

## Paramagnetic Relaxation of $\text{Fe}^{3+}$ in Potassium Cobalticyanide\*

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Relaxation time measurements have been made on the  $\text{Fe}^{3+}$  ion in  $\text{K}_3[\text{Co,Fe}](\text{CN})_6$  at low temperatures using the saturation-recovery method. Two distinct decay times have been observed; the longer decay time has been interpreted as the true spin-lattice relaxation time  $T_1$ , while the more rapid initial decay can be explained by a spin-diffusion process (cross-relaxation process) within the inhomogeneously broadened resonance line. The observed temperature dependence of  $T_1$  indicates that the Raman type of interaction dominates the relaxation process near 4.2°K while a  $1/T$  law of the simple "direct process" model is predominant at temperatures below 1.8°K. For iron concentrations between 0.1% and 3.0% the spin-lattice relaxation time was found to be nearly independent of concentration.

Spin-lattice relaxation rates have been calculated on the basis of the Van Vleck theory and are found to be in reasonable agreement with the experimental measurements.

The paramagnetic absorption spectra of the more concentrated crystals (0.5–3.0%) were often quite complicated with as many as 57 lines. The degree of complexity was uncorrelated with the degree of polytypism in the crystals and is most likely the effect of exchange coupling.

### I. INTRODUCTION

THERE have been relatively few comprehensive studies of the spin-lattice relaxation process in crystals. This is due in part to the fact that much of the interest has shifted to the cross-relaxation (C-R) phenomena which often accompany and even mask the basic spin-lattice relaxation effect. Another factor in the neglect of spin-lattice relaxation studies is the unfortunate circumstance that most convenient materials are multilevel systems, which greatly complicates the interpretation of results.<sup>1</sup> However, the basic spin-lattice relaxation is in our opinion worthy of more attention.

To study relaxation effects we chose potassium cobalticyanide doped with small concentrations of potassium iron cyanide.<sup>2</sup> This material seemed convenient for the study of spin-lattice relaxation since it is a spin- $\frac{1}{2}$  system, so that some of the problems occurring in multilevel systems could be avoided. Also, the line-width for cross-relaxation should be very small at low concentrations. As will be evident in the Appendix, the spectra of these crystals proved to be far more complex than we had anticipated.

The major objective of these experiments was the investigation of the temperature dependence of the spin-lattice relaxation time  $T_1$  as a function of temperature. The measurements were made on various crystals with iron concentration between 0.1% and 3.0%. In the low concentration crystals at low temperatures ( $\approx 1.6^\circ\text{K}$ ) two distinct relaxations were observed. We interpreted the initial rapid relaxation to be a "spin-diffusion" effect, while the slow relaxation we believe to be the spin-lattice relaxation. At higher temperatures,

where the "Raman" processes<sup>3,4</sup> proved to dominate, the two relaxations were of the same order of magnitude and so were difficult to untangle.

A brief description of the experimental setup is given in Sec. II, and the experimental results are presented and analyzed in Sec. III. A calculation of the spin-lattice relaxation rate, based on the Van Vleck theory, is given in Sec. IV.

### II. THE EXPERIMENT

The investigation of relaxation effects in  $\text{K}_3[\text{Fe,Co}](\text{CN})_6$  were carried out in the temperature range from 1.6° to 4.2°K using the saturation-recovery method. The experimental setup was similar to that described by Davis, Strandberg, and Kyhl.<sup>5</sup> The saturating pulse, however, was obtained by pulse modulation of the reflector of a V-58 Klystron whose peak power output was approximately 500 mW. The use of mutual coupling (bifilar wound single tuned coils) between stages in the i.f. amplifier of the superheterodyne detection system obviated the necessity of blanking circuits, pulsed ferrite attenuators, or other components which would otherwise be necessary to prevent the usual cascade i.f. strip from saturating on the pulse power. This feature of the system not only results in a reduction in the electronic circuitry but also eliminates any direct coupling between the pulse part of the system and the detection part. The fast recovery time of this i.f. amplifier allowed the relaxation signal to be displayed less than 2  $\mu\text{sec}$  after the termination of the saturating microwave pulse. An accuracy of within 10% was obtained for the spin-lattice relaxation time ( $T_1$ ) with this method.

The crystals were grown from a saturated aqueous solution by slow evaporation at a constant temperature. By this method we were able to grow large (20–65 g)

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<sup>1</sup> R. D. Mattuck and M. W. P. Strandberg, *Phys. Rev.* **119**, 1204 (1960).

<sup>2</sup> During the course of these studies we learned that D. H. Paxman [*Proc. Phys. Soc. (London)* **78**, 180 (1961)] also studied relaxation effects in  $\text{K}_3\text{Fe}(\text{CN})_6$ .

<sup>3</sup> I. Waller, *Z. Physik* **79**, 370 (1932).

<sup>4</sup> R. Kronig, *Physica* **6**, 33 (1939).

<sup>5</sup> C. F. Davis, Jr., M. W. P. Strandberg, and R. L. Kyhl, *Phys. Rev.* **111**, 1268 (1959).

crystals from which a small portion (100–300 mg) was used for an experiment. The  $\text{Fe}^{3+}$  content, as determined from spectro-chemical analyses,<sup>6</sup> of the crystals used in the experiments ranged from 0.1 to 3.0% (where percent  $\text{Fe}^{3+}$  = number of  $\text{Fe}^{3+}$  ions/number of  $\text{Fe}^{3+} + \text{Co}^{3+}$  ions).

