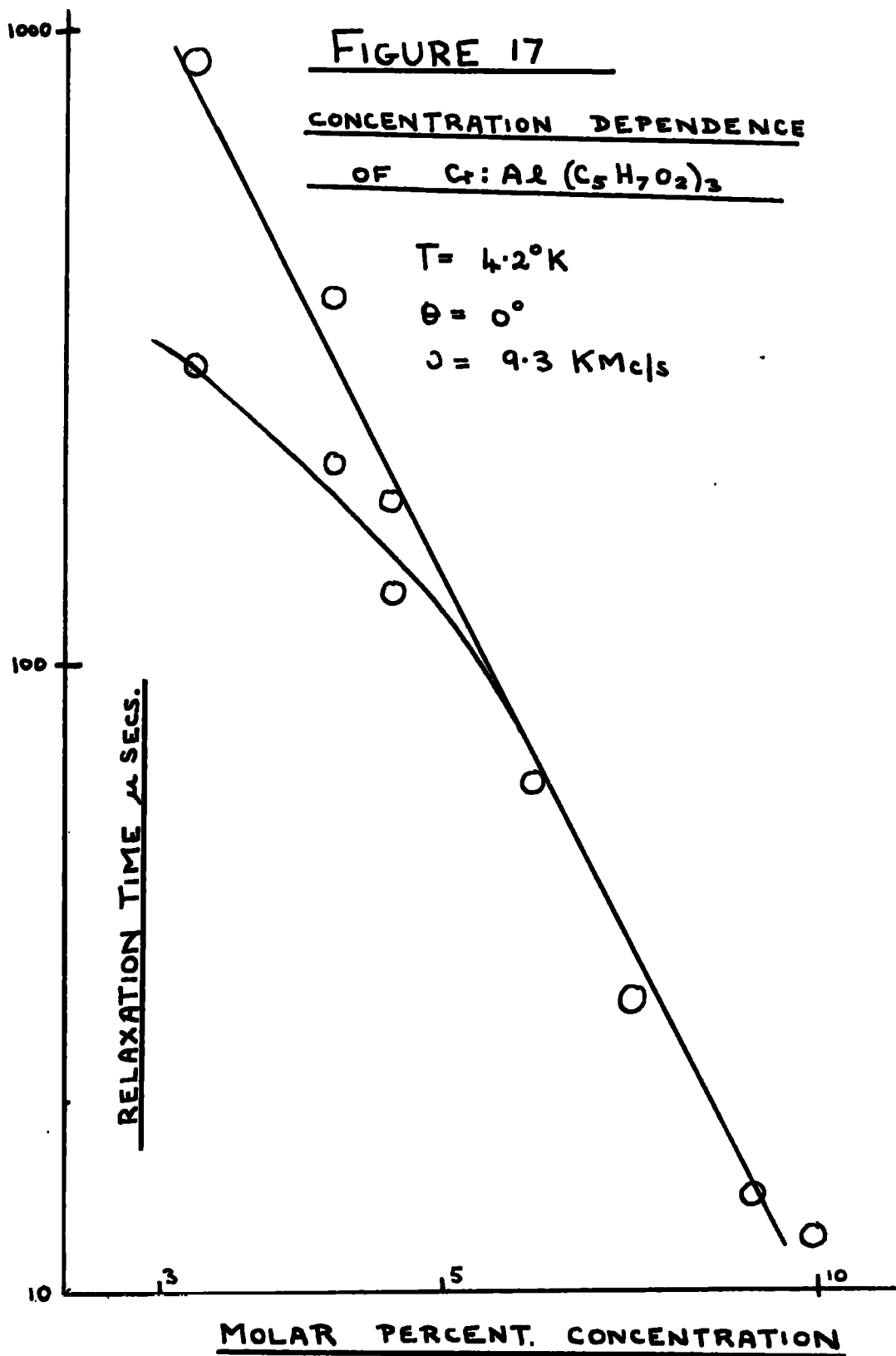
observed in concentration samples which was connected with a phonon

bottleneck in the relaxation process. In the spinel crystals it

appears that the hot phonons escape from the crystal by heat transfer

through the crystal surfaces, for, with liquid helium in contact with

the crystal, the long component disappeared discontinuously at the λ

point. Experiments were therefore made using the 8% and 10% samples

of the acetylacetonates with liquid helium inside the microwave cavity.

