contribution A_L, which is related to the g shift in ^2E by[21]

$$A_L = 2\gamma\mu_N\mu_B\Delta g\langle r^{-3}\rangle, \qquad (6)$$

where γ and μ_N are the nuclear gyromagnetic ratio and nuclear magneton, respectively, μ_B is the Bohr magneton, $\Delta g = g - 2.0023$, and $\langle r^{-3}\rangle$ is an average over the $3d$ wave function. Freeman and Watson[22] have calculated $\langle r^{-3}\rangle = 2.75$ a.u. from the free-ion Hartree-Fock wave functions. This value and the measured g shift with **H** along [111] used in Eq. (6) give a predicted orbital contribution $A_L = -17\times10^{-4}$ cm^{-1}, which is to be added to the core-polarization hyperfine interaction, which is also negative. The total calculated hyperfine constant thus obtained is $A = 91\times10^{-4}$ cm^{-1}. This is in excellent agreement with the measured value of 90×10^{-4} cm^{-1}, and implies that the calculated $\langle r^{-3}\rangle$ is accurate to at least 5% for this system.

ACKNOWLEDGMENTS

The author is indebted to Professor R. H. Silsbee and Dr. D. L. Cowan for many helpful discussions and suggestions concerning this work.

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Three-Spin Cross Relaxation in Cr^{3+}:K$_3$Co(CN)$_6$†

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An experiment designed to study the three-spin cross relaxation (CR) rate without interference from much faster two-spin CR processes is described. The study was performed on the electron spin system Cr^{3+} in K$_3$Co(CN)$_6$ and the CR rate was determined for a range of concentrations 0.036–1.030% and an energy imbalance range of ±680 MHz from the harmonic point. Comparison with Bloembergen's "hybrid" method (in the present application by an exact computation of the second moments of the shape functions) shows good agreement for concentrations in the range 0.036–0.384%. For higher concentrations, this theory does not explain the data. The experimental results are also in disagreement with a theory of Grant's, which gave a good account of several previous two-spin CR experiments.

I. INTRODUCTION

Two theories of cross relaxation (CR) in spin systems have been advanced. In both theories the dipolar and exchange interactions play dual roles; their secular parts broaden the energy levels of the system of uncoupled spins and the nonsecular parts cause transitions ("flip-flops") of spins. In 1958, Bloembergen *et al.*[1] introduced a theory of CR (the so-called "hybrid method") which was an extension of previous theories of paramagnetic line broadening. The CR rate in this theory is given as $W(\omega) = (2\pi/\hbar)\,|\langle i\,|\,H_{\text{dip}}{}^{\text{NS}}\,|\,f\rangle|^2 g(\omega)$, in which the nonsecular part $H_{\text{dip}}{}^{\text{NS}}$ is the interaction operator and $g(\omega)$ is the shape function, which Bloembergen *et al.*[1] compute (for a two-spin process) by the folding of two paramagnetic line shapes involved in the CR process. Instead of a convolution, Kiel,[2] Kopvillem,[3] and Hirono[4] have utilized the method of moments[5,6] of the theory of paramagnetic line broadening. In diluted spin systems, of concentration f, the moments of the shape function are polynomials in f with leading terms which are concentration-independent.[7] The shape of $g(\omega)$ in diluted systems has thus been assumed to be concentration-independent. The magnitude of the CR rate is proportional to f^{n-1}, where n is the order of the interaction (i.e., the number of spins involved in a single process); $n-1$ is also known to be the order of perturbation theory necessary to determine the matrix element of the transition operator. The hybrid method does not require exact conservation of Zeeman energy in a single process. CR transitions can occur away from the harmonic coincidence of the Zeeman transitions; the balance of energy is achieved by a dynamic rearrangement of the entire lattice. In practice, for systems in which S_z is not a good quantum number, only the first and second moments of $g(\omega)$ can be computed. The ratio of the two is then used as the criterion of whether

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the shape is well approximated by a Gaussian. However, the shape of $g(\omega)$ has little to do with the shapes of paramagnetic lines and the width of $g(\omega)$ may be an order of magnitude greater than the width of the paramagnetic lines. The hybrid method has been used extensively to explain the experiments of Bloembergen *et al.*,[1] Pershan,[8] Feng and Bloembergen,[9] Mims and McGee,[10] and others.

More recently, Grant[11] has developed an alternative theory. The main objection to the hybrid method raised by Grant concerns the origin and meaning of the shape function $g(\omega)$, which was introduced by analogy to the case of paramagnetic line widths.[12] Grant proceeds from the requirement that the differences in Zeeman energies of the n spins of the CR transition have to be equalized by shifts due to the dipolar and exchange effect of all the spins of the system. Each pair of spins (in the two-spin CR process) is subjected to the dipolar field of one of the members of the ensemble of spin-system configurations which arise from distributing N spins into M paramagnetic sites. Some of these configurations shift the levels of the pair in such a way that the energy is conserved in the flip. The interaction operator which is the nonsecular part of the dipolar interaction is the weight with which the configurations responsible for equalization of Zeeman energies enter the averaging over the ensemble of all configurations. As a result, the CR rate becomes proportional to the convolution of two functions, one related to the power spectrum of the transition operator, $\chi(\omega)$, and the other, $\varphi(\omega)$, to the dipolar broadening of paramagnetic lines. $\varphi(\omega)$ is in turn the convolution of the shapes of the paramagnetic lines. The CR rate is concentration-dependent through a statistical factor f^n (one order higher than in the hybrid method) and also through the dependence on concentration of the paramagnetic lines of the convolution $\varphi(\omega)$. No assumption about the shape has to be made and Grant's method is able to explain fine features of the concentration dependence in the two-spin CR experiments of Mims and McGee.[10] Recently Weissfloch[13] has applied Grant's theory to two-spin processes in cobaltihexacyanide doped with Cr^{3+}.