The resonance data given by Baker *et al.*,<sup>7</sup> show that the paramagnetic ions form two similar but differently oriented magnetic complexes. The crystal is pseudo-orthorhombic, and the spectra of the two ions are identical if the external uniform magnetic field ( $H_0$ ) lies in the ( $a,c$ ) or ( $b,c$ ) planes of the crystal. The measurements reported on here were made with  $H_0$  in the ( $a,b$ ) plane in order to investigate any cross relaxation effects. In this case the separation of the absorption lines of the two complexes can be varied from coincidence, where  $H_0$  is parallel to either the  $a$  axis or the  $b$  axis, to a maximum separation of approximately 1000 Mc/sec when operating at  $X$  band (8750 Mc/sec).

In order to avoid radiation damping effects the size of the crystal was so chosen that the paramagnetic losses were always less than 10% of the total cavity losses. The paramagnetic losses relative to the total cavity losses were determined by vertical standing wave ratio (VSWR) measurements for one crystal size and concentration at 1.6°K; for higher temperatures the relative loss is, of course, less. The proper size crystal to be used at other  $\text{Fe}^{3+}$  concentrations could then be calculated with sufficient accuracy.

### III. EXPERIMENTAL RESULTS

The paramagnetic absorption spectra of the more concentrated crystals (0.5 to 3.0%) were often extraordinarily complicated, with as many as 57 lines being

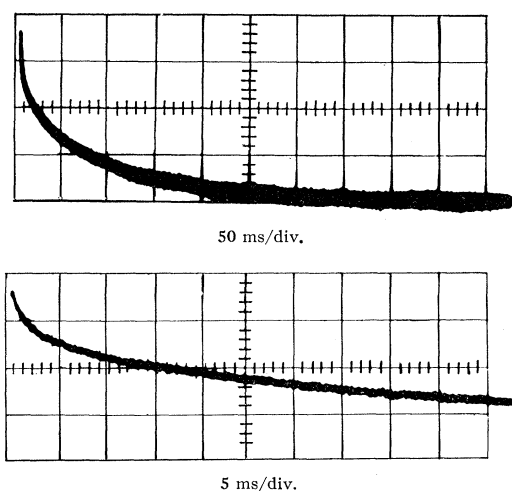


Fig. 1. Photograph of typical decay curve at  $T = 1.6^\circ\text{K}$ .

<sup>6</sup> Crystal analyses were performed by Spectrochemical Laboratories, Inc., Pittsburgh, Pennsylvania.

<sup>7</sup> J. M. Baker, B. Bleaney, and K. D. Bowers, *Proc. Phys. Soc. (London)* **B69**, 1205 (1956).

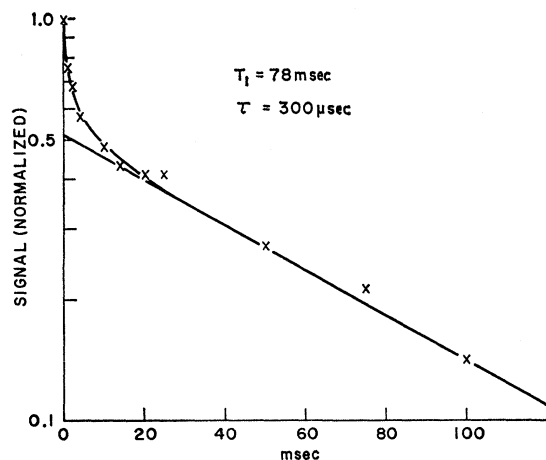


Fig. 2. Semilogarithmic plot of decay curve shown in Fig. 1.

present. Somewhat similar results were observed by Ohtsuka<sup>8</sup> and interpreted by him as being due to exchange coupling. It is probable that the complexity of our spectra resulted from this cause also. The spectrum in our case was so complicated and so orientation dependent that we did not attempt to investigate it in any detail. However, since this effect is of some interest, the absorption spectra of a few crystals are shown in the Appendix.<sup>9</sup>

The crystals used in this experiment were so chosen that the "extraneous" spectrum was absent altogether or there were only a few weak extraneous lines.

A typical decay at 1.6°K is shown in Fig. 1. The length of the saturation pulse was approximately 20  $\mu\text{sec}$  in this case. The sharp slope near the beginning of the decay is clearly evident; similar decay profiles have been observed by Bowers and Mims<sup>10</sup> in other paramagnetic crystals. On a semilog plot the different decay rates can be seen very clearly (Fig. 2). The rapid decay here was about 300  $\mu\text{sec}$  as compared to the slow decay time of 80 msec.

The rapid decay times were observed not to depend appreciably on crystal orientation, the effect being clearly evident even when the two magnetic complexes overlapped. Moreover, it was also present and largely undiminished when the separation between magnetic complexes was as great as 1000 Mc/sec (250 G). From recent work<sup>11,12</sup> the cross-relaxation linewidth for a spin- $\frac{1}{2}$  crystals of low concentration<sup>13</sup> is expected to be far less than 250 G. In fact, the C-R linewidth calcu-

<sup>8</sup> T. Ohtsuka, *J. Phys. Soc. (Japan)* **15**, 939 (1960).

<sup>9</sup> The question of whether polytypism can account for these results is also discussed in the Appendix.

<sup>10</sup> K. D. Bowers and W. B. Mims, *Phys. Rev.* **115**, 285 (1959).

<sup>11</sup> A. Kiel, *Phys. Rev.* **120**, 137 (1960).

<sup>12</sup> A. Kiel, *Phys. Rev.* **125**, 1451 (1962).

