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Electron Spin-Lattice Relaxation in Dilute Potassium Chromicyanide at Helium Temperatures*

J. G. Castle, Jr., P. F. Chester, and P. E. Wagner†
Westinghouse Research Laboratories, Pittsburgh 35, Pennsylvania

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Measurements have been made of the electron spin-lattice relaxation of the $-\frac{1}{2}$, $+\frac{1}{2}$ line of Cr^{+++} in $K_3Co(CN)_6$ at 9kMc/sec as a function of temperature, chromium concentration, and the proximity of the $-\frac{3}{2}$, $-\frac{1}{2}$ line. The experimental procedure, involving inversion of the line, is capable of distinguishing a "bottleneck" relaxation time from a true spin-phonon relaxation time, T_1. At Cr^{+++} concentrations up to 0.5%, the relaxation data are fitted well by single exponential functions of time. Between 1.3°K and 4.8°K, T_1 varies approximately as $T^{-1.2}$ indicating that the single phonon process is dominant. No phonon-bath bottleneck is observed, in agreement with calculations based on the measured parameters. A "proximity effect" is observed in which the relaxation rate of the $-\frac{1}{2}$, $+\frac{1}{2}$ line is enhanced when the $-\frac{3}{2}$, $-\frac{1}{2}$ line is within 20 linewidths. At one percent Cr^{+++}, the relaxation behavior is markedly different: the recovery is considerably faster and can no longer be described by a single time constant. This change and the proximity effect are interpreted qualitatively in terms of spin cross relaxation. The measured linewidth increases with concentration from 0.03% to 2% Cr^{+++}, even though the line is observed to be inhomogeneous at and below 0.5% Cr^{+++}.

I. INTRODUCTION

The existing theory[1–3] of the interaction between the electron spins of a paramagnetic solid and the crystal lattice postulates two relaxation processes: a direct process in which a spin absorbs or emits a single phonon at the frequency of the spin transition, and an indirect or "Raman" process in which one phonon is absorbed and another is emitted at a frequency differing by the frequency of the spin transition. The strength of the interaction is characterized by the spin-lattice relaxation time, T_1, which is, properly, the time constant for the equilibration of the spin system and those lattice modes with which it exchanges quanta. At temperatures low enough that only the direct process is active, T_1 for a two-level system is expected to be inversely proportional to the density of lattice modes at the spin transition frequency, to the occupation number of these modes including the zero point term, and to the square of the appropriate spin-phonon matrix element. A frequency or magnetic field dependence enters through all three factors and a temperature dependence through the second. For sufficiently high fields, there is no explicit dependence on the density of paramagnetic centers in the absence of exchange or other cooperative process.

Experimentally, a number of factors may complicate the task of determining T_1 and its dependence on temperature and magnetic field. This is particularly so where the spin-phonon coupling is strong and the spin density is high in relation to the number of interacting lattice modes. Here, if the spin system is heated, a phonon emitted by a spin in the center of a crystal has a high probability of being reabsorbed by another spin before it is scattered by a crystal boundary or by another phonon.[4,5] The recovery of the spin system is then retarded and is largely governed by the rate at which the "imprisoned"[6] phonons can escape. This rate, in turn, depends on the size, geometry, and physical perfection of the sample and on the mechanism of line broadening.[7] Such a situation is often termed a phonon-bath "bottleneck." Under such circumstances the recovery does not proceed with a single time constant nor does it reveal the true spin-lattice relaxation time.[7]

If the spin density is reduced sufficiently, by dilution, the phonon imprisonment can be made negligibly small, and the true T_1 should be observed. The effects of dilution have been studied by the Leiden school using the nonresonant technique.[8,9] In many cases dilution increases the measured relaxation time. This is the opposite of what one would expect from a phonon-bath bottleneck and may indicate the presence of yet other factors. No results have been reported for dilutions at which the measured times become independent of dilution. Unfortunately, in this method there is a limit to the permissible dilution, set by the breakdown of the Casimir-du Pré hypothesis.[8]

Microwave resonance techniques on the other hand are well fitted to deal with very dilute materials and have been applied in several ways.[10–20] In a recent micro-

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† Present Address: Department of Electrical Engineering, The Johns Hopkins University, Baltimore, Maryland.

[1] J. H. Van Vleck, Phys. Rev. **57**, 426 (1940).

[2] R. de L. Kronig, Physica **6**, 33 (1939).

[3] I. Waller, Z. Physik **79**, 370 (1932).

[4] J. H. Van Vleck, Phys. Rev. **59**, 724 (1941).

[5] M. W. P. Strandberg, Phys. Rev. **110**, 65 (1958).

[6] The close analogy with the imprisonment of resonance radiation in gas discharges [T. Holstein, Phys. Rev. **72**, 1212 (1947); and **83**, 1159 (1951)] has recently been pointed out by T. Holstein (private communication) and P. W. Anderson (reference 7).

[7] P. W. Anderson, Phys. Rev. **114**, 1002 (1959).

[8] C. J. Gorter, *Paramagnetic Relaxation* (Elsevier Publishing Company, Amsterdam, 1947).

[9] L. C. Van der Marel, J. Van den Broek and C. J. Gorter, Physica **23**, 361 (1957); and **24**, 101 (1958).

[10] A. H. Eschenfelder and R. T. Weidner, Phys. Rev. **92**, 869 (1953).

[11] A. M. Portis, Phys. Rev. **91**, 1071 (1953).

wave study of three diluted salts, $Gd_2Mg_3(NO_3)_{12}\cdot 24H_2O$, $K_3Cr(CN)_6$ and $Cu(NH_4)_2(SO_4)_2\cdot 6H_2O$, Giordmaine *et al.*[13] have concluded that the observed times are due to lattice-bath bottlenecks, even at dilutions of 100 or more, and that the true spin phonon times must be shorter than the observed times by some orders of magnitude. It was also suggested that the frequency width of the imprisoned phonons is much broader than the resonance linewidth[4] and that the lines, which they had expected to be inhomogeneously broadened, are in fact homogeneously broadened by the phonons.

Phonon imprisonment in a relatively narrow frequency band in dilute $K_3Cr(CN)_6$ and in ruby has been postulated by Strandberg *et al.*[21] and Morris *et al.*[22] on the basis of the operating characteristics of two different masers. On the other hand, relaxation measurements on three other dilute paramagnetic crystals, $Gd(C_2H_5SO_4)_3\cdot 9H_2O$, $(NH_4)Al(SO_4)_2\cdot 12H_2O$ and ruby, by Davis *et al.*,[16] and on dilute $K_3Cr(CN)_6$ by Collins *et al.*,[18] appear to show that there is no phonon-bath bottleneck.