Both CR theories have been extended to higher-order processes in diluted paramagnets, but experimental data is scarce. Feng and Bloembergen[9] have investigated five-spin and four-spin processes of Cr^{3+} in ruby and used the hybrid method to explain general features of the data. The reasons for the scarcity of data are clear: (a) CR rates in general are difficult to extract from time decays of saturated or inverted paramagnetic lines since these decays depend also on spin-lattice relaxations and in spin system with $S>\frac{1}{2}$ several of these rates are involved. (b) Higher-order CR processes are accompanied by lower-order CR processes which are usually stronger by a factor of $10^2/f$ per decreasing order. When the concentration increases they mask the higher-order processes even if their harmonic point is separated by a large (several hundreds MHz) frequency interval from the harmonic point of the higher-order process under study. (c) A precise determination of the concentrations is very important because of the f^{n-1} (or f^n) dependence of the nth-order CR rates. In most past experiments the concentration has been assumed to be that of the nominal ratio of materials used in the preparation of the crystals.

The present experiment on the three-spin CR rate has been designed to minimize these difficulties: (a) We investigate the three-spin processes in a range of ±680 MHz from their Zeeman energy balance. For all magnetic field values corresponding to this range two-spin CR processes occur at the exact harmonic ratio of their Zeeman energies. Thus we can eliminate two-spin processes from consideration. (b) In order to decrease the number of independent decay modes (of which there are 3 in a 4-level spin system) we apply saturating constraints to two of the Zeeman transitions. The decay of the monitored transition proceeds with a single time constant if the constraints are maintained during the experiment. It is then much easier to extract CR rates from these decay data and from the stationary-state absorption data. (c) The determination of the concentration was performed by spectral photometric method. By increasing the number of tested samples of each crystal we have reduced the probable error in concentration to 1 part in 10^4. Seven crystals were investigated with spin concentrations ranging from 0.036%–1.030% (atomic replacement of cobalt by chromium).

We hoped to be able to account for the present experimental results by an extension of Grant's theory. This was not the case, however. We, therefore, include for comparison computations based on the hybrid method.

The experimental setup and results are discussed in Sec. II. The application of the "hybrid" method is given in Sec. III, and an attempt to interpret the present data in terms of Grant's theory is presented in Sec. IV. Section V summarizes the work.

II. EXPERIMENTS WITH THREE-SPIN CR IN DILUTED $K_3[Cr, Co](CN)_6$

In the experiments to be described below we have concentrated our attention on the concentration dependence of the CR shapes and on the strength of the interaction, at high-dilution ratios of the paramagnetic ions. The experiments were performed with the spin system $Cr^{3+}:(S=\frac{3}{2})$ in potassium chromihexacyanide,

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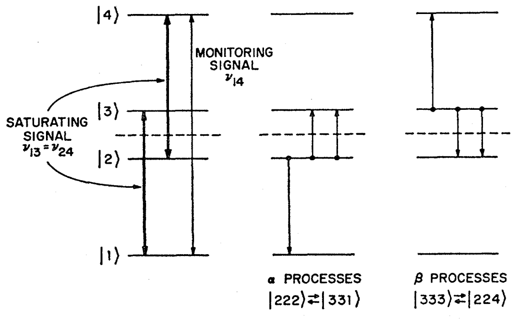
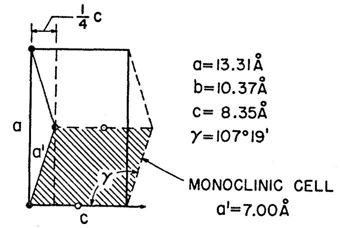


FIG. 1. The principle of the experiment and the two three-spin CR processes.

$K_3Cr(CN)_6$, diluted with potassium cobalti-hexacyanide, $K_3Co(CN)_6$. The general scheme of the experimental method is illustrated in Fig. 1. The four levels of Cr^{3+} have separations such that several types of three spin CR processes are possible. Application of saturating signals at frequencies ν_{13}, ν_{24} eliminates all but two types of three-spin processes from consideration. The pumping signals provide two constraints on the populations of the levels, reducing the number of independent rate equations to one. A weak monitoring signal is applied at a frequency ν_{14}. The behavior of the population difference n_1-n_4 is then studied in the stationary state (with pumping signals) and in the recovery to the stationary state after pulse saturation by a strong ν_{14} signal.

A. Unit Cell and Spin Hamiltonian of $K_3[Cr, Co](CO)_6$

An examination of older crystallographic literature[14–16] reveals a controversy about the crystal structure of $K_3Co(CN)_6$. Recent neutron diffraction studies,[17] x-ray diffraction work,[18] and correlation of x-ray-diffraction and paramagnetic-resonance results[19] have clarified the situation. The simple cell is monoclinic, as shown in Fig. 2. Four polytypes, arising from different ways in which simple cells are stacked upon one another have been observed[18,19]; they are denoted by *1M*, *2Or*, *3M*, and *7M*. The most prevalent ones are *1M* with a simple monoclinic unit cell, and *2Or* with an orthorhombic unit cell arising from a rotation around the *c* axis and a stacking in the direction of the *a* axis of one monoclinic cell on another. On the basis of the discussion presented in Ref. 19, we have identified the crystals used in our experiment as belonging to the type *2Or*. Figure 2 shows a cross section of a *2Or* unit cell, with the following lattice parameters (in Å): $a=13.31\pm0.04$, $b=10.37\pm0.02$, $c=8.37\pm0.01$. There are four cobalt ions[17,20] per unit cell with coordinates $(0,0,0)$, $(\frac{1}{2},0,\frac{1}{4})$, $(0,\frac{1}{2},\frac{1}{2})$, $(\frac{1}{2},\frac{1}{2},\frac{3}{4})$.



COBALT SITES:

ℓa	mb	nc
$(\ell+1/2)a$	mb	$(n+1/4)c$
ℓa	$(m+1/2)b$	$(n+1/2)c$
$(\ell+1/2)a$	$(m+1/2)b$	$(n+3/4)c$

FIG. 2. Orthorhombic $K_3Co(CN)_6$ (*b* axis perpendicular to the figure plane).