<sup>13</sup> In reference 12 the author has pointed out that the concentration-independent term [Eq. (1)] is zero for two species of ions with identical spin  $\frac{1}{2}$ . Hence, the C-R linewidth may be quite narrow if the concentration is small enough so that the exchange terms are not significant.

lated from Eq. (1) of reference 12 was approximately 8 G which is comparable to the homogeneous linewidth (5 G). These calculations were for cubic crystals; the linewidths would probably be smaller in the case of noncubic crystals.

With saturation pulses of the order of 1 msec the initial rapid decay was no longer observed. The slow decay rate was unaffected by this increase in pulse length. It might be pointed out that these long pulses were often used to avoid the complications of the cross-relaxation effect when the spin-lattice relaxation was alone of interest.

The experimental evidence above leads us to believe that the rapid initial decay is due to spin diffusion within the inhomogeneously broadened line. (A rigorous description of this process is given in reference 12.) We have interpreted the slow decay time as being the true spin-lattice relaxation time ( $T_1$ ).

For a crystal containing 0.1% ferricyanide, where  $T_1$  at 1.6°K was observed to be 99 msec, the measured spin-diffusion time  $\tau$  was 775  $\mu$ sec. This is comparable with the calculated value of  $\tau$  (860  $\mu$ sec) as given by Eq. (4) of reference 12. However, since this calculation used a cubic model with only a rough knowledge of the parameters, the agreement should be taken with some reserve. We have not attempted to investigate the spin-diffusion time as a function of concentration due to the probability of exchange effects at higher concentrations (>0.2%) and sensitivity problems at very low concentrations.

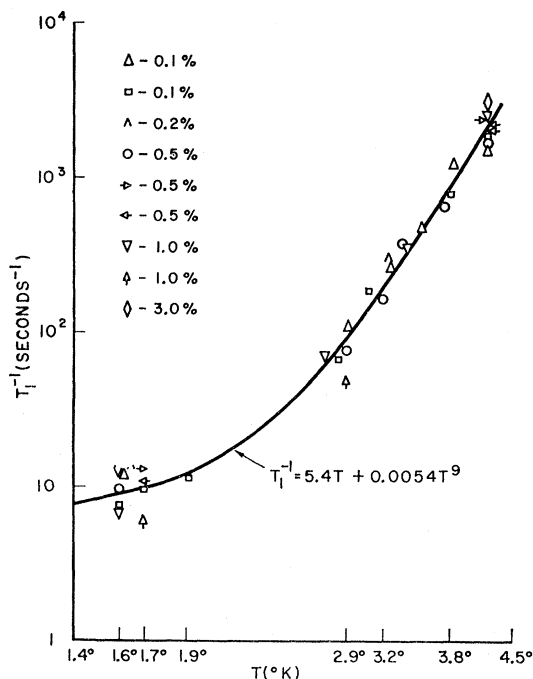


FIG. 3. Inverse spin-lattice relaxation time ( $T_1^{-1}$ ) as a function of temperature (log-log scale).

The most striking feature observed in the relaxation measurements was the temperature dependence of the spin-lattice relaxation time. Figure 3 shows a plot of the inverse spin-lattice relaxation time ( $T_1^{-1}$ ) as a function of the absolute temperature. Each point shown on the graph is an average of several experimental measurements; these data are listed in Table I. The experimental points were found to fit the empirical relation

$$T_1^{-1} = 5.4T + 0.0054T^9, \quad (1)$$

as shown by the solid curve in the previous figure. A quick calculation using Eq. (1), shows that the direct process and the Raman process contribute equally to the spin-lattice relaxation rate at 2.1°K. The spin-lattice relaxation time becomes inversely proportional to temperature below 1.8°K.

Attempts were also made to fit the experimental data with relations of the same form as Eq. (1) except with a smaller temperature dependence at the higher temperatures. A  $T^7$  dependence fits poorly, and a  $T^8$  dependence gives only a fair fit.

We might also point out at this time that in the rapid temperature-dependent region the data can also be fitted by an exponential. If an exponential law held, this would indicate that the Finn, Orbach, Wolf<sup>14</sup> relaxation mechanism was dominant. This mechanism attributes the rapid relaxation to consecutive emission and absorption of high frequency phonons. This requires that the splitting of the energy levels of the ground  $^2T_g$  state be less than the Debye cutoff, which is probably 80  $\text{cm}^{-1}$  or less in this crystal. However, it is extremely unlikely that the splitting is this small in  $\text{K}_3\text{Fe}(\text{CN})_6$  [see Eq. (6) of Sec. IV]. We have, therefore, not considered this mechanism further.

The data shown in Fig. 3 indicate that the spin-lattice relaxation time is nearly independent of iron concentration. The spread in the data at the lower temperatures is most likely due to inaccuracies in the temperature measurements. In the work of Paxman,<sup>2</sup> which has recently been brought to our attention,<sup>15</sup> a slight concentration dependence was observed at temperatures below 2.4°K. In this region the relaxation time  $T_1$  was found to increase approximately 30% when the  $\text{K}_3\text{Fe}(\text{CN})_6$  concentration was decreased from 6.6% to 1.7%. The results of Paxman are shown in Fig. 4, in which  $T_1$  (msec) is plotted as a function of temperature on a log-log scale. For purposes of comparison our empirical relation [see Eq. (1)] is also shown in this figure. Although there is seen to be fair agreement between our results and Paxman's at temperatures near 4.2°K, our less concentrated crystals show a definite tendency toward longer spin-lattice relaxation times at the lower temperatures. As pointed

<sup>14</sup> C. B. P. Finn, R. Orbach, and W. P. Wolf, Proc. Phys. Soc. (London) **77**, 671 (1961).