The assumptions and conclusions of Giordmaine *et al.*[13] have recently been questioned from several points of view. Anderson[7] has shown that the frequency distribution of the phonons interacting with the spins cannot be significantly broader than the resonance linewidth. Bloembergen[23] and Strandberg *et al.*[21] have pointed out that low frequency masers would not be able to operate if such broadening were significant.

Another factor in spin-lattice relaxation, called "cross relaxation," has recently been discussed by Bloembergen *et al.*[24] In this process excitation is transferred among the various lines of a multilevel system by means of multiple spin transitions. Although phonons are not directly involved, cross relaxation can strongly affect the pattern of thermalization of spin systems at low temperatures. It provides an explanation for the effects observed by Giordmaine *et al.* and may also account for some of the observations of Strandberg *et al.* Cross relaxation can be made negligible by sufficient dilution.

In addition to phonon imprisonment and cross relaxation, a further factor complicates the interpretation of spin-lattice relaxation measurements in multilevel systems. In such systems there are several transitions each with a distinct spin-phonon transition probability. A number of time constants, each compounded from these probabilities, is in general required to properly describe the relaxation.

The aim of the present study was to examine the relaxation, and its dependence on temperature and concentration, in a material that had been previously studied. In particular, it was desired to establish the presence or absence of a phonon-bath bottleneck and to delineate the effects of cross relaxation. Dilute potassium chromicyanide was chosen because it was, at that time, the most widely investigated[13,14,21] of the salts of interest and was available in rather a wide range of Cr^{+++} concentration.

II. EXPERIMENTAL TECHNIQUE

Of the various resonance techniques for investigating spin-lattice relaxation, the cw saturation method, developed in nuclear resonance,[25] has been most widely used[10–12,14] because of its simplicity. It consists of measuring the magnitude of the resonance absorption as a function of the microwave power incident on the sample. Only one relaxation time is taken into account and certain assumptions which are not always reliable are needed to deduce it from the data. The method does not directly distinguish between a genuine spin-phonon time and a phonon-bath bottleneck time.

Other methods rely on observation of the absorption as a function of time after the spin populations have been disturbed by microwave power. In the "saturation-recovery" method[16,26] the magnetic field is held constant at a value corresponding to maximum absorption, a pulse of microwave power of sufficient intensity and duration to saturate the absorption is applied, and the recovery of the absorption is then monitored as a function of time. Any multiplicity of relaxation times is in principle observable. This technique requires no assumptions regarding the paramagnetic system save that the line is uniformly saturated. Complications can arise with inhomogeneously broadened lines.[26] Under certain conditions the method can distinguish a bottleneck from genuine spin-lattice relaxation.[16]

In the "inversion-recovery" method,[15,17–19] the spin populations are inverted by rapid passage or by a 180° pulse. As used in the present study, the method consists of inverting a line by rapid passage[27,28] of the field through resonance and subsequently observing the

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[12] G. Feher and H. E. D. Scovil, Phys. Rev. **105**, 760 (1957).

[13] J. A. Giordmaine, L. E. Alsop, F. R. Nash, and C. H. Townes, Phys. Rev. **109**, 302 (1958).

[14] A. L. McWhorter and J. W. Meyer, Phys. Rev. **109**, 312 (1958).

[15] J. W. Culvahouse and F. M. Pipkin, Phys. Rev. **109**, 319 (1958).

[16] C. F. Davis, Jr., M. W. P. Strandberg, and R. L. Kyhl, Phys. Rev. **111**, 1268 (1958).

[17] P. F. Chester, P. E. Wagner, and J. G. Castle, Jr., Phys. Rev. **110**, 281 (1958).

[18] S. A. Collins, Jr., R. L. Kyhl and M. W. P. Strandberg, Phys. Rev. Letters **2**, 88 (1959).

[19] P. E. Wagner, J. G. Castle, Jr., and P. F. Chester, Bull. Am. Phys. Soc. **4**, 21 (1959).

[20] C. Kikuchi, J. Lambe, G. Makhov, and R. W. Terhune, J. Appl. Phys. **30**, 1061 (1959).

[21] M. W. P. Strandberg, C. F. Davis, B. W. Faughnan, R. L. Kyhl, and G. J. Wolga, Phys. Rev. **109**, 1988 (1958).

[22] R. J. Morris, R. L. Kyhl, and M. W. P. Strandberg, Proc. Inst. Radio Engrs. **47**, 80 (1959).

[23] N. Bloembergen, Phys. Rev. **109**, 2209 (1958).

[24] N. Bloembergen, S. Shapiro, P. S. Pershan, and J. O. Artman, Phys. Rev. **114**, 445 (1959).

[25] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).

[26] K. D. Bowers and W. B. Mims, Phys. Rev. **115**, 285 (1959).

[27] F. Bloch, Phys. Rev. **70**, 460 (1946).

[28] A. G. Redfield, Phys. Rev. **98**, 1787 (1955).

whole line as a function of time during its recovery toward thermal equilibrium. An important advantage of the inversion technique is the test that it provides for phonon imprisonment. When the spin system is at a negative temperature, a phonon interacting with it stimulates the emission of another phonon. If this phonon stimulates another emission before it reaches the boundary, the relaxation will be accelerated. The situation changes as soon as the spin temperature becomes positive, at which point the imprisonment sets in and the recovery is retarded. A marked decrease in the slope of the recovery curve at the point of saturation is therefore to be taken as evidence of imprisonment.

In the present technique, inhomogeneous broadening[11] is readily detected by the "hole burning" method[25] and, even if present, does not affect the results, as microwave energy is applied across the whole line. Since the shape of the whole line is observed, any gross effects of cross relaxation or spin diffusion within the line may be detected.