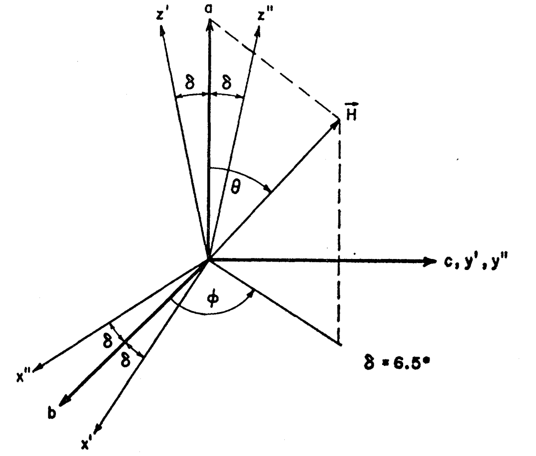


FIG. 3. Orientation of the axes of two nonequivalent magnetic complexes of *2Or*-type $K_3Cr(CN)_6$ with respect to the crystallographic axes.

The positions of the principal axes of the two magnetic complexes in the *2Or*-type crystals are illustrated in Fig. 3. There are two nonequivalent cobalt sites in the unit cell and two nonequivalent magnetic complexes of Cr^{3+}.[21–23]

The spin Hamiltonian has the form

$$H_i=\beta\mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S}+D[S_{zi}^2-\tfrac{1}{3}S(S+1)]+E(S_{xi}^2-S_{yi}^2). \qquad (1)$$

We have adopted as the values of the parameters those determined by Baker, Bleaney, and Bowers[23]:

$$D=0.0831\pm0.0010\ \mathrm{cm}^{-1},$$
$$E=0.0108\pm0.0010\ \mathrm{cm}^{-1}, \qquad (2)$$

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and $g_x=1.993$, $g_y=1.991_4$, $g_z=1.991$, with a probable error of ± 0.001. The abundance of ^{53}Cr as compared to ^{52}Cr is 9.5% and therefore the hyperfine-interaction term in the spin Hamiltonian has been neglected.

All our work has been performed with the magnetic field in the *ac* plane and we have adopted the value $g=1.991$. Corrections due to an angle of 6.5° formed by the $y'z'$ and $y''z''$ planes with the *ac* plane are below the value of the probable experimental error of the present experiment. With the external field in the *ac* plane the spins of the two complexes have the same energies. The eigenvalue equation is of the type

$$C_4\epsilon^4+C_2\epsilon^2+C_1\epsilon+C_0=0, \qquad (3)$$

where the C_i are functions of the parameters D, E, g, the magnetic field $|\mathbf{H}|$, and its orientation. We describe this orientation by polar angles θ, φ of $\mathbf{H}$ with respect to the crystallographic axes.

For our purposes, we choose the orientation at which Eq. (3) is quadratic in ϵ^2, that is, $C_1(\theta,\varphi)=0$. This condition results in a cone of directions for which $\epsilon_4=-\epsilon_1$, $\epsilon_2=-\epsilon_2$ for all values of $|\mathbf{H}|$. [Here ϵ_i label the four possible solutions of Eq. (3).] Since we also require $\varphi=\frac12\pi$ ($\mathbf{H}$ in the *ac* plane), the condition $C_1(\theta,\varphi)=0$ leads to

$$\cos^2\theta=\tfrac13[D+3E]/[D\cos^2\delta+E(1+\sin^2\delta)].$$

With the adopted values of D and E and with $\delta=\pm 6.5°$, we have

$$\theta=49°50' \qquad (\varphi=\tfrac12\pi).$$

The plot of eigenvalues for this orientation versus $|\mathbf{H}|$ is shown in Fig. 4. The value of the field of particular interest in the present investigation is indicated by the vertical line at $|\mathbf{H}|=0.735$ kOe. At this point the energy differences are related by

$$\nu_{14}:(\nu_{13}=\nu_{24}):(\nu_{12}=\nu_{34}):(\nu_{23})=5:3:2:1, \qquad (4)$$

where we have introduced the notation $h\nu_{ik}=|\epsilon_i-\epsilon_k|$.

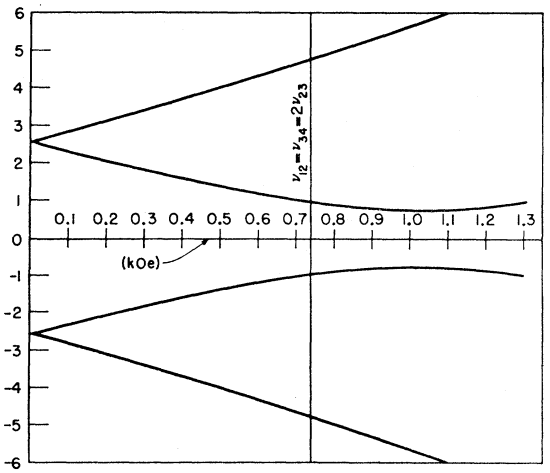

FIG. 4. Energy levels of Cr^{3+} in $K_3Co(CN)_6$ versus $|\mathbf{H}|$. $\mathbf{H}$ in *ac* plane at $\theta=49°50'$, $\varphi=\frac12\pi$.

B. CR Processes at $\varphi=\frac12\pi$, $\theta=49°50'$, $|\mathbf{H}|=735$ Oe

Equation (4) allows a very large number of kinds of CR processes to take place. In particular, we will investigate the possible two-spin and three-spin processes. Higher-order processes are of no importance since we are interested in diluted salts and in the range of concentrations studied four-spin processes result in relaxation times slower by at least three orders of magnitude than the three-spin processes. Even higher-order processes have a correspondingly smaller effect.

The possible two-spin processes are characterized in our case by $\epsilon_1+\epsilon_4=\epsilon_3+\epsilon_2$. It should be noted that this relation is independent of the particular field $|\mathbf{H}|=735$ Oe, and it is valid for all fields at the orientation considered. The two-spin processes are always operating at their exact harmonic relation.

There are 10 types of three-spin CR processes which conserve energy at the operation point $|\mathbf{H}|=735$ Oe. Of these, four are "cyclic" and do not change the population numbers; four are eliminated by application of the saturating signals at transition frequencies ν_{13}, ν_{24} (which are equal). The remaining three-spin processes are of the two types shown in Fig. 1. For the α processes, the condition for energy conservation is $3\epsilon_2=2\epsilon_3+\epsilon_1$, and for the β processes it is $3\epsilon_3=2\epsilon_2+\epsilon_4$. In terms of the paramagnetic transition frequencies, these become $2\nu_{23}=\nu_{21}$ and $2\nu_{23}=\nu_{34}$, respectively. In order to investigate the shape of the CR lines, we perform the experiment not only at exact coincidence of the energies, but also in the vicinity of the field point $|\mathbf{H}|=735$ Oe. We define the deviation from the harmonic ratio as

$$\Delta\nu=\nu_{12}-2\nu_{23}=\nu_{34}-2\nu_{23}.$$

$\Delta\nu$ is plotted versus $|\mathbf{H}|$ in Fig. 5. (For future use we have also plotted the frequencies ν_{14}, and $\nu_{13}=\nu_{24}$.)

