THE CONCENTRATION DEPENDENCE OF PARAMAGNETIC RELAXATION IN DILUTE POTASSIUM CHROMI- AND FERRI-CYANIDES AT LIQUID HELIUM TEMPERATURE[1]

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ABSTRACT

Measurements of the spin–spin relaxation time and of the effective, lattice-induced, transition probabilities are reported for magnetically dilute potassium chromicyanide in chemically analyzed concentrations ranging from 0.06 to 1.5%. In these measurements the c-axis of the cobalticyanide matrix was parallel to the static magnetic field. All measurements were made at a temperature of 4.2° K. Measurements made at a concentration of 1.5% did not fit into the same pattern as measurements made at lower concentrations, suggesting a change in the dominant mechanism of relaxation. Pulse and saturation measurements have been compared. The effective, lattice-induced transition probability by the pulse method for samples in the lower range of concentration was found to be independent of the concentration and of the transition involved and was found to have a value of

$$W = 65 \pm 7 \text{ sec}^{-1}.$$

The results for potassium ferricyanide were much less reliable and only two concentrations, 0.2 and 0.4%, have been examined. The static magnetic field was parallel to the b-axis and the temperature was 4.2° K. The value of W is probably between 1000 and 2000 sec^{-1}.

PARAMAGNETIC RELAXATION

Resonant methods of measurement applied to paramagnetic salts make it possible, as a first approximation, to consider only one pair of energy states, for example state i and state j, out of the manifold available for experiment. When thermal equilibrium exists, these two states are populated by N_i and N_j spins. When the salt is placed in the cavity of a spectrometer and subjected to microwave radiation of frequency ν_0, because of the probability $V(ij)$ that transitions will occur, the states take on an out-of-equilibrium population characterized by N_i' and N_j'.

It is customary in the literature of this subject to make use of a saturation factor $S(ij)$ when discussing the populations of the states. Lloyd and Pake (1954) define the saturation factor and show that its relation to the parameters of the salt and of the radiation is

$$S(ij) = (N_i' - N_j')/(N_i - N_j) = (1 + V(ij)/W(ij))^{-1}, \tag{1a}$$

$$W(ij) = U(ji) + C(ji)^{-1} \sum_{k \neq j} U(jk)C(jk). \tag{1b}$$

The quantity $W(ij)$ is defined as an effective, lattice-induced transition probability. In equation (1a), quantities of which $U(ji)$ is typical are lattice-induced, transition probabilities while quantities like $C(ji)$ are the cofactors of a determinant which appears in the Lloyd and Pake derivation. Equation

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(1*a*) makes clear the use of the word effective in connection with $W(ij)$; this quantity depends on lattice-induced, transition probabilities between all states unlike $U(ij)$, which is related to only two of them.

In the literature of nuclear magnetic resonance and sometimes in paramagnetic resonance there is defined a spin–lattice, relaxation time, T_1. Insofar as it is possible to characterize the complex process of relaxation by a single time constant, T_1 is related to W as in equation (1*c*).

$$T_1(ij) = 1/2W(ij). \tag{1c}$$

Andrew (1956, p. 22) has derived the imaginary component of the nuclear magnetic susceptibility. Andrew's method may be applied to the two levels of a paramagnetic salt of effective spin S containing a total of N spins in all states to find an effective susceptibility $\chi''(ij)$. Power P, incident on the coupling hole of the microwave cavity, sets up an alternating magnetic field, $H(\mathrm{rf})$, at the frequency ν_0 at which the spectrometer operates. The selected states are resonant with the radiation when the external static magnetic field has an amplitude $H_0(ij)$ but whatever the amplitude, the probability of a transition is $V(ij)$. In terms of these quantities the imaginary component of the effective susceptibility at a bath temperature T is as follows:

$$\chi''(ij) = Nh^2\nu_0 S(ij)\,V(ij)/\pi(2S+1)kT\,H(\mathrm{rf})^2. \tag{2}$$

It is convenient to be able to calculate the radiation-induced transition probability $V(ij)$, from the spin-Hamiltonian of the salt; this has been done for potassium chromicyanide by Chang and Siegman (1959). The first line of equation (3), which follows, is general and shows that the associated matrix element is to be calculated by applying the effective spin-operators to a set of wave functions for which the energy matrix derived from the spin-Hamiltonian is diagonal. Chang and Siegman give tables and graphs for the square of this matrix element which, however, include a factor of 2 as the spectroscopic splitting or g-factor for potassium chromicyanide; for convenience subscripts indicating direction have been omitted from the symbol g. The second line of equation (3) has been adjusted so that if $C(ij)^2$ is the value picked from one of Chang and Siegman's tables, $V(ij)$ has the correct value. In the third line, power P has been substituted for $H(\mathrm{rf})^2$; as indicated, power and the square of the field are related by the parameter K_p, which is mentioned later in connection with equation (8).

$$\begin{aligned} V(ij) &= (1/4\hbar^2)g(H)_{ij}|\langle i|\beta\mathbf{H}.g.\mathbf{S}|j\rangle|^2 \\ &= (1/16)(g\beta/\hbar)^2 g(H)_{ij}H(\mathrm{rf})^2 C(ij)^2 \\ &= (1/16)(g\beta/\hbar)^2 g(H)_{ij}K_\mathrm{p}P\,C(ij)^2. \end{aligned} \tag{3}$$

The transition probability $V(ij)$ depends on the static magnetic field H in two different ways. For a given orientation of the salt there is a slow dependence on a field contained in the matrix element itself; this field dependence is taken into account when the matrix element is picked from the tables. Secondly, an explicit dependence appears in the line-shape factor $g(H)_{ij}$. This function is normalized with respect to frequency and by definition has a maximum value equal to $2T_2(ij)$ where $T_2(ij)$ is the spin–spin relaxation time.