In the present work, resonances were observed with a superheterodyne spectrometer operating near 9 kMc/sec with an input power of 10^{-8} watt. This value was found to be low enough to have no effect on the recoveries. Relaxation measurements were made over the range 1.3–4.8°K. The cavity[29] was constructed of silvered C-8 epoxy resin to permit the rapid field sweeps required for inversion. A pair of Helmholtz coils mounted on the cavity in the liquid helium allowed sweeps up to 120 gauss in a time $\geqslant 20$ microseconds. Above the λ point of helium, bubbling in the cavity was reduced with a shaped insert of polystyrene foam which diverted bubbles away from the regions of strong E field and out of slots cut in the cavity walls. This arrangement allowed good circulation of liquid helium about the sample and ensured thermal contact between the crystal and a carbon resistance thermometer outside the cavity in the helium bath. Microwave power for rapid passage was provided by an auxiliary X-13 klystron, normally not oscillating, whose beam voltage was pulsed to 900 v for the duration of the inverting field sweep. In some of the later work, inverting power up to 12 watts was obtained from a pulsed traveling wave amplifier.

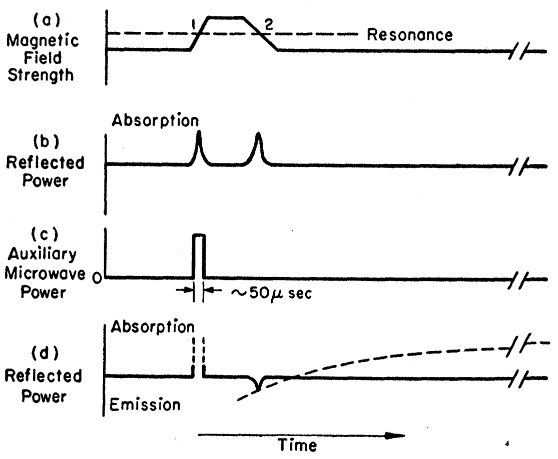

FIG. 1. Time sequence for observation of recovery after inversion by rapid passage. The magnetic field is swept through resonance at 1 and 2. On alternate cycles, rapid passage is effected by a pulse of microwave power applied during sweep 1. The resulting inversion is observed on sweep 2. The time interval between the sweeps is adjustable. Each cycle is much longer than T_1.

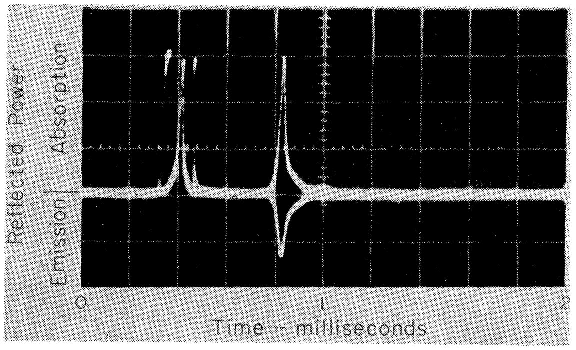

FIG. 2. Oscilloscope presentation of traces (b) and (d) of Fig. 1 superposed. The deviation of the absorption from equilibrium is read off directly.

The sequence of events in a measurement of T_1 is shown in Fig. 1. The steady magnetic field was held slightly below the resonant value. A current pulse of the form shown (a), applied to the Helmholtz coils, swept the field through resonance at times 1 and 2. The absorption line was seen twice at the output of the spectrometer as indicated in (b). For rapid passage, a pulse of microwave power was applied at the resonant frequency of the cavity during the first sweep.[30] Inversion of the line resulted and was observed on sweep 2 as in (d). By delaying the second passage to later times the recovery to normal absorption was followed. The quantity of interest is the deviation of the line height from its equilibrium value. By applying the inverting pulse only on alternate cycles this deviation was read directly from an oscilloscope presentation, Fig. 2. The duration of each cycle was much longer than T_1. An exact correction was applied to each reading, using the relationship between reflection coefficient and cavity Q's to give a quantity proportional to the deviation of the peak absorption from its equilibrium value. Care was taken to have the resonance loss a small fraction of the total cavity loss, in order to avoid the complications of radiation damping.[31] With one sample a direct check for radiation damping was made by altering the cavity Q.

The stability of the spectrometer with helium II in the cavity allowed line shapes to be obtained by record-

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[29] P. F. Chester, P. E. Wagner, J. G. Castle, Jr., and G. Conn, Rev. Sci. Instr. **30**, 1127 (1959).

[30] The conditions of rapid passage were typically: microwave field strength 0.5–2.0 gauss, time of passage through 10% points $\sim 10^{-4}$ sec with $T_1 \sim 10^{-2}$ sec. A field of 5 milligauss produced a saturation factor of 10 at Cr^{+++} concentrations below 1%.

[31] S. Bloom, J. Appl. Phys. **28**, 800 (1957), and references therein

TABLE I. Samples of dilute $K_3Cr(CN)_6$

Sample	Percent Cr:Co nominal (in liquor)	Percent Cr:Co chemical[a] analysis	Source Crystal[b]	Volume mm^3	Linewidth Mc/sec[c]
A	0.03	···	JHU359	35	8.8
B	0.1	0.06	LL45	40	15
C	0.1	0.06	LL45	40	22
D	0.1	0.06	LL45	35	···
E	0.5	0.24	JHU87	28	24
F	0.5	0.4	JHU131	15	46
G	0.5	0.5	LL21	27	45
H	1.0	1.0	JHU59	8	56
I	0.5	1.9	CRC	···	87

[a] On crystals cut from the same host crystal or grown from the same solution.

[b] JHU—Johns Hopkins Radiation Laboratory, courtesy of A. Kiel and J. Minkowski.
LL—Lincoln Laboratories, courtesy of J. W. Meyer.
CRC—Cambridge Research Center, courtesy of I. Lessin.

[c] Full width at half absorption.

ing the output of the spectrometer as the steady magnetic field was swept slowly through resonance. A small correction was made to the traces to allow for the effects of dispersion.

III. THE PARAMAGNETIC MATERIAL

Crystals of chromium doped $K_3Co(CN)_6$, grown from aqueous solution, were obtained from several sources as indicated in Table I. Most of the crystals were optically clear except for a few occlusions. Samples were prepared in several ways: *B*, *C*, and *H* were cut out with a wet string saw and sanded to size; *D* and *I* were sanded and then etched down; *E* and *F* were used as cut; *G* was reduced to size by etching only; and *A* was the crystal as grown with only a light surface etch. Samples *A*, *C*, *D*, and *F* were glued to styrofoam with rubber cement, the others to solid polystyrene.