C. Rate Equations

Saturating signals applied to the transitions $|1\rangle\rightleftarrows|3\rangle$ and $|2\rangle\rightleftarrows|4\rangle$ provide two constraints on the populations, $n_1=n_3$ and $n_2=n_4$. Together with the condition

$$\sum_1^4 n_r=N$$

(N is the total number of spins), these constraints reduce the number of independent rate equations to 1. The monitoring signal is applied at a frequency ν_{14}. The rate equation for the difference $\Delta=n_1-n_4$ then becomes[24]

$$\dot{\Delta}+\Delta(2U_+)+3(n_1^3-n_4^3)(1/N^2)W_{\mathrm{CR}}=\tfrac14 NU_-, \qquad (5)$$

where we have introduced the following abbreviations

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[24] Compare, e.g., W. J. C. Grant, J. Phys. Chem. Solids **25**, 751 (1964).

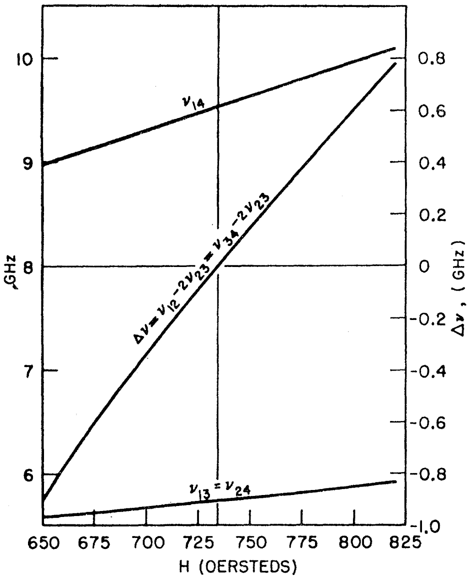

FIG. 5. Deviation $\Delta\nu$ from the harmonic point versus $|\mathbf{H}|$, at $\theta=49°50'$ and $\varphi=\frac{1}{2}\pi$. (Monitor frequency ν_{14} and pump frequency $\nu_{13}=\nu_{24}$ are shown above and below, respectively.)

for the functions of the spin-lattice relaxation rates u_{ik}:

$$2U_+=(u_{12}+u_{21})+(u_{41}+u_{14})+(u_{43}+u_{34})+(u_{32}+u_{23}),$$

$$U_-=(u_{21}-u_{12})+(u_{41}-u_{14})+(u_{43}-u_{34})-(u_{32}-u_{23}).$$

W_{CR} is the CR transition probability rate per single-flipping spin.

We linearize Eq. (5) by assuming that

$$(n_1^3-n_4^3)\simeq(n_1-n_4)\tfrac{3}{16}N^2$$

and obtain

$$\dot{\Delta}+\Delta[2U_++\tfrac{9}{16}W_{\mathrm{CR}}]=\tfrac{1}{4}NU_-. \qquad (6)$$

The decay constant of this equation is

$$\lambda=2U_++\tfrac{9}{16}W_{\mathrm{CR}} \qquad (7)$$

and the stationary solution is

$$\Delta_s=\tfrac{1}{4}NU_-/[2U_++\tfrac{9}{16}W_{\mathrm{CR}}]. \qquad (8)$$

One might expect that a determination of λ alone by the pulse-saturation method at various concentrations f, and then an extrapolation to $f=0$ (no CR) would lead to a determination of $2U_+$ and hence to the determination of W_{CR}. Such a procedure assumes the independence of U_+ on concentration. In addition, the pulse-saturation experiment with the system recovering to the stationary state after the pulse at ν_{14} becomes difficult at both extremes of the investigated concentration range. The pulse-saturation apparatus is not sensitive enough to provide good data at higher dilutions. On the other hand, at chromium concentrations larger than 0.8% the saturating pulse at the frequency of the $|1\rangle\rightleftarrows|4\rangle$ transition does not perturb the stationary state appreciably since this transition is already nearly saturated. Therefore much more weight has been assigned to the data obtained by the method of comparing the paramagnetic absorption in the stationary state, Eq. (8), with absorption at thermal equilibrium, that is, with constraints $n_1=n_3$, $n_2=n_4$ removed. If we denote the imaginary part of susceptibility as a function of power-saturating transitions $|1\rangle\rightleftarrows|3\rangle$ and $|2\rangle\rightleftarrows|4\rangle$ by $\chi_{14}''(P_{13,24})$, then the ratio of the susceptibility at complete saturation, $P_{13,24}\pm\infty$, to the susceptibility at $P_{13,24}=0$ (Boltzmann equilibrium) is

$$\begin{aligned}\eta&=\chi_{14}''(\infty)/\chi_{14}''(0)\\&=(n_1-n_4)_s/(n_1-n_4)_B=\Delta_s/\Delta_B.\end{aligned} \qquad (9)$$

Δ_s is given in Eq. (8) and the subscript B denotes Boltzmann equilibrium. We call η the relative index of absorption.

In the absence of CR the relative index of absorption is

$$\eta_0=NU_-/4\Delta_B. \qquad (10)$$

We discuss methods of determining this quantity in the next section. From Eq. (10) and Eqs. (7)–(9) we can obtain relations between the measured quantities λ, η, η_0, and the spin-lattice relaxation and CR rates:

$$2U_+=\lambda\eta/\eta_0, \qquad (11)$$

$$W_{\mathrm{CR}}=(16/9)(2U_+)(\eta_0-\eta)/\eta. \qquad (12)$$

The fourth measured quantity of interest is the concentration of the chromium ions. This is discussed in detail in the next section.