$$\int_0^\infty g(H)d\nu = 1, \tag{4a}$$

$$g(H_0)_{ij} = 2T_2(ij). \tag{4b}$$

Substitution into equation (2) of the quantities defined in equations (3) and (4) leads to the final expression for $\chi''(ij)$; this expression is general although the form of $V(ij)$ appropriate to Chang and Siegman's values for chromicyanide has been used in defining M, the maximum value of $\chi''(ij)$.

$$\chi''(ij) = (M/2T_2(ij))S(ij)g(H)_{ij}, \tag{5a}$$

$$M = C(ij)^2Nh^2\nu_0(g\beta/\hbar)^2T_2(ij)/8\pi(2S+1)kT. \tag{5b}$$

The object of an experiment in paramagnetic relaxation should be to determine the values of the lattice-induced transition probabilities that appear in equation (1*b*); this objective has not been reached but the effective, lattice-induced transition probabilities $W(ij)$ have been measured. The quantity $W(ij)$ enters the expression for the susceptibility (5*a*) through the saturation factor $S(ij)$. A useful analogy can be established between this subject and that of nuclear magnetic resonance by introducing a power-dependent parameter, σ, of the same general nature as that discussed by Andrew (1956, p. 108).

$$\sigma(ij) = T_2(ij)(g\beta/\hbar)^2K_0P\ C(ij)^2/8W(ij). \tag{6a}$$

In this relation K_0 is the value of K_p, appropriate to an empty cavity. In terms of σ, the expression for the saturation factor becomes:

$$S(ij) = [1+\sigma(ij)(K_p/K_0)g(H)_{ij}/2T_2(ij)]^{-1}. \tag{6b}$$

Feher (1957) has analyzed the response of spectrometers to changes in χ''. Although equation (7*a*), below, is not in his notation, Feher shows that the quality factor, Q_p, of a cavity when a paramagnetic salt in it is absorbing power, is related to the quality factor of an empty cavity, Q_0, in the following way:

$$Q_p = Q_0(1+4\pi\chi''(ij)\eta Q_0)^{-1}. \tag{7a}$$

The instrumental problem is to relate the instantaneous value of Q_p to the deflection of a recorder at the output of the spectrometer subject to the conditions under which the spectrometer is being used. Feher solves the problem with the aid of the assumption that $\chi''(ij)$ is so small that equation (7*a*) can be approximated by the first term of a binomial expansion. During the course of the experiments reported here, it was observed that for many crystals which were used, Feher's approximation was not valid.

It is convenient to characterize the reaction of the crystal on the microwave cavity by a constant, α, defined as follows:

$$\alpha = 4\pi M\eta Q_0. \tag{7b}$$

In terms of α, and the other variables which have been defined, equation (7*a*) can be rewritten:

$$Q_{\mathrm{p}}/Q_0 = (1+\alpha S(ij)g(H)_{ij}/2T_2(ij))^{-1}. \tag{7c}$$

Feher makes use of a coupling constant, β_0, related to the empty cavity; it is now necessary to introduce a variable coupling constant β_{p}, which is defined in relation to Q_{p} in the same manner as β_0 is defined in relation to Q_0. Meyer (1955, Appendix) has defined and discussed the constant, K_0, which relates the radio-frequency field in an empty cavity to the incident power. In a more exact analysis it is necessary to recognize that K_{p} is a variable that depends on Q_{p}; it is related to the measurable constant K_0 in the following way:

$$K_{\mathrm{p}}/K_0 = (Q_{\mathrm{p}}/Q_0)^2(1+\beta_0)^2(1+\beta_0 Q_{\mathrm{p}}/Q_0)^{-2}. \tag{8}$$

Reference to equations (6*b*), (7*c*), and (8) shows that the exact equation relating Q_{p} to the measurable constants of the spectrometer and of the crystal is cubic in Q_{p}. The complexity of the solution for Q_{p} has made it necessary to seek experimental methods which depend on valid approximations to the exact relations. These experimental methods are explained under the section heading, Saturation Measurements.

SPECIMENS

In these experiments the Cr^{3+} ions of potassium chromicyanide ($K_3Cr(CN)_6$) or the Fe^{3+} ions of potassium ferricyanide ($K_3Fe(CN)_6$) were carried by single crystals of diamagnetic, potassium cobalticyanide; this was arranged by dissolving a paramagnetic salt in water in the desired ratio to the diamagnetic salt. Single crystals whose weight ranged between 40 and 100 milligrams were picked from the solution as the excess water evaporated.

Crystals were selected from each batch and analyzed by the colorimetric method which has been described by Sandell (1959). The following table illustrates the typical relation between the nominal and the measured concentration of paramagnetic ions in the diamagnetic lattice for potassium chromicyanide.

TABLE I

Relation between nominal and measured concentrations. The number of chromium ions is expressed as a percentage of the cobalt ions

Nominal concentration, %	Measured concentration, %
0.1	0.071±0.008
0.5	0.20 ±0.01
1.0	0.44 ±0.07
3.0	1.57
5.0	2.60 ±0.17 1.55

Opposite the nominal concentration of 5%, there appear two values for the measured concentration. These entries represent the anomalous behavior of one batch of crystals which has not been explained.

The concentrations of iron ions in the diamagnetic lattices have not been determined. It is assumed in what follows that the relation between nominal and measured concentrations for potassium ferricyanide is the same as that given in Table I.

Information on the crystallography of the complex cyanides, on the electronic configurations, and on the constants of the spin-Hamiltonian can be found in a paper by Bowers and Owen (1955) and in the two papers by Baker, Bleaney, and Bowers (1956) and by Bleaney and O'Brien (1956). Tables relating to the energy level structure of potassium chromicyanide have been published by Chang and Siegman (1959) and very useful graphs of energy levels versus the magnitude of the static field for many orientations of the crystal have been published by Butcher (1957). The angular dependence of the paramagnetic resonance spectra of potassium ferricyanide has been calculated for the static magnetic field oriented in the three crystallographic planes by Kipling (1961).