The paramagnetic resonance spectrum of Cr^{+++} in $K_3Co(CH)_6$ has been studied by Baker *et al.*,[32] by Walsh,[33] and more recently by Artman *et al.*[34] The principal features of the spectrum in an external field H are ascribed to two nonequivalent ions with $S=\frac{3}{2}$ on the two Co sites in the monoclinic unit cell.[35,36] Orientation of the magnetic field is specified with respect to a set of orthorhombic axes.[32] Coincidence of the two spectra is expected when H is applied in the *ac* plane or in the *bc* plane.[37] Samples were mounted to permit rotation of H in the *ac* plane. The alignment was checked in each case[38] by plotting the values of field required for resonance as a function of magnet angle and comparing them with the calculations of Chang and Siegman.[39] Figure 3 shows the spectrum observed with sample *G*. The angle in the *ac* plane between H and the crystal *c* axis is labelled θ. The energy levels are numbered in order of increasing energy. The alignment of a sample was considered acceptable if the 2-3 line was observed to be a singlet over the range of angles used in the relaxation measurements. In order to make comparisons among samples, the relaxation measurements were made at a standard orientation where the field required for the 2-3 line is a maximum with respect to θ. This orientation is designated θ_s in Fig. 3.

The 2-3 absorption was found to be Lorentzian out to three linewidths for samples *B*, *E*, *F*, *H*, and *I*. For *A* and *G* the line was slightly narrower than Lorentzian. The observed width increases with concentration even at the lowest concentrations, as given in Table I. The nature of the broadening was investigated by attempting to burn or invert a hole in the line. By applying microwave power to only part of the line during the first field sweep, it was found possible to invert a hole for samples

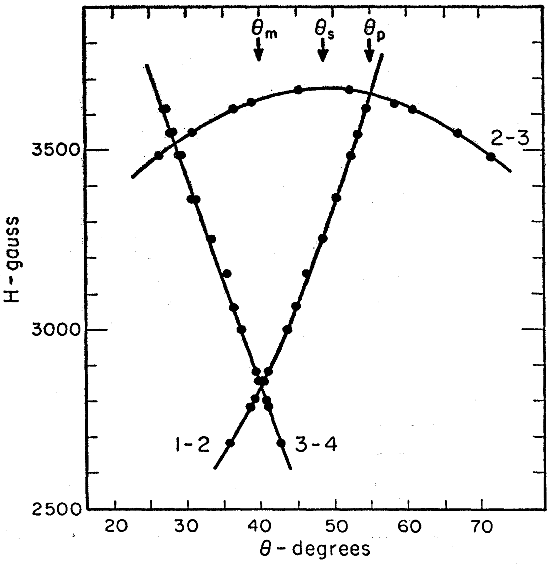

FIG. 3. Magnetic field strength, H, required for resonance of the 1-2, 2-3, and 3-4 lines as a function of angle between H and the *c* axis in the *ac* plane. The points were taken at 9200 Mc/sec with sample *G* at 4.2°K.

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[32] J. M. Baker, B. Bleaney, and K. D. Bowers, Proc. Phys. Soc. (London) **B69**, 1205 (1956).

[33] W. M. Walsh, Jr., Phys. Rev. **114**, 1485 (1959).

[34] J. O. Artman, J. C. Murphy, J. A. Kohn, and W. D. Townes, Phys. Rev. Letters **4**, 607 (1960).

[35] V. Barkhatov and H. Zdhanov, Acta Physicochim. U.R.S.S. **16**, 43 (1942); and V. Barkhatov, Acta Physicochim. U.R.S.S. **16**, 223 (1942).

[36] The positions of *C* and *N* have been observed with neutron diffraction by N. A. Curry and W. A. Runciman, Acta Cryst. **12**, 674 (1959).

[37] *Note added in proof.*—It has been pointed out by J. O. Artman and J. C. Murphy (private communication) that a splitting of the lines is to be expected even with H in the *ac* plane if two or more crystal polytypes (see reference 34) are present. It seems likely that the splitting of the 1–2 line and some of the inhomogeneous broadening of the 2–3 line in the present work arise in this way. A quantitative comparison must await measurements of polytype parameters at helium temperatures. A complete explanation of our results along these lines would seem to require that the polytype distribution be a function of concentration or at least vary from sample to sample. The presence of crystal polytypes does not affect the discussion of phonon imprisonment.

[38] In crystals *A*, *B*, *C*, *E*, *G*, and *H* x-ray photographs were also used.

[39] W. Chang and A. Siegman, Technical Report 156-1, Stanford Electronics Laboratory, May, 1958 (unpublished).

A, *B*, and *C*, [see Fig. 4(a)], and to saturate a hole for *E*. We conclude that in this concentration range most of the observed broadening is inhomogeneous. At higher concentrations the inhomogeneity was not as marked. Figure 4(b) shows the behavior of sample *G*. In sample *H* we were unable to detect any signs of a hole 50 μsec after passage. It is interesting that the linewidth is a strong function of concentration in a range where inhomogeneous broadening predominates. The inhomogeneous contribution to the linewidth is evidently a function of the Cr^{+++} concentration. This may be due to strains introduced by the larger chromium ion on the cobalt site.[37]

IV. RELAXATION RESULTS AND DISCUSSION

The recovery of the 2-3 line after inversion was measured at the standard orientation θ_s as a function of time, temperature, and concentration. Further measurements were made at the angle θ_m and in the vicinity of θ_p as defined in Fig. 3.

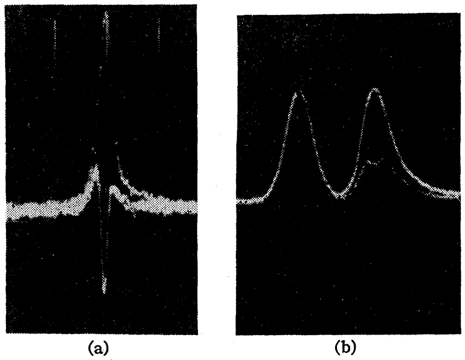
(a) (b)

FIG. 4. "Hole burning." In (a), an inverted hole in the 2-3 line of sample *C* at 2.16°K is seen 280 μsec after rapid passage. In (b), a hole in the 2-3 line of sample *G* at 2.0°K is seen 70 μsec after rapid passage.

Time Dependence

For samples *A* through *G* at θ_s the data at all temperatures can be fitted within the experimental error by single exponential functions. Figure 5 shows a typical recovery curve, starting from an inversion of ~20% and proceeding to ~2% of complete recovery.