<sup>15</sup> We are indebted to Dr. Paxman for several illuminating communications.

TABLE I. Results of relaxation time measurements on  $\text{K}_3[\text{Co,Fe}](\text{CN})_6$ .

Concentration	Temp. ( $^{\circ}\text{K}$ )	$T_1$	Concentration	Temp.	$T_1$
0.1%	4.2	620 $\pm$ 50 $\mu\text{sec}$	0.5%	4.2	610 $\pm$ 30 $\mu\text{sec}$
	3.85	830 $\pm$ 30 $\mu\text{sec}$		3.74	1.52 $\pm$ 0.04 msec
	3.55	2.10 $\pm$ 0.10 msec		3.35	2.70 $\pm$ 0.10 msec
	3.25	3.80 $\pm$ 0.20 msec		3.20	6.0 $\pm$ 0.3 msec
	2.92	9.1 $\pm$ 0.8 msec		2.90	13.0 $\pm$ 0.4 msec
0.1%	1.62	82 $\pm$ 5 msec	0.5%	1.60	103 $\pm$ 4 msec
	4.2	533 $\mu\text{sec}$		4.2	500 $\mu\text{sec}$
	3.8	1.27 msec		1.7	92 $\pm$ 2 msec
	3.08	5.33 msec		4.2	400 $\pm$ 30 $\mu\text{sec}$
	2.85	13.7 msec		3.4	2.81 msec
0.1%	1.92	87 $\pm$ 5 msec	1.0%	2.75	12.4 $\pm$ 0.3 msec
	1.70	104 msec		1.6	150 $\pm$ 10 msec
	1.60	132 $\pm$ 5 msec		4.2	400 $\pm$ 40 $\mu\text{sec}$
	4.2	460 $\pm$ 30 $\mu\text{sec}$		2.9	2.0 $\pm$ 0.2 msec
	3.25	3.2 $\pm$ 0.4 msec		1.7	156 $\pm$ 8 msec
0.2%	1.65	70 $\pm$ 5 msec	3.0%	4.2	330 $\pm$ 40 $\mu\text{sec}$
	4.2	410 $\pm$ 25 $\mu\text{sec}$		1.6	76 $\pm$ 5 msec
0.5%	4.2	75 $\pm$ 3 msec			
	1.7				

out earlier our experimental results indicate that the Raman process dominates the relaxation phenomena for temperatures down to approximately  $2.0^{\circ}\text{K}$ , while Paxman's measurements indicate that the transition temperature should be approximately  $2.5^{\circ}\text{K}$ . The disagreement between these two results appears to be connected with the concentration of the  $\text{Fe}^{3+}$  ions. It is also possible that the "exchange-packet" mechanism<sup>16</sup> introduced by Van Vleck may be playing an important role at the lower temperatures in the more concentrated crystals.

#### IV. CALCULATION OF THE SPIN-LATTICE RELAXATION RATE

As is well known, the ground manifold in  $\text{K}_3\text{Fe}(\text{CN})_6$  is not the  $^6A_1$  usually associated with  $\text{Fe}^{3+}$  in crystals with (nearly) octahedral symmetry, where  $A_1$  is the identity representation of the octahedral group. The ground state is instead a  $^2T_2$  state, where  $T_2$  is a three-dimensional cubic representation often designated  $\Gamma_5$ . This difference is due to the very strong crystal fields present in the cyanides. The dependence of the energy levels on the crystal field strength are shown in Fig. 7 of a paper by McClure.<sup>17</sup> (The approximate position of the energy levels of the  $\text{Fe}^{3+}$  ions in the cyanides in this diagram are at  $Dq/B=3.1$  when the cubic field approximation is used.) In our case the ground manifold is a  $^2T_2$  emanating from the  $^2I$  free ion term, which is approximately  $50\,000\text{ cm}^{-1}$  above the ground state in the free ion. The ground manifold is properly described in the strong-field case as a  $|t^5\ ^2T_2(^2I)\rangle$  state. This state is analogous to the ground manifold in the case of  $\text{Ti}^{3+}$  in the alums, where the ground manifold is

$|t^1\ ^2T_2(^2D)\rangle$ , with the difference that strong-field  $\text{Fe}^{3+}$  has one  $t$  orbital empty while titanium has one  $t$  orbital filled.

The sixfold degeneracy is lifted by the spin-orbit interaction and the rhombic field of  $\text{K}_3\text{Fe}(\text{CN})_6$ , leaving a Kramers doublet ground state. We can estimate the splitting of the ground manifold of iron as follows.

Following Griffith,<sup>18</sup> we assume the low-symmetry field separates the energies of the initially degenerate proper states ( $^2\zeta, ^2\eta, ^2\xi$ ) of  $^2T_2$  but does not mix them. If the energies of  $^2\zeta, ^2\eta, ^2\xi$  due to the rhombic field alone are  $\frac{1}{2}V, -\frac{1}{2}V, \Delta$ , the energy of the system including spin-orbit interaction  $\zeta(\mathbf{L}\cdot\mathbf{S})$  is obtained from the

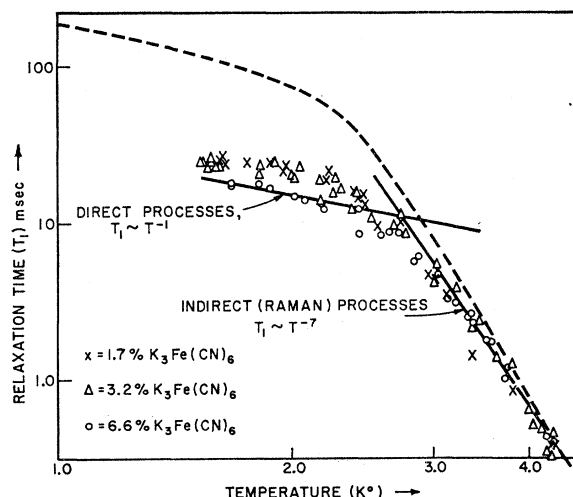


FIG. 4. Relaxation time vs temperature (from reference 2). For purposes of comparison Eq. (1) is also plotted here (dashed curve).