D. Experimental Results

Crystals of $K_3[Cr, Co](CN)_6$ were grown by suspending a small seed in the saturated water solution of the material. They were kept at a well-controlled temperature of 13.5°C for periods of several weeks. Large, well-formed crystals were obtained with easily identifiable directions of the crystallographic axes. The size of each crystal was sufficient to cut out the experimental sample and 2 to 4 additional samples for chemical analyses. These chemical analyses were performed by reducing the chromium with sodium peroxide and measuring the color concentration on a Fisher Electrophotometer with a No. 425 filter. A careful calibration of the photometer on 70 powder samples of known Cr:Co concentrations reduced the probable error to an estimated $1{:}10^4$. The results of analysis of the seven crystals used in the experiment are given in Table I.

The relative index of absorption is obtained from the ratio of the measured $\chi_{14}''(\infty)$ (under steady-state saturating powers at the frequency $\nu_{13}=\nu_{24}$) to $\chi_{14}''(0)$ (measured under Boltzmann equilibrium conditions). The apparatus consists in essence of two conventional paramagnetic-resonance spectrometers; a system for the weak monitoring power at the frequency of the $|1\rangle \rightleftarrows |4\rangle$ transition (X band) and a system which provides the saturating power to the $|1\rangle \rightleftarrows |3\rangle$ and $|2\rangle \rightleftarrows |4\rangle$ lines (C band). Both systems are provided with power monitoring arrangements. The control of power is of importance. The incident X-band power levels are kept low, of the order of 1 μW, while the C-band power levels are adjusted at each experimental point to provide sufficient saturation, without causing excessive heating, evaporation, and bubbling of the liquid helium. The saturating power depends not only on temperature, but also on the static field. Accordingly, we have to vary the saturating power in the range 5–15 mW.

The requirements on the microwave cavity are rather severe. This cavity has to be resonant at two bands (X band and C band) and tunable in both bands independently, in ranges of the anticipated width of the CR lines. All three quantities, ν_{14}, $\nu_{13}=\nu_{24}$, and $\Delta\nu$, are, of course, functions of the magnetic field (Fig. 5). We were able to cover a 1000-MHz range, from 9000 to 10 000 MHz, corresponding to $\Delta\nu = \pm 680$ MHz $(650 \leq |\mathbf{H}| \leq 820$ Oe). The requisite range of the frequency $\nu_{13}=\nu_{24}$ of the saturated lines is 450 MHz and was much easier to span. As the data to be discussed show, the range which we investigated was sufficient to display the main features of the CR processes under study. The loaded quality factors of the cavity were 3600 for C band and 2000 for X band.

Experiments were performed at 4.2 and at 1.6°K. The procedure used is as the following: The X-band frequency was changed by small (25–50 MHz) intervals. At each point the magnetic field was adjusted to resonance and the C-band power tuned to the frequency indicated in Fig. 5. The $|1\rangle \rightleftarrows |3\rangle$ and $|2\rangle \rightleftarrows |4\rangle$ transitions were then observed and small adjustments of frequencies were made to line up all three transitions at the same field value. The C-band power was then increased (to saturate the C-band transitions), the field-sweep amplitude and X-band power were reduced, the dc field shifted below the resonance value, and the ν_{14} line (with C-band power on) was recorded. The C-band power was then removed and the line was recorded twice without it. The fourth recording was made with C-band power on. This allowed us to observe any systematic drift of the system between the first and fourth recording. All the results of the steady-state measurements are shown in Figs. 6 and 7, for $T=4.2$ and 1.6°K, respectively. The curves are the result of theoretical computations of the CR rates to be described in Sec. III.

TABLE I. Concentrations of chromium in $K_3Co(CN)_6$ host crystals.

Crystal No.	Cr:Co
1	$(0.036 \pm 0.010) \times 10^{-2}$
2	$0.105 \quad \times 10^{-2}$
3	$0.153 \quad \times 10^{-2}$
4	$0.253 \quad \times 10^{-2}$
5	$0.384 \quad \times 10^{-2}$
6	$0.586 \quad \times 10^{-2}$
7	$1.030 \quad \times 10^{-2}$

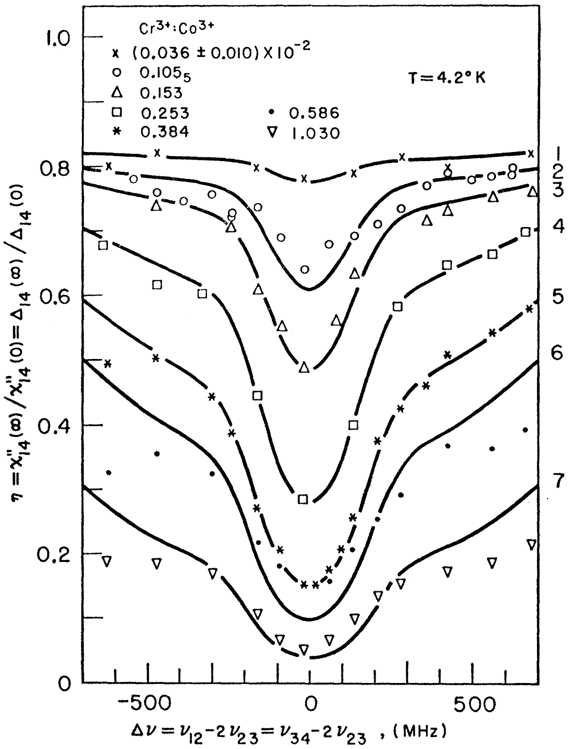

FIG. 6. Relative index of absorption versus $\Delta\nu$, $T=4.2$°K.

To determine η_0, we return to Eq. (12) and rearrange it to read $\eta = \eta_0 - F(f)\eta$. For crystals of low concentration (samples 1–5 of Table I), $F(f) \sim f^2$, so that

$$\eta = \eta_0 - \text{const.}\eta f^2.$$

For fixed values of $\Delta\nu$ plots of η versus (ηf^2) are straight lines and we have determined η_0 by a least-squares method. The results are shown in Table II.