No change in the relaxation behaviour was detected and there was no

discontinuity at the λ point, showing that if phonon bottlenecks are

present in the relaxation of these samples then the thermalisation of

the hot phonons proceeds by internal phonon-phonon scattering. The

occurrance of this extra relaxation component may however be a feature

of the concentration dependent relaxation process itself, arising for

reasons similar to those which give rise to the long component found

in the analysis of the single ion relaxation process.

Defect Relaxation.

Some experiments were made to test the effect of point defects on

the relaxation properties. According to the defect the theory it is the

interaction of the localised modes of vibration at each impurity para-

magnetic site which causes the concentration effects. The occurrance of

localised modes is not in any way dependent on the magnetic properties

of the impurity. Accordingly it can be argued that purely diamagnetic

impurities should have a marked influence on the relaxation properties,

if such effects are significant. Some aluminium acetylacetonate crystals

were therefore grown containing 0.1% and 1% chromium, with and without

the addition of 10% of the cobolt compound.

In neither case could any change in the relaxation properties be detected due to the presence of the diamagnetic cobolt compound. On the basis of the defect theory of Kochaleav (1960) one would expect these crystals to have relaxation properties similar to that found in the 10% doped chromium samples. The negative results obtained suggest that a single impurity molecule   is incorporated in the lattice without any appreciable disturbance of the vibrational spectrum. Such behaviour is to be expected in view of the similarity of the molecules involved, the isomorphous nature of the various crystal structures and the ease with which mixed crystals can be grown.

One can however develope a variation of the defect theory which may be consistent with these negative results. Despite the isomorphous crystal structures etc., it is not unreasonable to suppose that clusters of impurity molecules form vibrational defects. Such clusters could then form fast relaxing centres, in communication with the single ions by cross-relaxation processes. In this case the addition of 10% diamagnetic impurity is not equivalent to the addition of a similar amount of the paramagnetic species. In the former case only pairs of $Cr-Co$ or $Cr-Cr$ impurities can form fast relaxing centres, the more abundant $Co-Co$ pairs being magnetically inert. The number of such fast relaxing centres will be correspondingly reduced compared with samples doped entirely with the paramagnetic species. Even allowing for this fact some reduction in spin-lattice relaxation time should be observed in the diamagnetically doped crystals if this process is effective. The fact that no such reduction was observed shows that considerations of vibrational defects alone, at single ion sites or in clusters, is not sufficient to account for the results.

Exchange Coupled Clusters.

The fact that temperature independent relaxation is observed in the concentration dependent process strongly suggests that cross-relaxation is being observed. Spin-lattice relaxation in highly excited states is the only other known process that could give temperature independent relaxation over such a wide temperature range. In view of the known structure of the spin system in these materials, an explanation in these terms is not tenable. One is therefore led to conclude that the relaxation observed is characteristic of cross-relaxation between the single ions and some fast relaxing centres. Since there appears to be no stray paramagnetic impurity in the crystals studied, these fast relaxing centres can only be exchange coupled clusters of paramagnetic ions. In this interpretation it is the modulation of the exchange inter-actions within the clusters which produce the fast relaxation and any defect vibrations that may occur play a secondary role.