<sup>16</sup> C. H. Townes, *Quantum Electronics* (Columbia University Press, New York, 1960), p. 392.

<sup>17</sup> D. S. McClure, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1959), Vol. 9, p. 422.

<sup>18</sup> J. S. Griffith, *The Theory of Transition-Metal Ions* (Cambridge University Press, New York, 1961), Chap. 12, p. 364.

determinantal equation

$$\begin{vmatrix} \frac{1}{2}\zeta - \mathcal{E} & \frac{1}{2}\sqrt{2}\zeta & \frac{1}{2}V \\ \frac{1}{2}\sqrt{2}\zeta & \Delta - \mathcal{E} & 0 \\ \frac{1}{2}V & 0 & -\frac{1}{2}\zeta - \mathcal{E} \end{vmatrix} = 0. \quad (2)$$

We are working in the scheme complementary to  $t^5$ , that is, we assume a single  $t$  orbital.

The ground doublet wave functions are

$$\begin{aligned} \psi^{(+)} &= A|1^+\rangle + B|\zeta_1^-\rangle + C|-1^+\rangle, \\ \psi^{(-)} &= A|-1^+\rangle + B|\zeta_1^+\rangle + C|1^-\rangle \end{aligned} \quad (3)$$

(see Griffith<sup>18</sup> for notation). Then the  $g$  values (spectroscopic splitting factors) are given by

$$\begin{aligned} g_x &= 2[2AC - B^2 + kB(C-A)\sqrt{2}], \\ g_y &= 2[2AC + B^2 + kB(C+A)\sqrt{2}], \\ g_z &= 2[A^2 - B^2 + C^2 + k(A^2 - C^2)], \\ A^2 + B^2 + C^2 &= 1, \end{aligned} \quad (4)$$

where  $k$  is the reduction factor of the orbital moment.

From a knowledge of  $g$  ( $g_x = 2.35$ ,  $g_y = 2.10$ ,  $g_z = 0.91$ ) and using  $k = 0.87$  given by Baker *et al.*,<sup>7</sup> we can find  $A$ ,  $B$ , and  $C$ . Then  $V\zeta^{-1}$ ,  $\Delta\zeta^{-1}$ , and  $E$  may be computed from the following set of simultaneous equations ( $E$  is redundant here),

$$\begin{aligned} (\frac{1}{2}\zeta - E)A + \frac{1}{2}\sqrt{2}\zeta B + \frac{1}{2}VC &= 0, \\ \frac{1}{2}\sqrt{2}\zeta A + (\Delta - E)B &= 0, \\ \frac{1}{2}VA + (-\frac{1}{2}\zeta - E)C &= 0. \end{aligned} \quad (5)$$

Finally using Eq. (2) we can find the values of  $\mathcal{E}$ . To convert to  $t^5$  from the complementary  $t^1$  scheme we must replace  $\zeta$ ,  $\Delta$ ,  $V$  by  $-\zeta$ ,  $-\Delta$ ,  $-V$ . Taking a value of  $\zeta$  of  $278 \text{ cm}^{-1}$  we obtain as the best fit for the  $\mathcal{E}$

$$\begin{aligned} \mathcal{E}_1 &= -640 \text{ cm}^{-1}, \\ \mathcal{E}_2 &= -110 \text{ cm}^{-1}, \\ \mathcal{E}_3 &= +190 \text{ cm}^{-1}. \end{aligned} \quad (6)$$

We can now adapt the Van Vleck theory<sup>19</sup> to the present case. We will use Van Vleck's notation throughout.

To a first approximation, the two lowest states correspond to the  $E$  representation of a trigonal group<sup>20</sup>:

$$\langle E_a | H_{0L} | E_b \rangle = 6aQ_2 + (\frac{1}{3})^{\frac{1}{2}}Q_6'b, \quad (7)$$

where

$$\begin{aligned} a &= (12e\mu\langle r_0^2 \rangle_{av}/7R^5 - 150e\mu\langle r_0^4 \rangle_{av}/63R^7), \\ b &= -(24e\mu\langle r_0^2 \rangle_{av}/7R^5 - 40e\mu\langle r_0^4 \rangle_{av}/21R^7). \end{aligned} \quad (8)$$

For the spin-orbit interaction we have

$$\langle E_{a\pm} | H_{so} | E_{b\mp} \rangle = \frac{1}{2}i\zeta(l_{zx'} \pm il_{zy'}),$$

where  $C$  is along  $z$  and  $H$  is along  $z'$ .

<sup>19</sup> J. H. Van Vleck, Phys. Rev. **57**, 426 (1940).

<sup>20</sup> Obviously there is a large amount of mixing of all the states, which can alter the results considerably. However, in view of the many approximations required in this theory, it would be difficult to justify great exactness in the calculations.