In view of the extensive literature on these salts it is sufficient to say that the Cr^{3+} ions have an effective spin 3/2; there are therefore three transitions associated with single quantum jumps and measurements are reported on all three transitions. The iron ion, Fe^{3+}, in the cyanide environment exhibits an effective spin 1/2 only and there is only one transition to measure and discuss.

The symmetry of the intramolecular field (in fact covalent bonding plays a major role) in these complex cyanides is such that the energy states of the two non-equivalent complexes are superimposed when the static magnetic field vector lies in either the *ac* or *bc* plane of the crystal. This advantage is retained when the static field is oriented along the *c*-axis and with this orientation the resonant frequencies of the various transitions are so widely spaced that there is little danger of the experimental results being confused by the phenomena of cross relaxation that has been discussed at length by Bloembergen, Shapiro, Pershan, and Artman (1959). For these reasons, all results which are reported here on potassium chromicyanide were collected in experiments in which the static field was parallel to the *c*-axis of the crystal.

Since for potassium ferricyanide there exists only one transition, cross relaxation is not a problem and in fact meaningful results can be obtained with any orientation of the static field. Convenience, arising from the required magnitude of the static field for resonance at the frequency of the spectrometers (9400 megacycles/second), dictated that the static field be oriented parallel to the *b*-axis and this orientation has been used in all experiments.

In the case of potassium chromicyanide there is some confusion in the literature concerning the naming of the energy levels. To avoid this confusion in this report, the lowest level is called 1 and the others are numbered in sequence up to 4.

APPARATUS, EXPERIMENTAL CONDITIONS

The spectrometers used in these measurements were similar to those described by Feher (1957); the microwave sources were controlled by Pound stabilizers and operated at a frequency of 9400 megacycles per second. In order to describe the measurements it is necessary to note two basic modifications to the Feher-type spectrometer: (i) precision, microwave attenuators were added to the spectrometer immediately before and after the magic-T bridge. Compensating adjustments to the two permitted power to the microwave cavity to be varied over a range of 50 decibels, while the power to the balanced mixer that preceded the I.F. preamplifier remained approximately constant; (ii) in some of the measurements, a pair of gyroline, ferrite attenuators in series were interposed between the microwave source (a 2K39 klystron) and the first of the precision attenuators mentioned in (i). A pulse generator was used to supply pulses of current to these attenuators so that their attenuation of 60 decibels could be reduced in a time of 15 microseconds to 2 decibels during the pulse; at the conclusion of the pulse the attenuation returned to its original value in the same time interval. A bypass network, consisting of two directional couplers and an attenuator, permitted a very low level monitor signal to reach the microwave cavity in a manner quite independent of the pulse system.

As in the Feher-type spectrometer a pair of modulation coils were mounted on the pole pieces of the magnet and in saturation experiments (but not in experiments of other types) these coils were supplied with current alternating at a frequency of 200 cycles per second. By this means a small alternating component could be added to the otherwise static magnetic field, H_0, to which the crystal was subjected. In this mode of operation the recorder traced a derivative with respect to field as the static magnetic field was allowed to sweep through resonance.

In addition to the mode of operation described for saturation measurements, two other modes were made possible by the insertion of the gyroline attenuators; in these modes field modulation was not used. When the line-shape factor $g(H)$ and the spin–spin relaxation time T_2 was under investigation, the microwave power to the cavity was amplitude-modulated by pulsing the gyroline attenuators with square waves recurring at the rate of 200 p.p.s. In this mode of operation the resonance line itself was traced by the recorder as the static magnetic field was swept through resonance.

For the purpose of pulse measurements the gyroline attenuators were supplied with square waves of current at the rate of about 16 p.p.s. The output of the I.F. preamplifier passed through a special, main, I.F. amplifier whose gain was much reduced by the same pulse that decreased the attenuation of the gyrolines; the output of this amplifier was direct coupled through a crystal diode to a double beam oscilloscope. The more or less exponential return of $\chi''(ij)$ to its thermal equilibrium value, after the pulse was cut off, was monitored by a steady signal of very low power, supplied through the bypass circuit. The second beam of the oscilloscope was used to display the decay curve of an R-C network, the condenser of which had been charged by the same pulse that had decreased the attenuation of the gyroline. Since manipulation of the controls of the oscilloscope permitted this curve to be superimposed on the curve exhibiting the decay of the saturation of the salt, adjustment of the resistance in the R-C network permitted immediate evaluation of the time constant associated with the value of $W(ij)$. The decay curve of the

R-C network also provided a reference by which it could be decided whether one or more time constants were to be associated with the relaxation process.

Two different spectrometers were used in the experiments. In one of these, the 12-in. magnet that supplied the static field was rotatable and in consequence, errors in orientation made in placing the crystal in the microwave cavity could be compensated by external rotation of the magnet. In the other spectrometer, the 6-in. magnet could not be rotated. To avoid serious errors the crystal was usually cemented to the tuning plunger, which was then inserted in the cavity.

The cavities of both spectrometers were immersed in liquid helium which was boiling at atmospheric pressure. Throughout this report all measurements were made at a temperature of 4.2° K.