In the previous section it was shown that exchange interactions do occur to a significant extent in the acetylacetonates, despite the rather large interionic distances involved. The spectrum of the exchange coupled pairs is sufficiently complex to ensure that at all angles there are many satellite lines close to or coincident with the single ion transitions, thus satisfying the conditions necessary for rapid cross-relaxation. It can be shown (Atsarkin 1966) that modulation of the exchange interaction in pairs of this type can lead to sufficiently rapid spin-lattice relaxation to account, in a qualitative way, for the observed behaviour. Exchange interactions of similar magnitude can be expected in other materials and so this process is capable of accounting in a general way for concentration dependent relaxation. Such relaxation with a characteristic temperature

independence has in fact been observed before by several workers. In all cases, oddly enough, the Cr^{3+} ion is involved (i.e. Dugdale (1965) for Cr^{3+} in spinels, Atsarkin and Popov (1965) and Atsarkin (1966) for Cr^{3+} in various tungstate crystals). In the case of the spinels the relaxation time involved the concentration as c^{-2} and in the tungstates as c^{-3}. According to Elliot and Gill (1961) the cross-relaxation time for a two spin process connecting the single ions and ion pairs, should be inversely proportional to the concentration of ion pairs in the crystal. On the basis of a random paramagnetic distribution, the concentration of ion pairs can easily be shown to be proportional to the square of the total paramagnetic concentration. This is in accordance with the results obtained for the spinel crystals but not for those of the tungstates and acetylacetonates.

To account for the tungstate results, Atsarkin (1966) considered an exchange coupled pair of equivalent ions in some detail. With the magnetic field oriented along the trigonal axis the energy level structure of the pair and single ion spin systems is as shown in Figure 18 . A negative D value is assumed in the figure and the numbering of the pair states follows that of Atsarkin and Mash and Rodak (1965). The latter authors have given exact solutions for the pair states for this particular field orientation. Consider the situation, relevant to the present case, when the single ion transition $1-2$ is saturated by resonant microwave radiation. The simplest cross-relaxation process that can couple together the single ion and pair systems is a two spin process involving pair transitions such as $10-14$, $16-12$, $7-8$, etc., which have equal or nearly equal frequencies at this angle. Of these various pair transitions those

121.