In most of our experiments  $C$  is perpendicular to  $H$ , so that we can write

$$\langle E_{a\pm} | H_{so} | E_{b\mp} \rangle = \frac{1}{2}i\zeta. \quad (9)$$

Hence for *direct* processes we obtain the following expression for the spin-lattice relaxation rate  $W$ ,

$$W(E_{a+} \rightarrow E_{a-}) = \frac{2\pi^3 V(\bar{n}+1)g^6\beta^2\gamma^3 H^5}{3 h\nu^5 M(\mathcal{E}_2 - \mathcal{E}_1)^4} \zeta^2(6a^2 + \frac{1}{3}b^2), \quad (10)$$

where

$$\beta = eh/2mc = h\gamma,$$

and where we use the results

$$\begin{aligned} |Q_2|^2 &= |Q_6'|^2 = h\nu R^2(2\bar{n}+1\pm 1)/48M\nu^2, \\ \bar{n} &= [\exp(h\nu/kT) - 1]^{-1}. \end{aligned}$$

In the experiments described in Sec. III,  $T \geq 1.6^\circ\text{K}$ ,  $\bar{n} \approx kT/h\nu$ ,

$$W \approx \frac{2\pi^3 V \zeta^2 \nu^4 kT}{9 \nu^5 M (\Delta\mathcal{E})^4} [18(Ra)^2 + (Rb)^2]. \quad (11)$$

For our case

$$\begin{aligned} \nu &\approx 8.7 \times 10^9 \text{ sec}^{-1}, & \nu &\approx 2.0 \times 10^5 \text{ cm/sec}, \\ \zeta &= 280 \text{ cm}^{-1}, & V/M &\approx 0.5 \text{ cm}^3/\text{g}, \\ \Delta E &= 530 \text{ cm}^{-1}, \\ W &= 8.47 \times 10^{-9} [18(aR)^2 + (bR)^2] T. \end{aligned} \quad (12)$$

We may *also* use the relation  $Dq = e\mu\langle r_0^4 \rangle_{av} R^{-6}$ . We estimate the terms in  $\langle r_0^2 \rangle_{av}$  by assuming  $\langle r_0^2 \rangle_{av} R^2 / \langle r_0^4 \rangle_{av} \approx 2.5$ . Then  $aR = 2Dq$ ,  $bR = 7Dq$ . For the cyanide,<sup>5</sup>  $Dq \approx 2700 \text{ cm}^{-1}$ ,

$$\begin{aligned} W_{\text{direct}} &= 7.47 T, \\ T_1 &\approx 1/2W \approx 0.067 T^{-1}. \end{aligned} \quad (13)$$

It is well known that at higher temperatures a two-phonon process, generally called a "Raman process" dominates the spin-lattice relaxation. We may use the expression for the Raman type relaxation rate given in reference 19, with minor modification to take into account our new energy level picture.

Van Vleck's expression is

$$\begin{aligned} W \approx 64 \frac{(256V^2\zeta^2\pi^4 h^2)}{75(\Delta\mathcal{E})^6 M^2} \times (9/4)\nu^{-10} [(Ra)^4 \\ + (11/18)(Ra)^2(Rb)^2 + (11/648)(Rb)^4] I_8, \end{aligned} \quad (14)$$

where

$$\begin{aligned} I_8 &= \int_0^{\nu_D} [\nu^8 e^{h\nu/kT} (e^{h\nu/kT} - 1)^{-2}] d\nu \\ &\approx 8!(kT/h)^9 \text{ (for } kT \ll h\nu_D). \end{aligned}$$

Substituting the values for the parameters we used previously, we get

$$W_{\text{Raman}} \approx 5.0 \times T^9. \quad (15)$$

For our case we estimate that  $W$  is decreased by a factor of about 5–6 due to the splitting of  $E_a$  and  $E_b$  and the spin-orbit mixing. This would still leave  $W_{\text{Raman}}$  much bigger than  $W_{\text{direct}}$  even at temperatures well below 2°K. There is, however, another possible large error in Eq. (14).

In the derivation of Eq. (14) it is assumed that  $\rho(\nu)$  is a perfect parabolic function for  $\nu < \nu_D$ . Actually, this is not the case for ionic crystals. Specific heat studies have confirmed the theories predicting peaks in the lattice spectrum. In general the *peak* of the Debye spectrum is much less than  $4\pi V \nu_D^2 / v^3$ . If one considers the expression for  $I_8$  given above, it is easy to show that the major contribution to this integral comes from the region  $x^8 e^{-x} \approx 1$ , where  $x = h\nu/kT$  or  $h\nu \approx 25kT$ . In materials such as  $\text{K}_3\text{Co}(\text{CN})_6$  the Debye temperature is probably about 100°K or less. Hence, even for temperatures in the liquid helium<sup>21</sup> range the reduction of  $\rho(\nu)$  near  $\nu_D$  will affect the value of  $I_8$ .<sup>22</sup> The net effect of these considerations is to lead to an effectively larger value for  $\nu$  for Raman processes as compared to direct processes and a decrease in the value of  $I_8$ . It should be noted that the temperature dependence of  $W_{\text{Raman}}$  would also be altered since  $W$  is decreased more at 4°K than at 2°K in general.

We have no data concerning the Debye spectrum and velocity of sound in  $\text{K}_3\text{Co}(\text{CN})_6$ , so that we can make only a crude guess as to the magnitude of these effects. It seems likely that the spectrum deviations will cause a decrease<sup>23</sup> in  $W_{\text{Raman}}$  by an order of magnitude say, by a factor of between 10 and 100 or more. We therefore take  $W_{\text{Raman}}$  to have a value between  $0.01T^9$  and  $0.1T^9$ , that is,

$$W_{\text{Raman}} = 0.01T^9 \text{ to } 0.1T^9, \quad (15)$$

where we retain the  $T^9$  law only for lack of anything better. Combining Eqs. (13) and (15) we have  $T_1^{-1} \approx 15T + 0.1T^9$ .