SATURATION MEASUREMENTS

Figure 1 illustrates the saturation method of measuring $W(ij)$. Because of the field modulation, the recorder plotted a derivative with respect to the

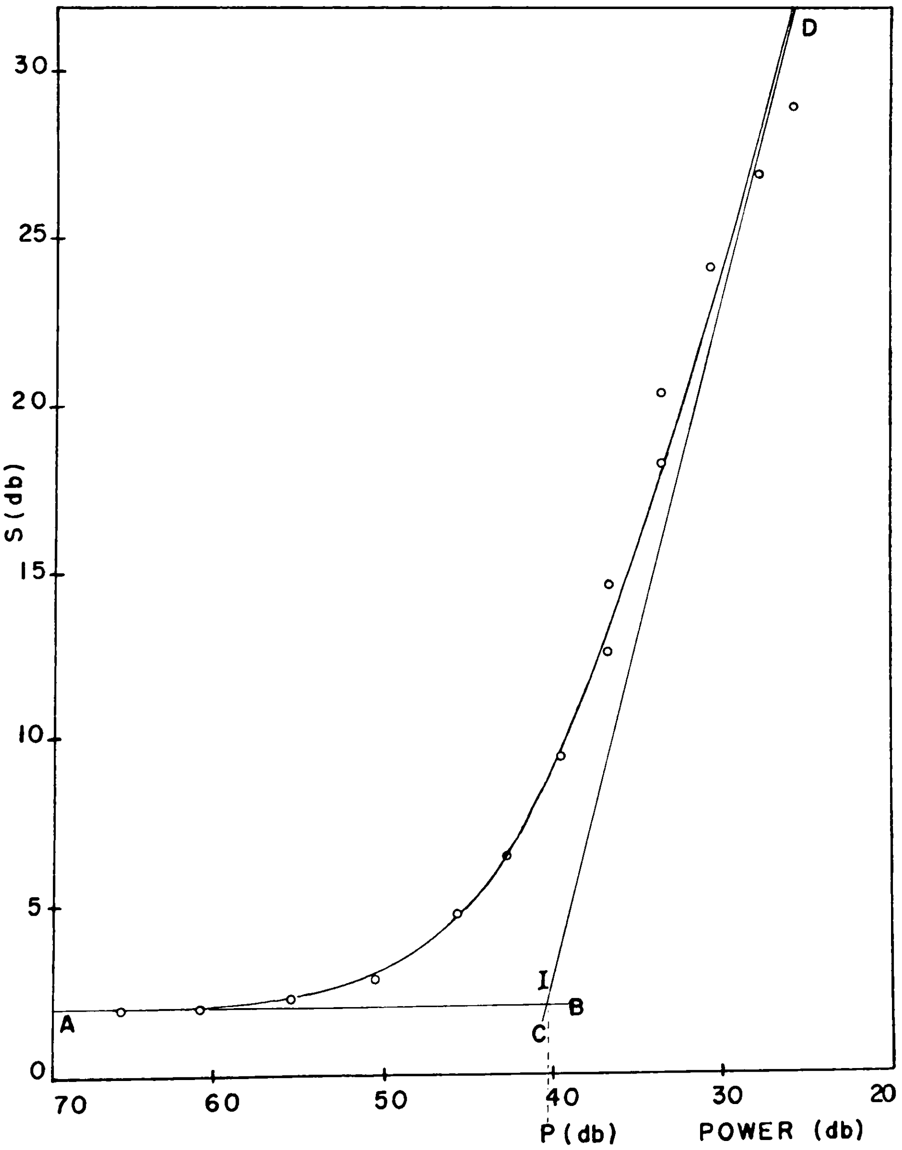

FIG. 1. A typical set of experimental points in a saturation measurement, fitted by a theoretical curve (solid line). The extrapolated linear regions, AB and CD meet at I. The power P_I, used in equation (9), is calculated from the logarithmic power ratio P(db).

field when the static field was allowed to sweep through the resonance line. In many cases a sample of D.P.P.H. was placed in the cavity along with the sample under investigation. The ordinates of Fig. 1 are:

$$S(\mathrm{db}) = 20 \log \left(\frac{\text{max. value of derivative for D.P.P.H.}}{\text{max. value of derivative for sample}}\right).$$

Since D.P.P.H. does not saturate, higher values of the ordinate express increased saturation of the sample. These ordinates are plotted against the power incident on the coupling hole of the cavity, expressed in decibels.

The curve which appears in Fig. 1 is typical of all saturation measurements. On the logarithmic plot, two linear regions always appear, one for the condition $S(ij) \doteqdot 1$, the other for $S(ij) \doteqdot 0$; the approach to a straight line for the latter condition is so slow that theoretical curves are required to establish the correct slope in any set of experiments. In Fig. 1, the two linear regions have been projected and are the straight lines AB and CD; these intersect at I, which provides a unique point on the diagram for determining $W(ij)$.

Andrew (1956, p. 108) provides enough information to determine the theoretical form of the saturation curves that appear in Fig. 1, when it is assumed that the line shape is of the Lorentz form and that the crystal characteristic α, equation (7*b*), is zero; there are two subcases appropriate to whether the saturation factor $S(ij)$ is able to follow the modulation or whether it should be considered a constant. The exact solution when α is not zero is a problem of considerable complexity and has not yet been solved. It is the purpose here to show that measurements based on the unique point of intersection, I, in Fig. 1 can be exact without a complete knowledge of the form of theoretical curves.

In a theoretical derivation, the location of the straight line AB is determined when the power P to the cavity is very small, that is for $\sigma(ij)$, equation (6*a*), approximately zero and $S(ij)$ very nearly unity. These approximations do not make Q_p equal to Q_0 but they do simplify all relations in such a way that the equation of the line AB can be found as a function of α. When the power to the cavity is large, the parameter $\sigma(ij)$ is large and the saturation factor $S(ij)$ approaches zero; in consequence the parameters of the empty cavity Q_0, β_0, and K_0 are excellent approximations for Q_p, β_p, and K_p. The resultant equations are simple enough to permit the determination of the straight line CD and hence to determine P_I, the actual power (not its logarithm) appropriate to a perpendicular dropped from the point I to the axis of abcissae.