It is instructive to see under what conditions a single exponential is to be expected from the six possible relaxation paths in a four-level system. The rate equations, neglecting any cross relaxation, are

$$\dot{n}_i=\sum_{i\neq j} w_{ji}n_j-w_{ij}n_i, \qquad (1)$$

where w_{ji}=spin-phonon transition probability from level *j* to *i* and $w_{ji}=w_{ij}\exp(h\nu_{ji}/kT)$. The solutions can be written

$$n_i=\sum_\alpha a_\alpha \exp(-\lambda_\alpha t).$$

Because of the conservation condition $\sum \dot{n}_i=0$, only three of Eqs. (1) are independent, and there are in general three values for λ_α. Only in special cases should a single time constant result. However, in many cases the recovery may proceed in a fashion indistinguishable in practice from a single time constant.

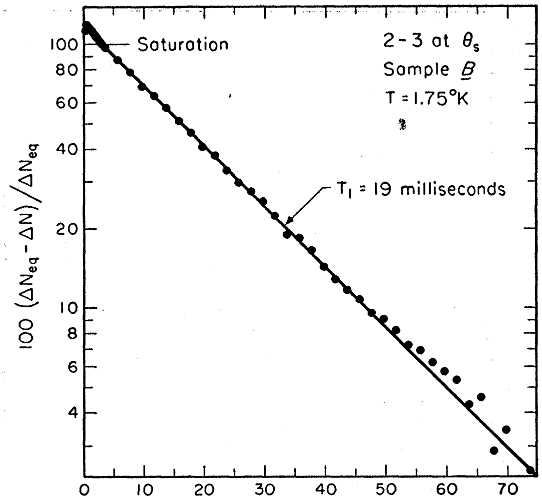

FIG. 5. Recovery of absorption as a function of time after inversion in dilute $K_3Cr(CN)_6$.

A comparison with experiment is facilitated by considering the case of $\nu_{12}=\nu_{34}$. This adds a further constraint to the system by tending to produce a common spin temperature in the coincident lines in a time of the order of T_2, the spin-spin relaxation time. When $w_{ij}T_2\ll 1$, the thermal relaxation has to take place in a way that closely maintains the equality of spin temperature of the coincident lines. To take account of the constraint we add the following spin-spin rates $(\dot{n}_i)_s$ to Eqs. (1)

$$\begin{aligned}(\dot{n}_1)_s&=-A(n_1-n_2-n_3+n_4),\\ (\dot{n}_2)_s&=A(n_1-n_2-n_3+n_4),\\ (\dot{n}_3)_s&=A(n_1-n_2-n_3+n_4),\\ (\dot{n}_4)_s&=-A(n_1-n_2-n_3+n_4), \qquad (2)\end{aligned}$$

where $A\sim 1/T_2$ and it is assumed that $h\nu\ll kT$. The precise form of the spin-spin terms is not crucial, since we are concerned with the behavior of the system only for times much longer than T_2.

The values of λ obtained from the augmented equations are

$$\lambda_\alpha\sim A\sim 1/T_2$$

$$\begin{aligned}\lambda_\beta,\lambda_\gamma=&\bar{w}_{23}+\bar{w}_{14}+\tfrac{1}{2}(\bar{w}_{24}+\bar{w}_{13})+\tfrac{1}{2}(\bar{w}_{12}+\bar{w}_{34})\\ &+[(\bar{w}_{14}-\bar{w}_{23})^2+\tfrac{1}{4}(\bar{w}_{24}+\bar{w}_{13}-\bar{w}_{12}-\bar{w}_{34})^2]^{\frac{1}{2}}, \qquad (3)\end{aligned}$$

where $\bar{w}_{ij}=(w_{ij}+w_{ji})/2$, and terms of order $w(h\nu/kT)$ have been neglected. λ_α is presumed to occur too quickly to be seen. λ_β and λ_γ characterize the two possible thermal relaxation modes consistent with the constraint.

Recoveries were measured with samples *C* and *G* at 2.16°K at the orientation for which $\nu_{12}=\nu_{34}$, shown as

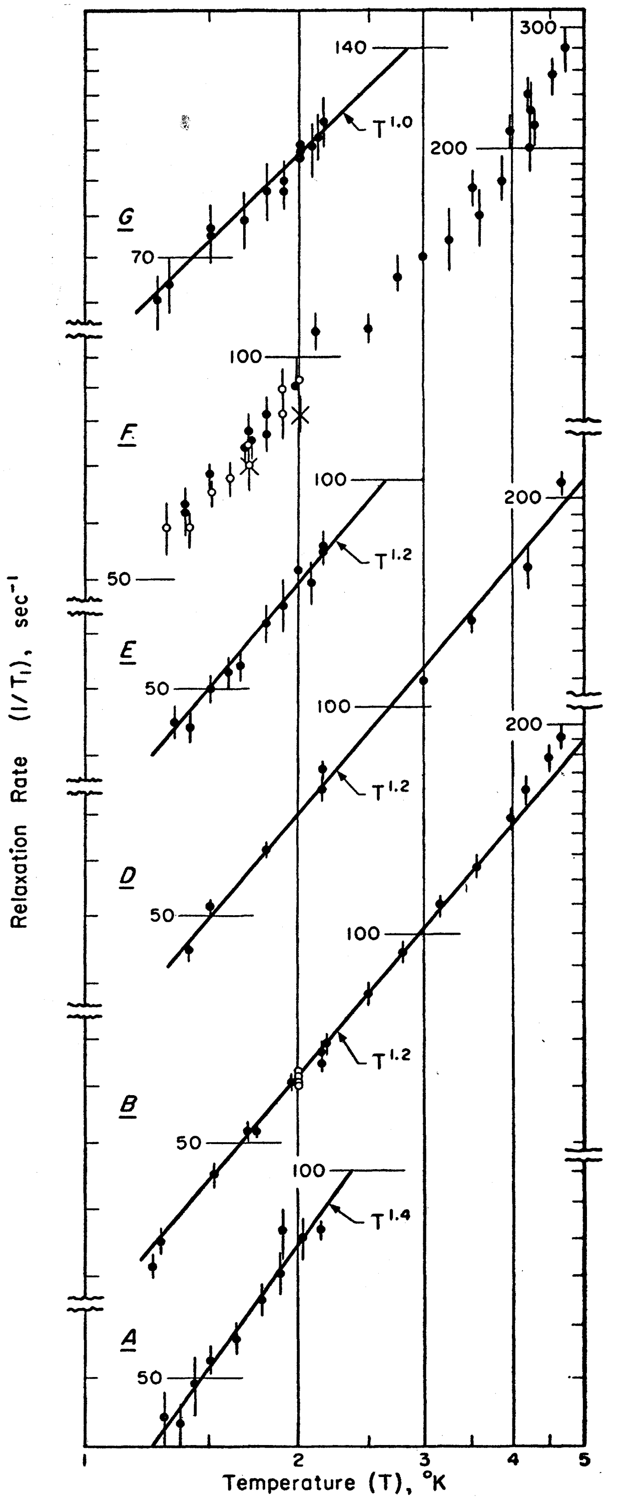

FIG. 6. Reciprocal of T_1 vs temperature for six samples of dilute $K_3Cr(CN)_6$. Samples are described in Table I. For sample F only, T_1 was measured in three cavities having different Q's (solid circles $Q_m/Q_e \sim 7$, open circles $Q_m/Q_e \sim 23$, crosses $Q_m/Q_e \sim 4$). $\theta = \theta_s$ for A, B, D, E, and F; $\theta = 82°$ for G.