We have also attempted to determine η_0 theoretically by estimating the spin-lattice relaxation rates by a method discussed by Mattuck and Strandberg.[25] The resulting values are $\eta_0 = 0.823$ at 4.2°K and $\eta_0 = 0.859$ at 1.6°K. The approximations necessarily made were rather drastic and therefore we have adopted the average experimental values from Table II:

$$\eta_0 = 0.820 \pm 0.010 \qquad (4.2°\text{K}),$$

$$\eta_0 = 0.863 \pm 0.010 \qquad (1.6°\text{K}).$$

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[25] R. D. Mattuck and M. W. P. Strandberg, Phys. Rev. **119**, 1204 (1960).

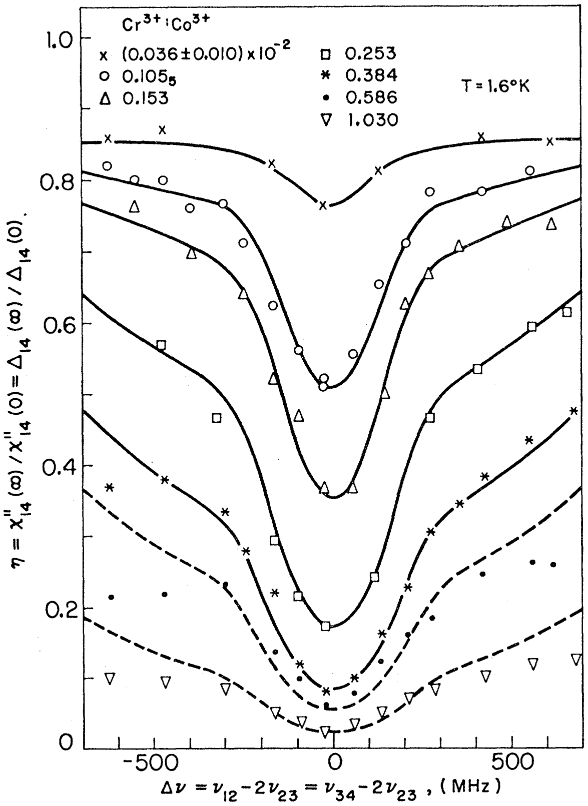

FIG. 7. Relative index of absorption versus $\Delta\nu$, $T = 1.6$°K.

Determination of the time constant was performed by the pulse-saturation method, first introduced by Davis, Strandberg, and Kyhl[26] and subsequently used in many experiments. The apparatus used has been described in detail by Bray, Brown, and Kiel.[27] The new feature introduced in the application of the pulse-saturation method has already been indicated; whereas in previous experiments the spin system recovers to thermal equilibrium, in the present experiment it recovers to a stationary state. Transitions $|1\rangle\rightleftarrows|3\rangle$ and $|2\rangle\rightleftarrows|4\rangle$ are held at saturation during the recovery of a pulsed-saturated transition $|1\rangle\rightleftarrows|4\rangle$. The system recovers with a single time constant provided no complications arise from spin diffusion[27] within inhomogeneously broadened lines.

The experimental procedure was similar to that followed during the steady-state experiments, but instead of recording the ν_{14} line, the field-sweep and synchronous-phase detection were replaced by the superheterodyne detection system to increase the sensitivity. The fast recovery of the IF amplifier permitted the monitoring signal to be displayed as early as 2 μsec after the pulse.

Mims and McGee[10] and Bray *et al.*[27] have observed spin diffusion within inhomogeneously broadened lines. At a concentration of 0.1% of the paramagnetic ion Bray *et al.* observed spin-diffusion times of the order of 0.75 msec. This value agrees well with theoretical estimates of Kiel.[28] At higher concentrations spin-

TABLE II. Experimental relative index of absorption η_0 (in the absence of CR).

$\Delta\nu$(MHz)	η_0(4.2°K)	η_0(1.6°K)
−475	0.816	0.855
−300	0.821	0.859
0	0.821	0.865
+275	0.827	0.860
+550	0.824	0.867

TABLE III. Decay constants and spin-lattice relaxation rate at 4.2°K.

Cr:Co	$\Delta\nu$ (MHz)	λ (sec^{-1})	$2U_+$ (sec^{-1})
0.035×10^{-2}	622	54	52
	−15	62	47
0.15×10^{-2}	682	51	48
	137	76	46
	−462	49	45
0.38×10^{-2}	682	74	53
	157	155	53
	−468	75	46
1.03×10^{-2}	682	185	49
	−5	736	46
	−468	202	48

TABLE IV. Decay constants and spin-lattice relaxation rate at 1.6°K.

Cr:Co	$\Delta\nu$ (MHz)	λ (sec^{-1})	$2U_+$ (sec^{-1})
0.15×10^{-2}	682	22	19
	60	45	19
	−463	24	20
0.38×10^{-2}	682	39	21
	127	117	19
	−468	42	18
1.03×10^{-2}	682	128	18
	−15	826	21
	−468	171	18

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

[27] T. M. Bray, G. C. Brown, and A. Kiel, Phys. Rev. **127**, 730 (1962).

[28] A. Kiel, Phys. Rev. **125**, 1451 (1962).

diffusion times are shorter. In order to avoid the complications connected with spin diffusion, the saturating pulses used in our experiment were 1 msec long. The measured values of the decay constant λ and the resulting [Eq. (11)] spin-lattice relaxation ($2U_+$) rate for four crystals at various intervals from the center of the CR line are given in Table III for 4.2°K. The data obtained at 1.6°K are shown in Table IV.

The measurements were difficult to perform at the lowest concentrations because of sensitivity limitations of the apparatus. They were also difficult at the center of the CR line for crystals of the highest concentration since for these conditions the index of absorption is only 0.04 at 4.2°K and 0.02 at 1.6°K (Figs. 6 and 7). The saturation transferred from the C-band lines by CR to the monitored ν_{14} line is nearly complete, even without the saturating pulse.

Tables III and IV show that $2U_+$ is independent of the magnetic field within the investigated interval of 150 Oe. In terms of Mattuck and Strandberg[25] analysis applied to the present case, this is consistent with the assumption that the quadrupole term in the matrix elements of direct spin-phonon processes dominates the dipole term.[25] In the following we have adopted the average values of the spin-lattice rates from Tables III and IV:

$$2U_+=49\pm5\ \text{sec}^{-1}\qquad(4.2°\text{K}),$$

$$2U_+=19\pm2\ \text{sec}^{-1}\qquad(1.6°\text{K}).$$

These values, the values of η_0, and the data of Figs. 6 and 7 provide all the information needed to determine, from Eq. (12), the CR rate at various concentrations for a range of $\Delta\nu$.