The analysis shows that in terms of the power P_I

$$W(ij) = \Lambda(2T_2(ij)\,V(ij)/H_{\mathrm{rt}}^2\,g(H)_{ij})\,K_0P_I. \tag{9}$$

The multiplier Λ is a function of the crystal constant, α, and the cavity coupling constant β_0. Figure 2 represents a graph of the values of Λ plotted against the composite variable $\alpha/(1+\beta_0)$. Four lines appear on the graph corresponding to the four subcases appropriate to a Lorentz or Gaussian model and to $S(ij)$ invariant or variable with modulation.

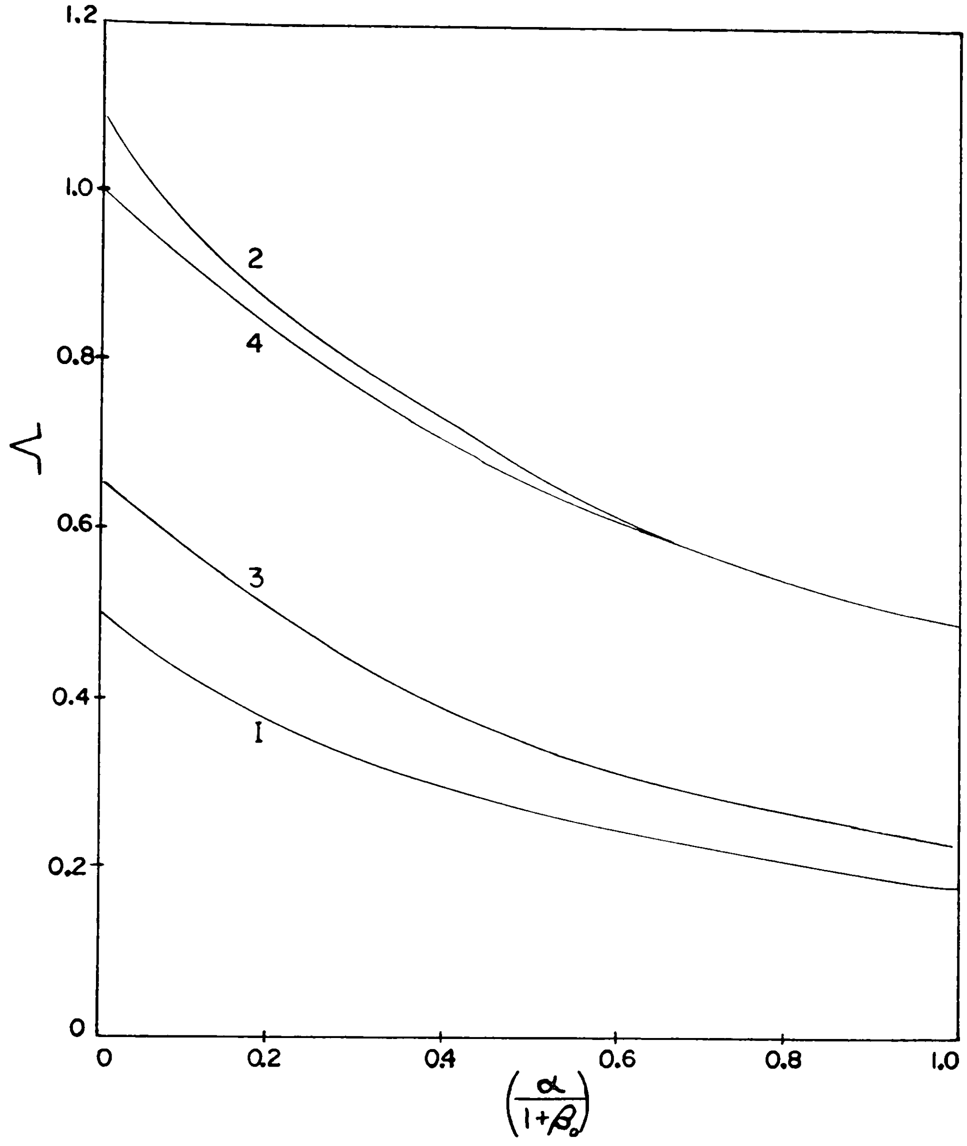

FIG. 2. The multiplier, Λ, from equation (9) plotted as a function of the variable α, equation (7*b*), and β_0 the coupling constant for the empty cavity. The curves are plotted for different models: (1) Gauss, $S(ij)$ invariant; (2) Gauss, $S(ij)$ variable; (3) Lorentz, $S(ij)$ invariant; (4) Lorentz, $S(ij)$ variable.

In order to improve the accuracy of the measurements, experimental points should be fitted by a theoretical curve in order to determine the location of the line AB and the location and particularly the slope of the line CD (see Fig. 1). This has been done with the approximate theoretical curves ($\alpha = 0$) which were available to the authors. It is from the fit and shape of these curves that conclusions have been drawn about whether or not the saturation factor $S(ij)$ was to be regarded as a constant or a variable with modulation.

PULSE MEASUREMENTS

The same argument that has been used in connection with saturation measurements shows that, provided $\sigma(ij)$ is large, the pulse measurements correspond to the decay of saturation. This restriction requires that the decay curve be fitted in its earlier portion for not too many time constants after the termination of the saturating pulse.

All pulse data correspond to a single relaxation time. It is possible that later slow relaxation processes have been missed but since the circuits were operative 15 microseconds after the termination of the saturating pulse, it is unlikely that there were unobserved fast, initial relaxations.

EXPERIMENTAL RESULTS FOR $T_2(ij)$, THE SPIN-SPIN RELAXATION TIME

In line-shape measurements, errors were avoided by picking crystals of such weight, in relation to the concentration of the paramagnetic ions, that there were too few spins to make necessary a correction for the reaction of the spins on the microwave cavity. In all measurements of line shape except one (on a ferricyanide sample) the spectrometer was operated so that the recorder traced line shapes rather than derivatives.