θ_m in Fig. 3. By adjusting the magnetic field either the 2-3 line or the (1-2, 3-4) line could be inverted. A single time constant fits the data over the whole range of observation from $\sim 40\%$ inversion to $\sim 6\%$ of thermal equilibrium.[40] On the basis of plots of composite exponential functions made for comparison, it is estimated that two components, with comparable coefficients and with time constants differing by a factor of two, could just have been distinguished. Within this limitation the following possibilities are compatible with our observations at θ_m.[41]

(a) All $\bar{w}_{ij}$ comparable;
(b) One of the $\bar{w}_{ij}$ negligible, special relationships among the others;
(c) Certain cases with two $\bar{w}_{ij}$ negligible and a special relationship between the others.

The case that any one $\bar{w}_{ij}$ dominates is ruled out. Evidently at θ_m, and probably at other angles most of the six paths are effective in relaxation.

Temperature Dependence

The dependence of T_1 on temperature was measured at θ_s in the range 1.3 to 4.8°K. Temperatures were measured to an accuracy of 0.02°K with a calibrated carbon resistance thermometer, but were generally regulated to within $\sim$.001°K. The results are shown in Fig. 6. The length of the vertical bars gives an estimate of the uncertainty in determining the time constant of a given recovery curve. The points at 2°K for sample B were taken after warming to room temperature. The points for sample F include measurements in three different cavities. Measurements of T_1 at 2.16°K on five samples with 0.06% Cr^{+++} showed a spread of about ±10%.

For the data at θ_s a T^{-1} law is not an acceptable fit over the whole temperature range. If all these data are to be described by a single T^{-n} law, then the best value for n is 1.2. However, there are signs of a faster dependence near 4°K.

Even with the single-phonon process, there are two possible reasons for a small deviation from a T^{-1} law in a multilevel system. When $h\nu \sim kT$ for some paths, the zero point motion weakens the temperature dependence. In the present work, however, this effect is not expected to be noticeable above the scatter for any reasonable relationship between the $\bar{w}_{ij}$'s. The second factor is the redistribution of the spins toward the lowest energy levels as the temperature is reduced. Depending on the relative importance of the various transitions, this could lead to an increase or a decrease in the exponent

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[40] At 2.16°K T_1 for the (2-3) line at 3680 gauss is 14.5 milliseconds and T_1 for the (1-2, 3-4) line at 2840 gauss is 18.0 milliseconds.

[41] It is conceivable that either λ_β or λ_γ might be too fast for us to observe. This, however, is not compatible with the observed degrees of inversion.

of T. The law is closer to T^{-1} in sample G, for which the level separations were different.

It is concluded that in dilute $K_3Cr(CN)_6$ the direct process predominates in this temperature range,[42] but that an additional mild temperature dependence is also present.

Discussion of Phonon-Bath Bottleneck

Whatever the relative importance of the several spin-lattice paths discussed above, the fact that the curve of Fig. 5 is linear throughout the whole range of observation on both sides of infinite spin temperature, implies that there can be no serious phonon-bath bottleneck. This remains true down to 1.3°K and for concentrations up to and including 0.5% Cr^{+++}.

We may ask whether such a bottleneck is to be expected for the direct relaxation process in these crystals. A crude estimate of the mean lifetime (τ_{ph}) and therefore the mean free path (λ) of a phonon against reabsorption by the spin system is given for a two-level system, by the expression

$$\lambda = c\tau_{ph} \simeq c[(T_1)_0/\Delta N]\rho(\nu)\Delta\nu,$$

where $(T_1)_0 = (2n+1)(T_1)_T$, and c is the velocity of sound, $\rho(\nu)$ is the density of lattice modes at frequency ν, n is their occupation number, $\Delta\nu$ is the frequency width of interaction, $(T_1)_0$ is the spin-lattice relaxation time at 0°K, and ΔN is the excess of spin population in the lower state at any temperature T. In a multilevel system we must take into account the several possible relaxation paths. In the present case, if we assume that all six transitions are active in relaxation the appropriate $(T_1)_T$ to use for a given transition is of the order of six times the observed T_1. The mean free path for phonons at ν_{23} is then given by

$$(\lambda_{23})_T \simeq \frac{6(2n+1)T_1}{(\Delta N)_{23}} \frac{8\pi}{c^2} \nu_{23}{}^2 \Delta\nu_{23},$$

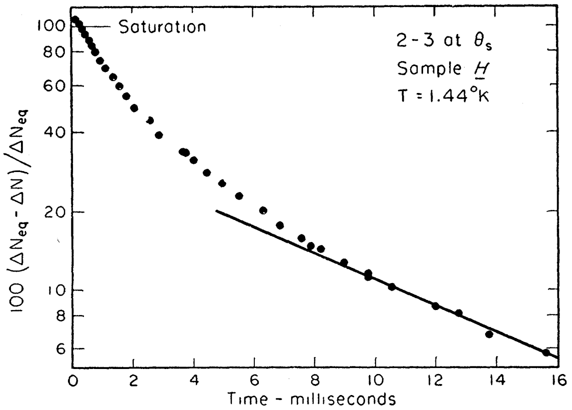

FIG. 7. Recovery as a function of time after inversion in one percent potassium chromicyanide.