FIGURE 18

ENERGY LEVELS FOR H ∥ TRIGONAL AXIS

SINGLE ION

ION PAIR

RELAXATION ALLOWED
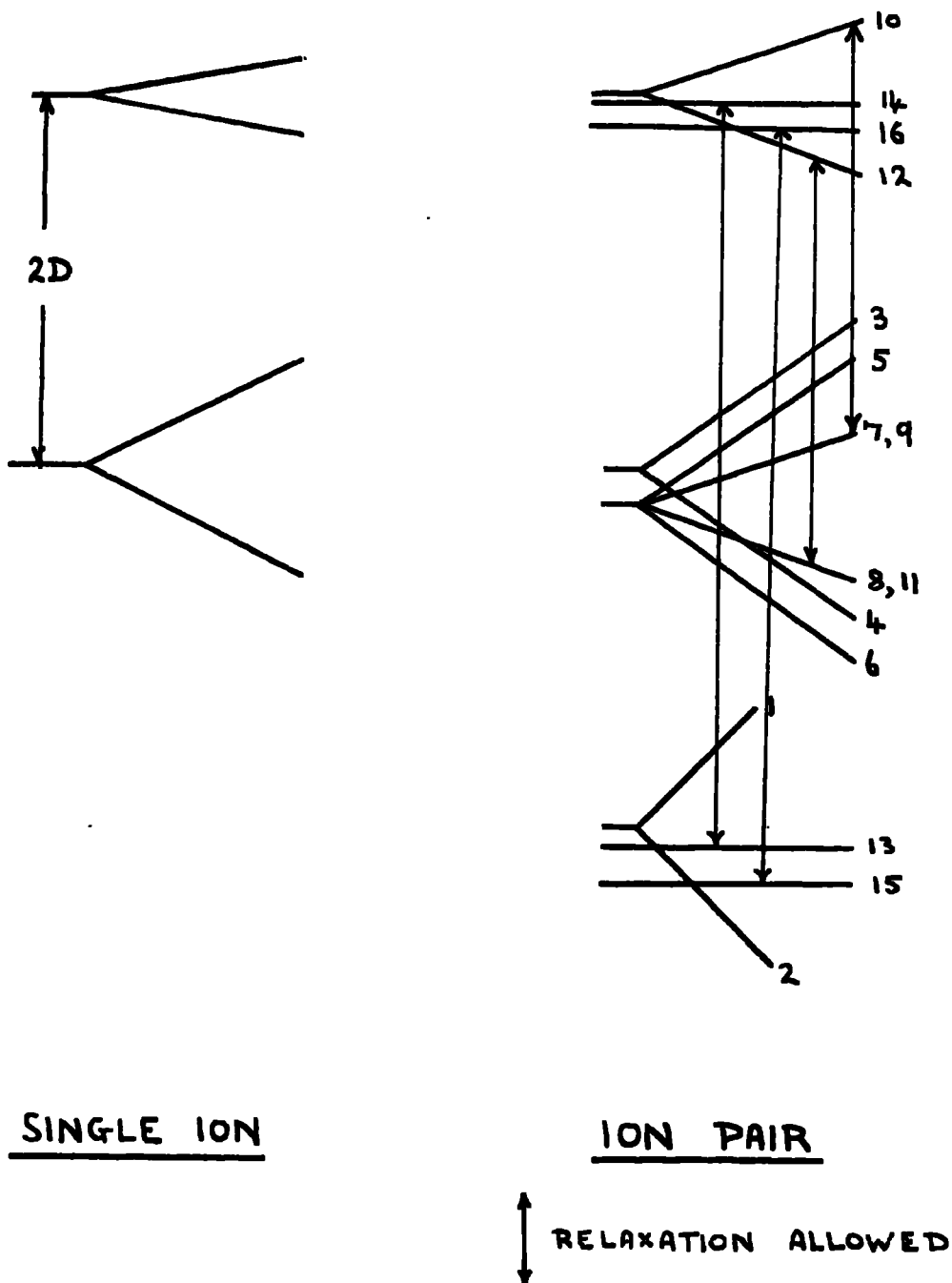
corresponding to 5-7, 6-8, 7-8, 9-11, are particularly suitable, since the transition frequencies coincide exactly with that of the single ions. The perturbation calculations of the pair spectrum made by the author for other orientations of magnetic field, show that this correspondance in transition frequency is approximately maintained at all angles, for the transitions 5-7 and 6-8. Thus cross-relaxation between these transitions is expected to be strongly allowed. Unfortunately, because of the special symmetry present at this particular field orientation, no matrix elements of the exchange interaction connect these particular pair states, directly or indirectly. Thus there can be no rapid spin-lattice relaxation between these states due to exchange modulation. In fact at this field orientation only those transitions shown in Figure 18 have strongly allowed spin-lattice relaxation. Because of these facts Atsarkin considered higher order cross-relaxation processes in which a single ion makes a transition from $1 \rightarrow 2$ simultaneously with another single ion making a transition from $1 \rightarrow 3$. Energy balance is achieved by a simultaneous pair transition $11 \rightarrow 12$ or $9 \rightarrow 10$. Such a process has the merit of predicting a stronger concentration dependence of the order C^{-3}, as was found in the tungstate crystals.

This process is rather peculiar in that it does not by itself allow the single ion system to achieve thermal equilibrium, since excess populations are built up in levels 3 and 4. However such a process, acting together with the single ion relaxation process, could conceivably lead to a reduction in the observed relaxation times of transition $1-2$. A computer calculation was therefore carried out to test this possibility. The rate equations (6.11) were augmented by terms to describe this cross-relaxation process, of the type

$$\frac{\partial n_1}{\partial t} = -2X\left(n_1^2 n_p - n_3 n_2 n_p'\right) + X\left(n_2^2 n_p - n_1 n_4 n_p'\right)$$

where $n_p = n_{11} + n_9$; $n_p' = n_{12} + n_{10}$

and X represents the cross-relaxation transition probability.
After making the approximation of linearising these terms, the augmented
rate equations were solved as before for the time constants and amplitudes
of the three exponential terms. The assumption was made that the relaxa-
tion of the pair transitions was so rapid that n_p and n_p' could be
assumed constant during the relaxation of the single ions. Calculations
were carried out for various values of X at various temperatures in the
helium range. Although the cross-relaxation transition probability, X ,
is independent of temperature the observed cross-relaxation time will not
in general be so, since the populations of the various participating
transitions change with temperature significantly in materials with such
large zero field splittings. Surprisingly enough the results of these
calculations show all the features of concentration dependent relaxation.
As the parameter X is increased so the amplitude of the shortest relaxa-
tion component grows quickly, from an insignificant value to become
dominant. At the same time the relaxation time of this component decreases.