There are available two methods for determining the value of T_2 to be associated with an experimental line. The direct application of the definitions contained in equations (4*a*) and (4*b*) require that the area under the curve be measured with a planimeter; the error in this method may not be negligible if the line exhibits wide wings whose areas are difficult to determine. As a second method, the normalized Lorentz and the normalized Gaussian line shapes may be fitted at (for example) the half-height of the normalized experimental curve. This procedure has the advantage of not requiring a determination of the area under the wings but is approximate since few experimental lines fit the models with precision. The result of both procedures applied to potassium chromicyanide appears in Table II.

TABLE II

Expressions for T_2

Transition	(1–2)	(2–3)	(3–4)
$T_2 = g(H_0)/2$	$2.9C^{-0\cdot 55}$	$6.8C^{-0\cdot 55}$	$2.9C^{-0\cdot 55}$
Lorentz model	$1.9C^{-0\cdot 63}$	$5.6C^{-0\cdot 63}$	$1.9C^{-0\cdot 63}$

Results measured for potassium chromicyanide, when the *c*-axis was parallel to the static magnetic field and the temperature was 4.2° K. The entry expresses $T_2(ij)$ in units of 10^{-9} seconds. The measured magnetic concentration C is to be expressed in per cent and the table is valid for $0.06 \leqslant C \leqslant 1.5$. At the lowest concentration the half-width in magnetic field was $\Delta H(1,2) = \Delta H(3,4) = 10.5$ oersteds; $\Delta H(2,3) = 3.95$ oersteds.

The statements in Table II are to be regarded as predicting a mean value for T_2 appropriate to a concentration C. The average deviation in the experimental results for each of the measured concentrations was ± 2 and in consequence the following statement is typical of the meaning of any entry:

$$T_2(2,3) = (6.8C^{-0\cdot 55} \pm 2) \times 10^{-9}\ \text{seconds}.$$

Precision is expressed, using average deviation, in this manner in connection with experimental results that appear elsewhere in this report.

It will be observed that results by the two methods overlap in view of the limits set by errors. In the process of fitting the experimental shapes, it was observed that when the concentration was below 1% the experimental shapes approximated that of Lorentz. The higher concentrations departed from the Lorentz shape but could not be fitted by a Gaussian line.

Bleaney and Ingram (1951) measured the line width of cobalt tutton salt as a function of concentration; they have reported that the line reached an approximately constant width for all nominal concentrations below 0.1% and have suggested that the limiting width is set by the magnetic moment of the protons. It is interesting to note that in Table II there is no indication that a constant width is being approached, probably because of the small magnetic moment associated with the CN radicals.

Castle, Chester, and Wagner (1960) have measured the line widths associated with the (2–3) transition in dilute chromicyanide for measured concentrations ranging from 0.06% to 1.9%. For many of the samples, the line was found to be Lorentzian out to three line widths. The line width increased with concentration even at the lowest concentrations. Evidence in their experiment suggests that the line is broadened inhomogeneously. The line widths of samples of the same concentration but from different sources were different from each other by ratios of more than 2:1. For purposes of comparison, using a Lorentzian model, the authors of the present paper have expressed the results of Castle *et al.* in the same form as that used in Table II; the result is displayed for comparison in Table III.

Swarup (1959) has made a study of the line shapes to be associated with the resonances in dilute chromicyanide. Most of the nominal concentrations are greater than have been considered in the present paper and further an error was made in reporting the measured concentrations which was later corrected; the relation between nominal and measured concentration, after correction, is not the same as the results in Table I of the present paper. Swarup finds $\Delta H(34)$ to be nearly the same as $\Delta H(12)$ and both of these to be somewhat greater than $\Delta H(23)$. Marr and Swarup (1960) report values of $T_2(23)$ for three nominal concentrations of chromicyanide. The present authors have assumed that the nominal and measured concentrations are related as in Table I and on this basis have converted the Marr and Swarup results into the form displayed in Table III.

TABLE III

Comparison of various measurements of $T_2(23)$ for $K_3Cr(CN)_6$

Author	$T_2(23)$ seconds
Castle, Chester, and Wagner	$5.4C^{-0\cdot44}\times10^{-9}$
Marr and Swarup	$7.5C^{-0\cdot43}\times10^{-9}$
KSVW (Lorentz model)	$(5.6C^{-0\cdot63}\pm2)\times10^{-9}$
KSVW ($g(H_0)/2$)	$(6.8C^{-0\cdot55}\pm2)\times10^{-9}$

The measurements by several authors have been converted to comparable form by (KSVW).

In Table IV are listed the measured values of T_2 for ferricyanide; the values were computed from the experimental lines using the Lorentzian approximation. Values of $T(23)$ for chromicyanide computed from a Lorentz model are given for comparison.

TABLE IV

Values of T_2

Concentration, %	T_2 in units of 10^{-9} seconds	
	$K_3Fe(CN)_6$	$K_3Cr(CN)_6$
0.2	14±1	15±2
0.4	6.2±1	8.6±2

EXPERIMENTAL RESULTS FOR $W(ij)$, THE EFFECTIVE, LATTICE-INDUCED TRANSITION PROBABILITY

Both pulse and saturation measurements of $W(ij)$ have been made on potassium chromicyanide. A very marked change in $W(ij)$ for the higher concentrations suggests the appearance of a new relaxation mechanism; accordingly, the results are reported separately for the range of concentrations 0.49% and less and for a concentration of 1.5%. In the region of lower concentrations, it has not been possible to identify any pattern in the results which would lead to the statement that one transition behaves in a manner different from the others; for this reason all values of $W(ij)$ have been averaged into a single W and the value of this parameter is taken to be representative of all transitions.