Comparing this result with the empirical relation [Eq. (1)] it is seen that the calculation agrees to within a factor of 3 to 5, which is as good as one would expect for this case. The theory also predicts (quite accurately in this case) that the Raman and direct processes contribute equally to the spin-lattice relaxation rate near 2.1°K. These results, so far as they go, are among the best so far obtained in confirmation of the Van Vleck theory.

## V. CONCLUSIONS

The measured spin-lattice relaxation times in  $\text{K}_3[\text{Co}, \text{Fe}](\text{CN})_6$  are in agreement with the values calculated on the basis of the Van Vleck theory. The tem-

perature dependence of the spin-lattice relaxation time was found to follow the empirical relation  $T_1^{-1} = 5.4T + 0.0054T^9$ . In the range of iron concentrations from 0.1 to 3.0% the spin-lattice relaxation time was found to have little, if any, concentration dependence.

Comparison of our results with similar measurements by Paxman<sup>2</sup> at higher ferricyanide concentrations would indicate a small concentration dependence at temperatures below 2.5°K. From a comparison of the two data, it would appear that the Raman process dominates the spin-lattice relaxation down to lower temperatures ( $\sim 2.0^\circ\text{K}$ ) in the more dilute crystals.

Two distinct decay times were observed in the relaxation curves at temperatures near 1.6°K. The initial rapid decay of the saturated spin system has been interpreted as spin diffusion in an inhomogeneous line rather than cross relaxation between adjacent lines since the effect was independent of the separation of these lines. For a crystal containing 0.1% ferricyanide, where  $T_1$  at 1.6°K was observed to be 99 msec, the measured spin-diffusion time  $\tau$  was 775  $\mu\text{sec}$ .

## ACKNOWLEDGMENTS

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## APPENDIX. PARAMAGNETIC ABSORPTION MEASUREMENTS

The effects of exchange coupling, as exemplified by the appearance of a number of weak lines<sup>24</sup> in the paramagnetic spectrum, may be of some importance in the spin-lattice relaxation processes in crystals of relatively high ferricyanide concentrations ( $>0.5\%$ ). [The spin-lattice relaxation time for a 0.5% crystal showing this very strong exchange coupling was found to be only slightly temperature dependent ( $T_1 \propto 1/T$  from 1.6° to 4.2°K).] We have therefore felt it worthwhile, at this time, to report on some measurements of the absorption spectra of a few such crystals. The measurements were carried out at X band (8750 Mc/sec) using a high-gain superheterodyne receiver system; a phase-sensitive detection system was used in recording the spectrum.

The paramagnetic resonance lines for a crystal containing one percent ferricyanide are listed in Table II. The magnetic field  $H_0$  was in the  $a$ - $b$  plane of the crystal

<sup>21</sup> The inequality actually required for validity of the expression given for  $I_8$  should be  $h\nu_D \geq 30kT$ .

<sup>22</sup> The direct process is unaffected by these considerations since the high-frequency phonons do not contribute.

<sup>23</sup> Under some conditions, this effect could cause  $W_{\text{Raman}}$  to increase.

<sup>24</sup> Reference 8 gives a theoretical argument explaining the dependence of a few of these lines on crystal orientation.

TABLE II. Paramagnetic resonance spectrum of a  $K_3[Co,Fe](CN)_6$  crystal containing one percent  $Fe^{3+}$ . Data were taken at  $1.5^\circ K$  with  $H_0$  in the  $a$ - $b$  plane of the crystal at  $6^\circ$  from the  $a$  axis. The frequency was 8.8 kMc/sec.

$H_0$ in kilogauss	Relative intensity	Remarks	$H_0$ in kilogauss	Relative intensity	Remarks
5.52	2	Very broad	2.63	100	One of 2 main lines
5.00	2		2.61	20	On edge of main line
4.91	2		2.60	20	On edge of main line
4.06	2	Doublet	2.47	4	Doublet
3.99	2		2.42	6	
3.96	2		2.39	6	
3.93	2		2.33	4	Doublet
3.92	2		2.23	6	
3.89	2		2.20	4	
3.34	4		2.15	4	Two doublets
3.27	1		2.13	4	
2.88	12		2.10	4	
2.86	3		2.06	3	
2.85	10		2.03	3	
2.81	6		1.29	1	
2.75	2		1.25	1	
2.74	3		1.21	0.5	
2.70	20		0.45	2	
2.64	100	One of 2 main lines	0.39	2	Broad
			0.35	1	Broad

making an angle of approximately six degrees with the  $a$  axis. In this particular experiment 38 lines were observed over a range in field strength of 5000 G. The ratio of line intensities was as high as 500 to 1. The broad lines in this spectrum may be two or more unresolved lines, since we have observed as many as 57 lines in another 1% crystal. There has also been some indication that the line intensities decreased when the temperature was lowered from  $4.2$  to  $1.5^\circ K$ .

Figure 5 is a recording of the spectrum of a three percent crystal at  $4.2^\circ K$ . The magnetic field  $H_0$  is in the  $a$ - $b$  plane and nearly parallel to the  $a$  axis. It is seen that there are only about 11 absorption lines. It may be that at this high concentration the smaller lines are too broad to be detectable.