III. DETERMINATION OF CR RATES BY THE METHOD OF MOMENTS

A. CR Contribution to the Rate Equation

In this section we compute the CR term appearing in the rate equation, Eq. (5), by the hybrid method of Bloembergen *et al.*[1,7] We consider a spin system of N Cr^{3+} spins distributed at random into M lattice sites. The spin Hamiltonian, Eq. (1), contains crystalline terms and it is therefore convenient to work in the representation in which H_i is diagonal. We mark the states satisfying $H_i\,|\,r\rangle=\epsilon_r\,|\,r\rangle$ by an index r running through integers $1, 2,\cdots, 2S+1$ in order of increasing energy, $\epsilon_1<\epsilon_2<\cdots<\epsilon_{2S+1}$. In the following we denote the crystalline axes (b, c, a) by x, y, z. The eigenstates of H_i at the orientation of the magnetic field $\theta=49°50'$ and $\varphi=\frac{1}{2}\pi$ were determined for $|\mathbf{H}|=600$, 700, 735, 800, 900 Oe (Fig. 4). Their composition in terms of the eigenstates of S_{zi} varies very little in this range and we have adopted the following approximate wave functions:

$$\begin{aligned}
|\,1\rangle&=\tfrac{1}{2}\sqrt{2}(|+\tfrac{1}{2}\rangle+i\,|-\tfrac{1}{2}\rangle),\\
|\,2\rangle&=\tfrac{1}{2}\sqrt{2}(i\,|+\tfrac{1}{2}\rangle+|-\tfrac{1}{2}\rangle),\\
|\,3\rangle&=|-\tfrac{3}{2}\rangle,\\
|\,4\rangle&=|+\tfrac{3}{2}\rangle.
\end{aligned}\tag{13}$$

The operators S_{zi}, S_{+i}, S_{-i} are transformed into this representation by the unitary transformation $U=\langle r\,|\,S_{zi}\rangle$. We call $T_{1i}=US_{zi}U^+$, $T_{2i}=US_{+i}U^+$, $T_{3i}=US_{-i}U^+$. It is expedient to split the pair interaction into six terms $H_{ij}=A_{ij}+B_{ij}+C_{ij}+D_{ij}+E_{ij}+F_{ij}$ and express it in terms of the operators T and in Cartesian coordinates:

$$\begin{aligned}
A_{ij}&=a_{ij}T_{1i}T_{1j}, & a_{ij}&=g^2\beta^2(r^2-3z^2/r^5)_{ij},\\
B_{ij}&=b_{ij}(T_{3i}T_{2j}+T_{2i}T_{3j}), & b_{ij}&=-\tfrac{1}{4}a_{ij},\\
C_{ij}&=c_{ij}(T_{1i}T_{2j}+T_{2i}T_{1j}), & c_{ij}&=-\tfrac{3}{2}g^2\beta^2(zy-izx/r^5)_{ij},\\
D_{ij}&=d_{ij}(T_{1i}T_{3j}+T_{3i}T_{1j}), & d_{ij}&=c_{ij}^*,\\
E_{ij}&=e_{ij}T_{2i}T_{2j}, & e_{ij}&=\tfrac{3}{4}g^2\beta^2[(y^2-x^2)-i2xy/r^5]_{ij},\\
F_{ij}&=f_{ij}T_{3i}T_{3j}, & f_{ij}&=e_{ij}^*.
\end{aligned}\tag{14}$$

In these expressions we have written the indices of the pair i, j outside the bracket. The use of Cartesian coordinates, rather than the more conventional spherical coordinates, was prompted by the facility of programming the computation of the lattice sums (to be discussed shortly) on the IBM-7094 computer for the orthorhombic cell of $K_3Co(CN)_6$. In Eq. (14) we have neglected exchange interactions because of a lack of any direct evidence of its effects in $K_3Cr(CN)_6$.

In the following, the product states $|\,r_i\rangle\,|\,s_j\rangle\,|\,t_k\rangle$, in which r, s, t mark the eigenstates of the single spin Hamiltonian and i, j, k mark the spins, will be abbreviated as $|\,rst\rangle$, the alphabetic order of spin indices being understood. Similarly a bra $\langle r_i\,|\,\langle s_j\,|\,\langle t_k\,|$ will be written as $\langle rst\,|$.

According to the hybrid method the transition probability rate, w_{ijk}, for a single three-spin CR process is given by

$$w_{ijk}=(1/\hbar^2)\,|\,\langle rst\,|\,O_{ijk}\,|\,r's't'\rangle\,|^2g(\Delta\nu).\tag{15}$$

Here O_{ijk} and $g(\Delta\nu)$ are the transition operator and the shape function, respectively. $|\,rst\rangle$ is the initial state of the three spins and $| r's't' \rangle$ is the final. It is understood that $r \neq r'$, $s \neq s'$, $t \neq t'$ and that $\epsilon_r + \epsilon_s + \epsilon_t = \epsilon_{r'} + \epsilon_{s'} + \epsilon_{t'}$. The matrix element of the transition operator is to be computed at the exact coincidence of the Zeeman (and crystalline) energies. The decrease of the interaction strength at the magnetic field values for which the energy condition is not exactly satisfied is absorbed into $g(\Delta\nu)$. In Eq. (15), $\Delta\nu = (\epsilon_r - \epsilon_{r'}) + (\epsilon_s - \epsilon_{s'}) + (\epsilon_t - \epsilon_{t'})$.