Despite these results however this interpretation cannot be valid in
the present case for a temperature dependence is also predicted, of the
form T^{-1} in the temperature range $1.6^{\circ}K$ to $4.2^{\circ}K$, in contradiction to
the experimental results. Other objections can also be raised against this
interpretation. The energy unbalance involved in the assumed cross-
relaxation process is of the order of J the exchange constant and from the

results of the previous section, this is large compared with the line-widths of the transitions involved. For this reason, as well as the high order of the cross-relaxation process involved, it is doubtful if sufficiently large cross-relaxation transition probabilities can be obtained to account for the experimental results. Also for other orientations of magnetic field fast spin-lattice relaxation becomes allowed for all transitions in the pair system, thus allowing two spin cross-relaxation processes to participate. The strong angular dependence that this leads to is not in fact observed. No doubt in materials with a positive zero field splitting the objection concerning the temperature dependence can be overcome. The other objections remain however and in any case it is clearly unsatisfactory to have different explanations for the behaviour of materials which are in all essential features similar.

A more satisfactory interpretation may be found in terms of the pairs of inequivalent ions, which so far have received no attention. It is surely not without some significance that in the materials which show this kind of concentration dependence (i.e. spinels, tungstates, acetyl-acetonates) there are at least two inequivalent ion sites. In the well known case of Ruby, which has only one type of ion, the concentration dependence appears to be of a more complicated nature and does not exhibit temperature independence over a wide range (Gill 1962). In the spinel crystals on the other hand there are four inequivalent ion sites and so inequivalent ion pairs will be by far the most numerous type. It is also a fact (Dugdale 1965) that the concentration effects in the spinels are most pronounced, extending to much lower concentrations than in either the tungstates or acetylacetonates, which both have two equivalent ion sites. Because of the lack of axial symmetry in pairs of this type, all

transitions will be allowed for spin-lattice relaxation, at any arbitrary angle. Thus there is no need to invoke high order cross-relaxation processes of the type considered by Atsarkin. Also, because of the smaller number of transitions involved, the temperature dependence will now be weak in the range of interest, especially if intermediate pair levels such as 7, 8, 9, 11 are involved.

The different functional dependence of the relaxation time on concentration found in these materials may be raised as an objection to this interpretation. The most recent theoretical analysis of Grant (1964) shows however that the concentration dependence of cross-relaxation processes may be more complicated and variable than is suggested by the considerations of Elliot and Gill (1961). Grant's theory for two spin processes shows that there is an explicit dependence, inversely proportional to the concentrations of the two spin species participating. Assuming that the density of pairs is quadratically related to the total paramagnetic concentration C, this leads to a cross-relaxation time varying as C^{-3}. The observed concentration dependence may however be different because there is also an implicit concentration dependence contained in the various integrals which occur in the theory, whose value depend to some extent on the linewidths of the transitions involved. It was observed by the author that in the case of the spinels there was no variation in linewidth in the concentration range studied whereas the linewidth in the acetylacetonates increased monotonically with concentration.

Also the assumption of a random paramagnetic ion distribution may be incorrect, especially at the high concentrations involved in the acetylacetonates. Thus the exact nature of the relationship between cross-relaxation times and concentrations can be much more complicated than is

usually supposed. In view of the lack of any detailed analysis of this special type of cross-relaxation, no definite form for this relationship can be given.

CHAPTER 7.

RUTHENIUM ACETYLACETONATE.