Within the precision of the pulse measurements, relaxation in the range of concentrations from 0.061% to 0.49% is characterized by a single time constant and this time constant is independent of concentration. The value of W calculated from the pulse measurements is:

$$W = 65\pm7 \text{ sec}^{-1}.$$

In applying saturation analysis to the low concentration measurements, it was necessary to decide on a model line shape and also to decide whether or not, at a modulation frequency of 200 c.p.s., the saturation factor varied with the modulation. Line-shape studies have shown that the best approximation is the Lorentz line. In order to decide the question concerning the saturation factor, experimental results were fitted to theoretical curves and the excellence of fit given a score; the evidence was about two-to-one in favor of a saturation factor, $S(ij)$ invariant at the modulation frequency. Subject to these decisions the value of W was found to be:

$$W = 64\ C^{0.28}\pm10 \text{ sec}^{-1}.$$

In this relation, C is the measured concentration and the relation is known to apply over the range of concentration expressed by $0.06\% \leqslant C \leqslant 0.49\%$.

There is as yet no explanation for the fact that the pulse measurements yield a value of W which is independent of concentration while the saturation measurements indicate a small but unmistakable dependence on concentration.

The measurements on samples containing 1.5% chromicyanide are summarized in Table V.

There are three reasons why the Lorentz and Gauss assumptions, applied to saturation data, lead to the different values of $W(ij)$ displayed in Table V, although the differences are not as great as might have been supposed. The greatest difference arises in the value chosen for P_I because of the different shapes of the theoretical curves which were used to fit the experimental data in the manner shown in Fig. 1. Less important are the different values of Λ obtained from Fig. 2 and the different values of T_2 which resulted from fitting the experimental line shapes with either a Lorentz or Gauss model.

TABLE V

Values of $W(ij)$ for $K_3Cr(CO)_6$

Transition	Pulse measurements	Saturation measurements		
			Dependence of $S(ij)$ on modulation	
		Model	Invariant	Variable
(3–4)	460	Lorentz	240	770
		Gauss	190	970
(2–3)	450	Lorentz	470	1800
		Gauss	380	2000
(1–2)	190	Lorentz	380	1200
		Gauss	270	1200

Values of $W(ij)$ in units of $\sec^{-1}$ for potassium chromicyanide in a concentration of 1.5%. The crystals were at a temperature of 4.2° K and were oriented with the c-axis parallel to the static magnetic field. H(rf) was parallel to the b-axis of the crystal; transition probabilities $V(ij)$ correspond to this arrangement. Saturation results have been analyzed subject in turn to each of the four possible ideal assumptions concerning the experiment.

The pulse measurements of $W(ij)$ are considered to be the most reliable, partly because no assumptions are required and partly because the measurements are so rapid that instrumental instabilities have little effect on the result. All the results, including the pulse measurements, were repeated on different days; it is believed that there is good justification for reporting that, at a concentration of 1.5%, the (1–2) transition does not respond in the same manner as do the other two.

Comparable data on chromicyanide have been published by Marr and Swarup (1960) and by Castle, Chester, and Wagner (1960). Marr and Swarup have reported that, in nominal concentrations of 0.1% and 0.5%, the spin–lattice relaxation time, T_1, of chromicyanide is a function of the power used in saturating the salt. The authors of the present paper have not been able to repeat this result; $W(ij)$ appears to be independent of the saturating power. Values of W computed from the Marr and Swarup, thermal-equilibrium, spin–lattice relaxation time (which they call T_1^0), are all higher than are reported in the present paper and this is particularly true for their nominal concentration of 1.0%.

Castle, Chester, and Wagner (1960) report an increase in the rate and a marked change in the nature of the recovery in passing from a measured concentration of 0.5 to 1.0% Cr^{3+} ion. Values of $1/T_1$ appropriate to 4.2° K can be picked for two concentrations from their Fig. 6: for a concentration of

0.06%, $1/T_1$ is reported to be about 180 and for a concentration of 0.4% to be 200 sec^{-1}, thus indicating a very slow increase in $1/T_1$ with concentration. In the present results, for low concentration W has been found to be 65 sec^{-1}, which yields for comparison a somewhat lower value of 130 sec^{-1} for $1/T_1$.

Potassium ferricyanide relaxes very rapidly; measurements have shown that T_1 for chromicyanide is about 30 times as great as that for ferricyanide. This rapid relaxation has made measurements difficult and has led the writers to be suspicious of the accuracy of the experimental results on this salt. The results in Table VI are to be regarded as order-of-magnitude figures; until further work is reported no great significance should be attached to the fact that W for the higher concentration is smaller than W for the lower concentration. These measurements were made by the saturation method. The fit of the theoretical curves suggests that the saturation factor, S, did not vary with the field modulation.

TABLE VI

Values of W for $K_3Fe(CN)_6$

Concentration, %	Dependence of S on modulation	
	Invariant	Variable
0.2	2200±660	6500±2100
0.44	960±360	3100±1400

Values of W in units of sec^{-1} for potassium ferricyanide. The crystals were at a temperature of 4.2° K and were oriented with the b-axis parallel to the static magnetic field. The direction of H(rf) was parallel to the c-axis of the crystal and the transition probability, V, was calculated for this arrangement. A Lorentz line has been assumed.

Bray, Brown, and Kiel (1960) have reported, briefly, on pulse measurements of T_1 for ferricyanide at temperatures between 2.6 and 4.2° K. The concentration of the sample is not mentioned in their abstract. They suggest that at a temperature of 4.2° K the Raman process is dominant. They find that the relaxation process is characterized by two relaxation times; it is possible that the uncertainties associated with the measurements in Table VI are related to this result of Bray *et al.*

DISCUSSION

The main purpose of this paper has been to report and collate experimental measurements; a second purpose has been to examine the relation between pulse and saturation measurements. The results give support to the idea that in a concentration of 1.5%, the Cr^{3+} ion in a cyanide environment relaxes by way of some mechanism which is not present or at least not dominant when the concentration is 0.5% or less. It would appear that if the results are to be understood, separate theories corresponding to the two different ranges of concentration are required.