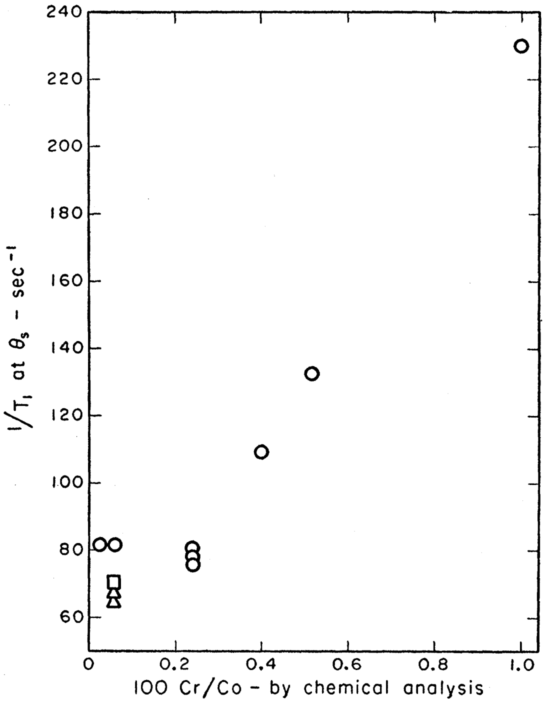

FIG. 8. Reciprocal of T_1 at 2.16°K vs concentration of Cr^{+++}.

where T_1 is the observed relaxation time at temperature T. Taking the equilibrium value for ΔN_{23}, we have for sample F at 4.2°K: $\nu = 9.3 \times 10^9$ sec^{-1}, $\Delta N \simeq 4 \times 10^{17}$/cc, $n \sim 9$, $T_1 = 4.5 \times 10^{-3}$ sec, $c \sim 2 \times 10^5$ cm/sec, and $\Delta\nu \simeq 10^8$ sec^{-1}, giving $\lambda \sim 2.8$ cm. At 1.3°K, $\lambda \sim 8$ mm. In this sample the mean distance of a spin from the surface is about one mm. If the phonon excitation is transferred to the helium bath upon one collision with the surface, we should not expect severe imprisonment. However, a slight degree of imprisonment is possible and might have given rise to a small change in the slope of the recovery at the point of saturation, if the relaxation had taken place entirely through the 2-3 transition. In fact, the recovery is compounded from several paths and the change may not be detectable. Moreover, since most transitions are at positive temperatures, the overall effect may even be a slowing, when the 2-3 line is itself inverted.

Since imprisonment becomes relatively more important as the temperature is lowered, it would give rise to a dependence faster than T^{-1}, the exponent increasing with sample dimension. A check on this is afforded by the data for samples B ($\sim$3 mm) and D (0.5 mm), which were cut from the same host. As seen in Fig. 6 there is no significant difference in temperature dependence between the two sets of data. While the rates in the thin sample are about 10% faster, this is within the sample to sample reproducibility. If phonon imprisonment had been responsible for the $T^{-1.2}$ law in sample B, one would have expected a noticeable change toward $T^{-1.0}$ in sample D.

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[42] This conclusion is also reached in S. Shapiro and N. Bloembergen, Phys. Rev. **116**, 1453 (1959).

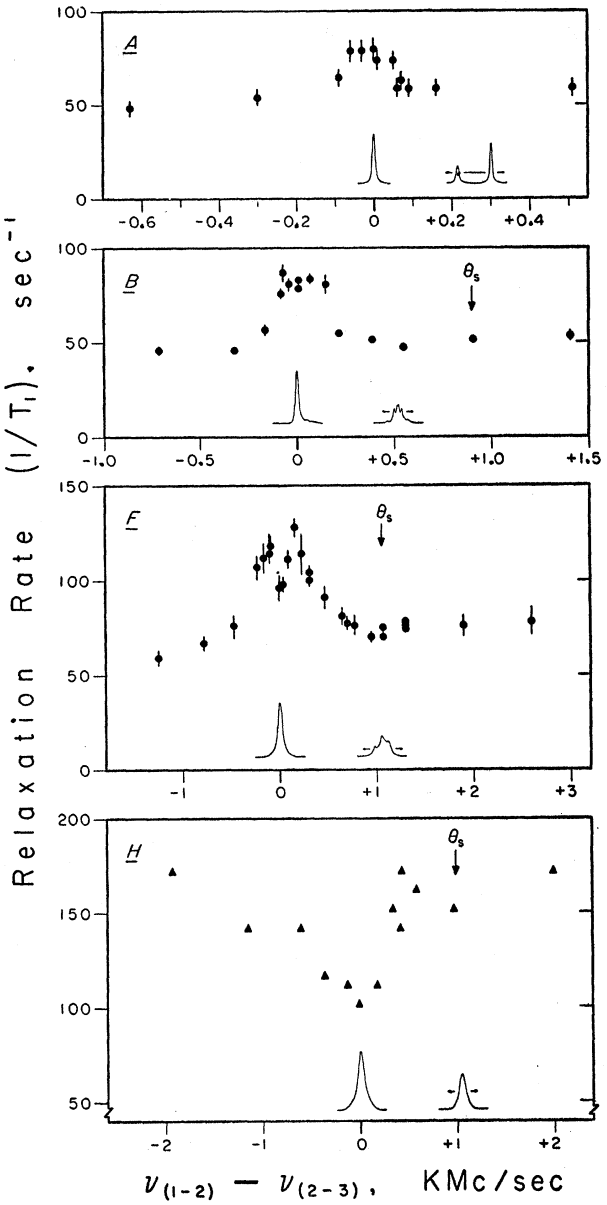

FIG. 9. Reciprocal of T_1 for the 2-3 line vs proximity (in frequency) of the 1-2 line for samples A, B, F, and H at 1.70°K. The normal appearance of the two lines is shown in each case to correct frequency scale.

Concentration Dependence

Between 0.5% and 1% Cr^{+++}, the nature of the recovery appears to change. A recovery curve for sample H is shown in Fig. 7. The rate of recovery is faster than at the lower concentrations and no longer proceeds with a single time constant. Even the asymptotic time constant is shorter than those observed in the more dilute materials at the same temperature. As the temperature is lowered, this time constant varies roughly as T^{-1} but accounts for a decreasing fraction of the recovery, 85% at 4.2°K and 35% at 1.7°K. It seems highly improbable that the onset of phonon imprisonment could be responsible for this new behavior, since imprisonment is expected to reduce the rate of recovery rather than to increase it. Radiation damping cannot be responsible since at 4.2°K the resonance absorption amounts to only 3% of the total cavity loss.