The E.P.R. data for the Ru^{3+} acetylacetonate (Jarrett 1957) shows, that in these materials, this ion must be described in terms of strong crystal field theory. The crystal field ground states then arise from the excited ^2I term of the free ion, producing a low spin electron configuration with $S = 1/2$. The orbital degeneracy of the ground state is only removed by the low symmetry rhombic terms in the crystal field. The g tensor is therefore quite anisotropic with principal values

$$g_z = 2.32, \quad g_x = 1.28, \quad g_y = 1.74$$

This situation is exactly analogous to that found for Fe^{3+} in $K_3Co(CN)_6$; in fact Ru^{3+} is the $4d^5$ analogue of the $3d^5$ Fe^{3+}.

Relaxation measurements were made on ruthenium doped crystals to compare with the rather exceptional results obtained for the corresponding case of Fe^{3+} in $K_3Co(CN)_6$. The results of Paxman (1961) and Bray, Brown and Kiel (1962) at X band frequencies, show that the relaxation time in the latter material is independent of concentration up to 6%. Such a range of concentration independent relaxation is probably the largest yet observed for any iron group material. Measurements at lower frequencies do however show concentration dependence in this concentration range (Rannestad and Wagner 1963).

Because of the strong dependence of the Ru^{3+} E.P.R. spectrum on the rhombic terms in the crystal electric field, the effects of the phase change noted previously (Chapter 6) is now very marked. This is consistent with the previous interpretation of this phase change in terms of molecular

rotations about the trigonal Z axis. Measurements were therefore made with the magnetic field in the a c crystal phase at an angle such that two of the three observed resonances were coincident. Three different samples were investigated with nominal concentration of 0.5%, 2% and 6% (measured concentrations 0.63%, 2.8% and 6.7%). No difference in relaxation behaviour was observed. In the helium temperature range the relaxation time could be fitted by a sum of Raman and direct terms, characteristic of the single ion process, of the form

$$\frac{1}{T_1} = 50\,T + 10^{-2}\,T^9$$

The magnitude of the relaxation time is similar to that of the corresponding Fe^{3+} ion in $K_2 C_o (CN)_6$, which has been shown to be in order of magnitude agreement with the single ion theory (Bray, Brown and Kiel 1962). The absence of any concentration effects is particularly interesting. It shows that analogous spin systems also have analogous relaxation behaviour, supporting the idea that a mechanism of concentration dependence exists common to all materials. It also shows that such a mechanism cannot be due to defect vibrations alone, at single ion sites or in clusters. One would expect such a process to be operative in both ruthenium and titanium doped crystals and hence equally pronounced in both cases. The observed behaviour is however consistent with the exchange coupled cluster theory. If it is assumed that clusters of Ru^{3+} ions have relaxation times similar to those of corresponding Ti^{3+} clusters then it can be seen that this mechanism only becomes competitive with the single ion process in Ru^{3+} doped crystals at concentrations in excess of 6%.

CONCLUSION.

The results obtained in dilute crystals of aluminium
acetylacetonate, doped with corresponding titanium, chromium
and ruthenium compounds are in good agreement with the predictions
of the single ion theory described in Chapter 4. In all cases the
magnitude of the relaxation time is in agreement with theoretical
expectations, as is the observed temperature independence. In the
case of chromium doped crystals the angular dependence of the
relaxation time was also found to be in accord with this theory.
The agreement found for the titanium samples is particularly inter-
esting since this ion has received little attention, and indeed has
previously been considered somewhat anomalous. It is gratyfying to
find that when Van Vleck's assumptions concerning excited orbital
state splittings are satisfied, then good agreement with theory is
obtained. From these and other results it can be concluded that in
general the single ion theory gives a correct description of the
relaxation properties of dilute paramagnetic materials.

The same can hardly be said of the relaxation behaviour found
at higher concentrations, where concentration dependent relaxation
times are found. The two mechanisms proposed to account for these
concentration effects have been compared with the present results and
those of other workers. Neither proposal is entirely satisfactory.
For the reasons stated in Chapter 5, considerations of defect
vibrationsat single ion sites do not lead to the type of concentration
dependence found. The observed behaviour does however support an
interpretation in terms of fast relaxing centres, such as exchange

coupled clusters of paramagnetic ions.