It may be supposed that the mechanisms are different in the two ranges of concentration because of differences in the amount of coupling throughout the spin system. For the higher concentrations, the spins constitute one thermodynamic system, the lattice another; relaxation is a co-operative phenomena. For the lower concentrations, to a first approximation, the paramagnetic ions are completely uncoupled from each other; each ion is on its own and relaxes to the lattice as an individual. This idea as it has appeared in the literature has been surveyed by Woonton in a review article to be published (written in the spring of 1960 and containing references only up to that time).

For the lower range of concentrations, Kittel (1958) suggested a form for coupling between the individual spins and the lattice. Mattuck and Strandberg (1960) worked out a detailed analysis of this type of coupling. Shiren and Tucker (1961) have produced experimental evidence which tends to validate the theory. The operator, $\mathscr{H}$, which Mattuck and Strandberg have called the spin–lattice Hamiltonian can be used to yield values of the lattice-induced transition probabilities such as $U(ji)$. Among other terms, the leading term of $\mathscr{H}$ is the anticommutator of the effective spin operators. This leading term applied to the wave functions of ferricyanide yields matrix elements which are identically zero, but this is not true in the case of chromicyanide. From this fact it must be concluded that it is unsafe to attempt to extrapolate the behavior of one salt as an explanation of phenomena related to the other.

The leading term of the Mattuck and Strandberg operator applied to the wave functions of chromicyanide yields very small values for $U(2,3)$, $U(3,2)$, $U(1,4)$, and $U(4,1)$. It had been hoped that differences in the values of $W(ij)$ might appear because of these differences in the U's; it has been shown that within experimental error, the values of the W's are all the same and so no specific statements can be made yet about the U's by the methods reported in this paper. It is now clear that the experiments should have been arranged so that the forbidden transitions could have been measured.

Van Vleck (1960, p. 398) has discussed ideas which apply in the range of higher concentrations: irregularities in the lattice constitute localized centers of very rapid relaxation which form a strong coupling between the lattice and the spin system. Van Vleck explains that by irregularities he means unusual situations for the paramagnetic ions such that an ion experiences an unusual stark splitting or that the ions happen to be in close-spaced groups of three or more, resulting in "exchange pockets". As Van Vleck says, "There is the difficulty of getting enough energy transport from the average atom to one which is a fast relaxer. The intermediary for doing this would have to be dipolar coupling". Van Vleck and others have suggested that the coupling mechanism is cross relaxation as worked out by Bloembergen *et al.* (1959). The experiments of Castle, Chester, and Wagner (1960) reinforce this suggestion. Presumably the region of concentrations over which the mechanism of relaxation changes could be controlled by varying the orientation of the crystal with respect to the static magnet field, thus controlling the onset of strong cross relaxation.

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REFERENCES

ANDREW, E. R. 1956. Nuclear magnetic resonance (Cambridge University Press, London and New York).
BAKER, J. M., BLEANEY, B., and BOWERS, K. D. 1956. Proc. Phys. Soc. London, **69**, 1205.
BLEANEY, B. and INGRAM, D. J. E. 1951. Proc. Roy. Soc. London, A, **208**, 143.
BLEANEY, B. and O'BRIEN, M. C. M. 1956. Proc. Phys. Soc. London, **69**, 1216.
BLOEMBERGEN, N., SHAPIRO, S., PERSHAN, P. S., and ARTMAN, J. O. 1959. Phys. Rev. **114**, 445.
BOWERS, K. D. and OWEN, J. 1955. Repts. Progr. in Phys. **18**, 310.
BRAY, T. M., BROWN, G. C., and KIEL, A. 1961. Bull. Am. Phys. Soc. Ser. II, **6**, 233.
BUTCHER, P. N. 1957. Electron Tube Laboratory, Tech. Rept. No. 155–1, Stanford Electronics Laboratories, Stanford, California.
CASTLE, J. G., CHESTER, P. F., and WAGNER, P. E. 1960. Phys. Rev. **119**, 953.
CHANG, W. S. and SIEGMAN, A. E. 1959. Electron Tube Laboratory Tech. Rept. No. 156–1, Stanford Electronics Laboratories, Stanford, California.
FEHER, G. 1957. Bell System Tech. J. **36**, 449.
KIPLING, A. L. 1961. M.Sc. Thesis, Dept. of Physics, McGill Univ., Montreal. Unpublished.
KITTEL, C. 1958. Phys. Rev. Letters, **1**, 5.
LLOYD, J. P. and PAKE, G. E. 1954. Phys. Rev. **94**, 579.
MARR, G. V. and SWARUP, P. 1960. Can. J. Phys. **38**, 495.
MATTUCK, R. D. and STRANDBERG, M. W. P. 1960. Phys. Rev. **119**, 1204.
MEYER, J. W. 1955. Lincoln Laboratory, Group Report M35–46, Mass. Inst. of Tech.
SANDELL, E. B. 1959. Colorimetric determination of traces of metals (Interscience Publishers Inc., New York).
SHIREN, N. S. and TUCKER, E. B. 1961. Phys. Rev. Letters, **6**, 105.
SWARUP, P. 1959. Can. J. Phys. **37**, 848.
VAN VLECK, J. H. 1960. Quantum electronics, *edited by* C. H. Townes (Columbia Univ. Press, N.Y.).
WOONTON, G. A. 1962. Advances in electronics and electron physics, Vol. XV (Academic Press, New York and London), p. 163. To be published.