Figure 8 shows the concentration dependence of relaxation rate at 2.16°K. It should be noted that the point for sample H corresponds to the asymptotic time constant. It is clear that the rate of relaxation increases with concentration particularly above 0.5% Cr^{+++}. Further light is shed on this matter by the results of the next section.

Angular Dependence

A series of experiments was carried out at 1.7°K in which the value of H and θ were varied about the point θ_p so as to alter the frequency separation between the 2-3 line and the 1-2 line. At each setting a measurement of T_1 was made for the 2-3 line. The results for four samples are plotted in Fig. 9. The normal appearance of the lines is shown in correct frequency scale for each case. In most cases the 1-2 line appeared split in spite of attempts to make it coallesce by small adjustments of angle.[43]

A general feature for samples A, B, and F is an increase in the rate of relaxation as the lines approach each other. The rate reaches a maximum when the lines overlap substantially and falls somewhat when they coincide and are inverted together. This "proximity effect" extends over a frequency range of approximately ±80 Mc/sec in A, ±300 Mc/sec in B, and ±550 Mc/sec in F.[44] In most cases, even within the proximity region, recovery takes place with a single time constant over the whole range of observation. In cases of actual line overlap a second, shorter, time constant is observed for the first few percent of recovery.

Since we have shown that there is no serious phonon-bath bottleneck in these samples, the explanation of the proximity effect cannot lie along these lines. The effect can be explained on the basis of cross relaxation. The process of inversion heats the 2-3 transition and cools the 1-2 transition. When the frequencies come within a few linewidths of each other, simultaneous spin flips become possible.[24] The simplest case is a double spin flip in which a state 1 spin flips up to state 2 while a state 3 spin simultaneously flips down to state 2. The effect of such cross relaxation is to increase the observed rate of recovery of the 2-3 line.

At separations such that the cross coupling rate is significant but does not dominate over the spin-phonon rates, we may not be able to resolve it as a separate time constant. When the lines are sufficiently close, the cross coupling rate should appear as a fast component in the

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[43] See note added in proof (reference 37).

[44] A similar result is obtained by a cw method by Shapiro and Bloembergen (reference 41) for 0.5% Cr^{+++}.

recoveries. A fast component is indeed observed at partial overlap.

The interpretation of the behavior of sample H is not as clear cut. There still appears to be a dip in the (asymptotic) relaxation rate at coincidence. The region of accelerated relaxation is not clearly defined but appears to extend over at least 1 kMc/sec, a value compatible with an extrapolation of the data for lower concentrations. At θ_s, $(\nu_{12}-\nu_{23})=1.2$ kMc/sec and $(\nu_{24}-\nu_{13})=1.9$ kMc/sec. Thus, in sample H, cross relaxation extends far enough to couple together all the levels[45] and to alter their spin temperature distribution during recovery. Consequently the pattern of spin-lattice relaxation is drastically affected. Cross relaxation is undoubtedly responsible for the marked change in behavior between 0.5% and 1.0% Cr^{+++} and is probably responsible for the slight concentration dependence of T_1 below 0.5% Cr^{+++}.

V. CONCLUSIONS

The present study resolves some of the problems associated with spin-lattice relaxation in dilute $K_3Cr(CN)_6$. In particular, for samples of the size and concentration used in masers, there is no serious phonon-bath bottleneck. The same conclusion is reached on the basis of an approximate analysis. A bottleneck may not set in even at higher concentrations because the increased spin density may be offset by the increased number of lattice modes provided by the greater linewidth and by cross relaxation. As the Cr^{+++} concentration is increased, maser action will evidently be impaired by cross relaxation before it is by a phonon-bath bottleneck.

By working with crystals sufficiently dilute to avoid cross relaxation, the true spin-phonon relaxation has been examined for one crystal orientation. The observed, apparently single-exponential, recoveries are consistent with multipath relaxation. Cross relaxation involving an adjacent line appears to speed up the recovery even at a separation of 20 full linewidths, and consequently cannot be avoided at concentrations of 1% Cr^{+++} and greater.

The temperature dependence confirms the expectation that the single phonon process is dominant, but the deviation from $T^{-1.0}$ appears to be real and to require an explanation.

The linewidths depend on concentration over the whole range in spite of the inhomogeneity observed at and below 0.5% Cr^{+++}. An explanation of the broadening mechanism would be of interest.[37] Homogenization by phonons is certainly ruled out below 0.5% Cr^{+++}.

In discussing the discrepancies between results obtained by different techniques, it should be borne in mind that the true spin-phonon time may be obscured by complicating factors in all of them. The discrepancies undoubtedly reflect the relative influence of these factors. The most reliable values will be obtained by methods that measure a time directly and require the fewest assumptions regarding the paramagnetic system. In this respect the recovery methods, and in particular the field sweep inversion method, are much to be preferred.

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[45] A similar conclusion is reached by Shapiro and Bloembergen (reference 42) for 2% Cr^{+++}.

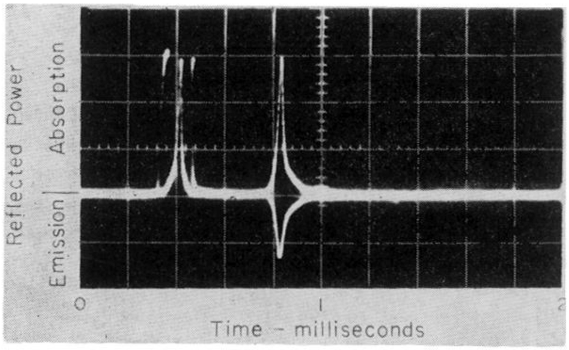
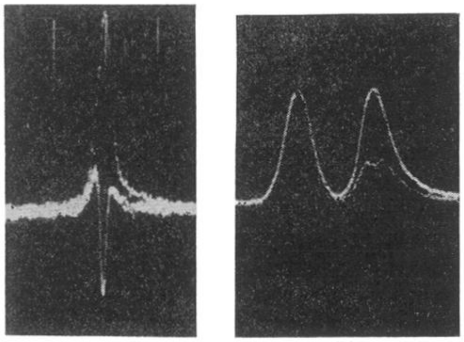


FIG. 2. Oscilloscope presentation of traces (b) and (d) of Fig. 1 superposed. The deviation of the absorption from equilibrium is read off directly.



(a) (b)

FIG. 4. "Hole burning." In (a), an inverted hole in the 2-3 line of sample C at 2.16°K is seen 280 μsec after rapid passage. In (b), a hole in the 2-3 line of sample G at 2.0°K is seen 70 μsec after rapid passage.