It was indeed found that there are significant exchange inter-
actions in the acetylacetonates and that these interactions are very
susceptible to modulation by the lattice vibrations. There are
difficulties in this interpretation however, which arise basically
from the commutation of the exchange and Zeeman interactions. In the
case of chromium samples this leads to the vanishing of certain
relaxation transition probabilities when the magnetic field lies
along the special symmetry direction (trigonal axis). Because of this
feature an interpretation of the results was developed in terms of
interacting pairs of inequivalent ions. The lack of axial symmetry
within such a pair ensures that, in general, relaxation will be allowed
between all states of the pair system. This interpretation was also
shown to be compatible with similar results obtained in other materials.
These selction rules are however particularly serious in the titanium
samples. It was shown that it is necessary in this case to consider
clusters of at least three interacting ions to obtain any allowed
relaxation within a cluster, in agreement with the observed concentration
dependence. The allowed relaxation is such however, that the Zeeman
levels of the triads are not connected, one must therefore consider
mixing of Zeeman levels by anisotropic or dipolar interactions. The order
of magnitude of the resulting relaxation rate is then rather small, unless
somewhat doubtful assumptions are made concerning the amount of exchange
modulation. Mixing of Zeeman states does however lead to a similar form
of frequency dependence to that generally observed.

The generally rapid temperature dependence observed in titanium samples suggest that Raman relaxation of some kind is operative, such as could arise through large exchange modulation. The peculiar nature of this temperature dependence cannot be understood unless it is assumed that some sort of distortion of the normal lattice vibrations is also present. Such effects on the lattice vibrations could occur through the appearance of defect vibrational modes within the ion clusters. The absence of any concentration effects in ruthenium doped crystals makes it extremely unlikely that defect vibrations within clusters can by themselves account for the observed concentration dependence. They must therefore be considered as secondary effects within the exchange coupled cluster theory.

An interpretation as complicated as this seems to be necessary quite generally, in view of the manifest complexity of the concentration effects usually observed. Future work in this field should therefore be concerned with the simplest $S = 1/2$ spin systems. In particular measurements on the titanium ion in crystals with large interionic distances would be most interesting. If suitable materials could be found with interionic distances of at least $10A^{\circ}$ then measurements could be made similar to those discussed here, in crystals where exchange interactions are insignificantly small. In this way one might then be able to clearly and unambiguously assign the essential features of concentration effects to the presence or lack of significant exchange interaction. It seems doubtful though if these interactions alone can also account for the anomalous frequency and temperature dependencies with which concentration dependent relaxation is associated.

REFERENCES.

ANDERSON and WEISS Rev. Mod. Phys. 25 269 (1953)

ASTBURY Proc. Roy. Soc. (London) 112 448 (1926)

ATSARKIN Sov. Phys. J.E.T.P. 22 106 (1966)

ATSARKIN and POPOV Sov. Phys. J.E.T.P. 20 578 (1965)

BARNUM J. Inorganic and Nucl. Chem. 21 221 (1961)

BENZIE Proc. Phys. Soc. (London) A64 507 (1951)

BENZIE & COOKE Proc. Roy. Soc. (London) A209 269 (1951)

BIJL Proc. Phys. Soc. (London) A63 405 (1950)

BLEANEY, BOGLE, COOKE, DUFFUS, O'BRIEN and STEVENS

        Proc. Roy. Soc. (London) A236 549 (1956)

BLEANEY and STEVENS Rep. Prog. Phys. 16 108 (1953)

BLOEMBERGEN and PERSHAN "Advances in Quantum Electronics"

        Columbia Univ. Press (1961)

BLOEMBERGEN, SHAPIRO, PERSHAN and ARTMAN Phys. Rev. 114 415 (1959)

BOWERS and MIMS Phys. Rev. 115 285 (1959)

BOWERS and OWEN Rep. Prog. Phys. 18 304 (1955)

BRAY, BROWN and KIEL Phys. Rev. 127 730 (1962)

CASTLE, FIELDMAN, KLEMENS and WEEKS Phys. Rev. 130 577 (1963)

DAVIDS and WAGNER Phys. Rev. Letters 12 141 (1964)