One might, perhaps, expect that the extraneous lines are connected somehow with the existence of polytypism in the cyanides.<sup>25</sup> Polytypism<sup>26</sup> is known to cause a doubling of the paramagnetic resonance lines in  $K_3[Co,Cr](CN)_6$ . In  $K_3[Co,Cr](CN)_6$ , Artman and Murphy's paramagnetic resonance results could be perfectly correlated with the x-ray diffraction studies of Kohn and Townes. However, the splittings in chromocyanide were only of the order of tens of gauss.

Kohn has made a complete study of seven of the crystals used in our work. His results<sup>27</sup> together with the rough resonance results are presented in Table III. Some of the crystals showed up to four polytypes. However samples  $F$  and  $G$ , which had very complicated resonance spectra, were of a single type. In general, it

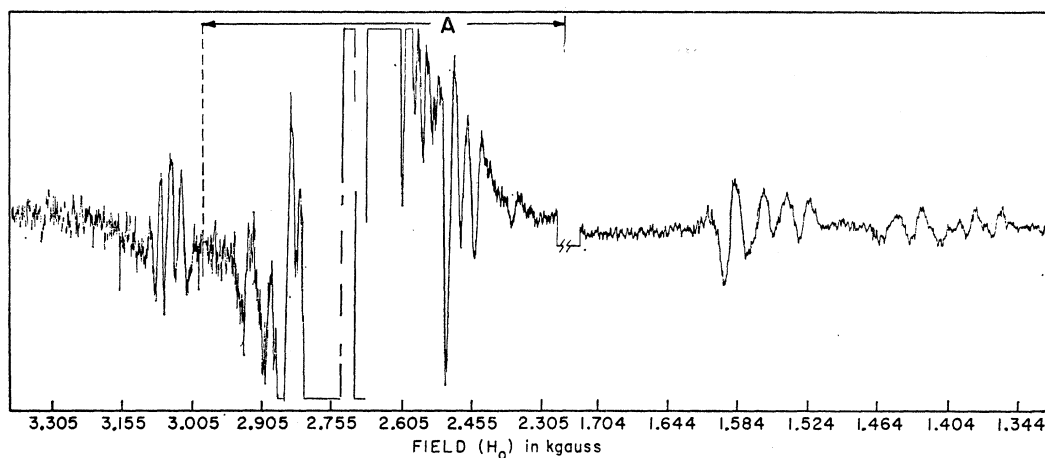


FIG. 5. Recording of the paramagnetic absorption lines (differentiated) of a  $K_3[Co,Fe](CN)_6$  crystal containing 3% ferricyanide.  $H_0$  is in the  $(a,b)$  plane. In the range  $A$  the gain is down 3 dB.

<sup>25</sup> J. A. Kohn and W. D. Townes, Acta Cryst. 14, 617 (1961).

<sup>26</sup> J. O. Artman, J. C. Murphy, J. A. Kohn, and W. D. Townes, Phys. Rev. Letters 4, 607 (1960).

<sup>27</sup> J. A. Kohn (private communication).

TABLE III. X-ray diffraction studies on Fe-doped  $\text{K}_3\text{Co}(\text{CN})_6$ .<sup>a</sup>

Crystal No.	Polytypes 2 Or:1 <i>M</i> :1 <i>M</i> ( <i>T</i> ):3 <i>M</i>	Disorder, multiplicity, etc.	Nominal % Fe	Resonance results
(A)	55:15:30:--	2 Or. and most of 1 <i>M</i> ( <i>T</i> ) show slight (few degrees) multiplicity.	0.2	2 normal, strong lines
(B)	55:25:--:20	slight to considerable stacking disorder throughout 70% of crystal.	5.0	up to 8 strong lines (Columbia)
(C)	60:40:--:--		0.5	2 normal, strong lines; temp. depend. relaxation time
(D)	40:35:5:20	stacking disorder through 15%; 2 Or. multiple (few degrees) through 50% of crystal.	1.0	4 strong lines (2 doublets)
(E)	60:30:10:--		0.5	7 strong, 23 weak lines; no temp. depend. of relaxation time
(F)	100:--:--:--	rotational disorder <i>b</i> through 15%; radial disorder normal to <i>b</i> through entire crystal	1.0	6 or 7 strong, many weak lines
(G)	100:--:--:--	rotational disorder <i>b</i> through 15%	1.0	4 strong, many weak lines

<sup>a</sup> See references 25 and 26 for notation.

can be said that the degree of polytypism and the degree of spectral complexity is uncorrelated.

As Kohn has pointed out, it is surprising that samples *A* and *C* do not show more than the two normal lines in view of the results of reference 26.

We have observed some correlation of the spectral results with concentration of  $\text{Fe}^{3+}$ . However the exceptions to this are striking. For example, *C* and *E* in Table II were found to have very nearly equal concentration, yet their spectra were very different. Several 1% crystals were found to have little or no anomalous lines and one 0.2% showed several extra lines.

Kohn's investigation removes the slight possibility that polycrystalline samples were responsible for our

results. Chemical analysis showed no significant impurities and it is difficult to imagine any impurity being responsible for such a spectrum as shown in Fig. 5.

This leaves us only with the explanation of Ohtsuka<sup>8</sup> based on exchange effects. Ohtsuka could explain the 5 strong lines of the 11 lines observed in his experiments. We have observed anywhere from 2 to 8 strong lines and up to 50 weak lines and, as stated above, different crystals of the same concentration had entirely different spectra.

The resolution of this problem would be of considerable interest, but at present no further effort along these lines can be attempted at this laboratory.