DE HAAS and DU PRE Physica 5 969 (1938)

DU PRE Physica 7 79 (1940)

DUGDALE Phys. Letters 16 226 (1965)

ELLIOT and GILL "Advances in Quantum Electronics"

Columbia Univ. Press (1961)

EMELYANOVA et al Sov. Phys. J.E.T.P. $\underline{17}$ 591 (1963)

ERDOS J. Phys. Chem. Solids $\underline{27}$ 1705 (1966)

FAULKNER Lab. Practice Nov. 1065 (1964)

FIERZ Physica $\underline{5}$ 433 (1938)

GILL Proc. Phys. Soc. London $\underline{79}$ 58 (1962)

GRANT Phys. Rev. $\underline{134}$ 1554 (1964)

GORTER, TUENISSEN and DIJKSTA Physica $\underline{5}$ 1013 (1938)

HAYWARD and DUGDALE Phys. Letters $\underline{12}$ 88 (1964)

HARRIS and YNGUSSON Phys. Letters $\underline{21}$ 252 (1966)

HEITLER and TELLER Proc. Roy. Soc. (London) $\underline{155}$ 629 (1936)

JARRETT J. Chem. Physics $\underline{27}$ 1298 (1957)

KASK, KORIENKO, MANDEL'SHTAM and PROKHOROV

Sov. Phys. Sol. State $\underline{5}$ 1677 (1964)

KOCHELAEV Sov. Phys. Doklady $\underline{5}$ 349 (1960)

KLEMENS Phys. Rev. $\underline{138}$ 1217 (1965)

KORNIENKO and PROKHOROV Sov. Phys. J. E. T. P. $\underline{38}$ 1651 (1960)

KRONIG Physica $\underline{6}$ 33 (1939)

KRONIG and BAUKAMP Physica $\underline{5}$ 521 (1938)

MANENKOV and ORBACH "Spin-Lattice Relaxation in Ionic Solids"

Harper and Row (1966)

MASH and RODAK Sov. Phys. Sol. State $\underline{7}$ 576 (1965)

MATTUCK and STRANDBERG Phys. Rev. $\underline{119}$ 1204 (1960)

McGARVEY J. Chem. Physics $\underline{38}$ 388 (1963)

McGARVEY J. Chem. Physics $\underline{40}$ 809 (1964)

MIMS and McGEE Phys. Rev. $\underline{119}$ 1233 (1960)

MURPHY Phys. Rev. $\underline{145}$ 241 (1966)

ORBACH Proc. Roy. Soc. (London) $\underline{A264}$ 458 (1961)

ORBACH and BLUME Phys. Rev. Letters $\underline{8}$ 478 (1962)

PAXMAN Proc. Phys. Soc. (London) $\underline{78}$ 180 (1961)

PERSHAN Phys. Rev. $\underline{117}$ 109 (1960)

PIPER and CARLIN Inorg. Chem. $\underline{2}$ 260 (1963)

PIPER and CARLIN J. Chem. Phys. $\underline{36}$ 3330 (1962)

PROKHOROV and FEDOROV Sov. Phys. J.E.T.P. $\underline{19}$ 1305 (1964)

RANESTAD and WAGNER Phys. Rev. $\underline{131}$ 1953 (1963)

ROOF Acta. Cryst. $\underline{9}$ 781 (1956)

SINGER J. Chem. Phys. $\underline{23}$ 379 (1955)

VAN DER MAREL, VAN VEN BROEK, GORTER Physica 22 361 (1957)

VAN VLECK "Electric and Magnetic Susceptibilities" (1932)

VAN VLECK J. Chem. Phys. $\underline{7}$ 72 (1939)

VAN VLECK Phys. Rev. $\underline{57}$ 426 (1940)

VAN VLECK Phys. Rev. $\underline{74}$ 1168 (1948)

VAN VLECK "Advances in Quantum Electronics" Columbia Univ. Press (1960)

VAN VLECK "Advances in Quantum Electronics" Columbia Univ. Press (1961)

WALLER Zeit. Fur. Phys. $\underline{79}$ 370 (1932)