If at a given time there are n_r, n_s, n_t spins in states $| r \rangle$, $| s \rangle$, $| t \rangle$, respectively, the total number of spin processes $| rst \rangle \rightarrow | r's't' \rangle$ is

$$\sum_{i=j}^{n_r} \sum_{j=1}^{n_s} \sum_{k=1}^{n_t} w_{ijk}.$$

This expression implies that we know exactly which sites are occupied by the spins and that we know the spin state at the occupied site. It is necessary to introduce the probability for the ith site to be occupied by a spin in the $| r \rangle$th state. This probability is $(n_r/N)(N/M) = (n_r/N)f$. When proper care is taken of the multiplicities of initial and final states, the total number of processes $| rst \rangle \rightleftarrows | r's't' \rangle$ becomes

$$(1/\hbar^2) n_r n_s n_t (f^2/N^2) \Big(\sum_{j,k\neq}^{M} K_{ijk} \Big) g(\Delta\nu). \qquad (16)$$

The summation over ith sites has been performed and $j, k \neq$ means $j \neq k$ and, of course, $j \neq i$, $k \neq i$. In Eq. (16),

$$K_{ijk} = [\sigma(r's't')/m_r! m_s! m_t!] \, | \langle rst | O_{ijk} | r's't' \rangle |^2. \qquad (17)$$

$\sigma(r's't')$ is the summation over distinguishable permutations of the final states $| r' \rangle$, $| s' \rangle$, $| t' \rangle$ and $m_r! m_s! m_t!$ is the number of indistinguishable permutations of the states $| r \rangle$, $| s \rangle$, $| t \rangle$. In the two (Fig. 1) processes, $| 331 \rangle \rightleftarrows | 222 \rangle$ and $| 224 \rangle \rightleftarrows | 333 \rangle$, we have $r' = s' = t'$ and $m_r! m_s! m_t! = 2$. Therefore for both processes

$$K_{ijk} = \tfrac{1}{2} \, | rrt | O_{ijk} | r'r'r' \rangle |^2. \qquad (18)$$

The change of the population number of a Zeeman level, e.g., n_r, is given by the number of processes per unit time multiplied by the number of spins in states $| r \rangle$ participating in a single CR process. Denoting this last quantity by $\alpha(r)$, the rate of change of n_r due to the processes $| rst \rangle \rightleftarrows | r's't' \rangle$ becomes

$$(\partial n_r/\partial t)_{\mathrm{CR}} = \alpha(r) (n_{r'} n_{s'} n_{t'} - n_r n_s n_t)(1/N_2) W_{\mathrm{CR}}, \qquad (19)$$

with

$$W_{\mathrm{CR}} = (f^2/\hbar^2) \Big(\sum_{j,k\neq} K_{ijk} \Big) g(\Delta\nu).$$

The summations in the last expression are over the lattice sites. We have treated α and β processes as independent. With this assumption the contribution of CR to the rate equation, Eq. (5), is

$$(\partial\Delta/\partial t)_{\mathrm{CR}} = 3(n_1^3 - n_4^3)(W_{\mathrm{CR}}/N^2) = \tfrac{9}{16} W_{\mathrm{CR}} \Delta,$$

with

$$W_{\mathrm{CR}}(f, \Delta\nu) = (f^2/\hbar^2) \Big[\sum_{j,k\neq} K_{ijk}^{(\alpha)} g_\alpha(\Delta\nu) + \sum_{j,k\neq} K_{ijk}^{(\beta)} g_\beta(\Delta\nu) \Big]. \qquad (20)$$

B. Transition Operator

The dipolar interaction does not cause three-spin flipping in first-order perturbation theory because terms like $\langle rst | H_{ij} | r's't' \rangle$ vanish when $r \neq r'$, $s \neq s'$, $t \neq t'$. The terms resulting from second-order theory are of the type

$$\frac{\langle rstu | H_{ij} | r''s''t''u'' \rangle \langle r''s''t''u'' | H_{lk} | r's't'u \rangle}{E(r's't'u) - E(r''s''t''u'')}.$$

It can be shown[7,8] that all intermediate states $| r''s''t''u'' \rangle$ occur in pairs whose contributions cancel out. One of the spin indices of H_{lk} must be the same as in H_{ij} occurring in the first factor. It follows also that four-spin processes cannot be described by second-order perturbation theory, but require third-order theory. In general, m-spin processes require the $(m-1)$st order of perturbation theory.

The interaction operator can be written as

$$O_{ijk} = \sum_{u,v,w} \times \frac{(H_{ij} + H_{jk} + H_{ik}) \, | uvw \rangle \langle uvw | \, (H_{ij} + H_{jk} + H_{ik})}{E(r's't') - E(uvw)}. \qquad (21)$$

The summation is over the intermediate states $| u \rangle$, $| v \rangle$, $| w \rangle$ of the i, j, k spins.

The matrix elements of the transition operator for the α and β processes were determined by making use of the representation of the dipolar energy given by Eq. (14). Their explicit form in terms of the geometric coefficients of the lattice are given in the Appendix. With these results the lattice sums of Eq. (20) have been programmed for the 7094 computer. The indices (l, m, n) of Fig. 2 were allowed to run through $(\pm 2, \pm 2, \pm 2)$. The resulting values are

$$\begin{aligned} \sum_{j,k\neq} K_{ijk}^{(\alpha)} &= 1.523 \times 10^2 \text{ MHz}^2, \\ \sum_{j,k\neq} K_{ijk}^{(\beta)} &= 2.501 \times 10^2 \text{ MHz}^2. \end{aligned} \qquad (22)$$

C. Shape Functions

For undiluted spin systems Bloembergen *et al.*[1] and Pershan[8] compute the shape functions of the CR processes by evaluating the convolution of the shapes of paramagnetic lines participating in the CR process. For diluted salts the shape functions are determined by the method of moments by an extension of the method introduced by Van Vleck[5] and Pryce and Stevens[6] in the study of paramagnetic line shapes. The main result of the method of moments is the conclusion that the shape functions of the CR in diluted spin systems is concentration-independent. We summarize the reasoning below.

The Hamiltonian of the entire spin system is given by

$$H=H_0+H_{\text{dip}}=\sum_{i}^{N} H_i+\sum_{i>j}^{N} H_{ij}. \tag{23}$$

When the populations $(n_1^\Gamma, n_2^\Gamma, \cdots, n_{2S+1}^\Gamma)=\{n^\Gamma\}$ of single-spin Zeeman energies have been prescribed, the manifold Γ of eigenstates of H_0 with the energy $E_\Gamma=\sum n_r^\Gamma \epsilon_r$ is degenerate ($N!/\prod_r n_r!$-fold). The dipolar energy plays a dual role: It removes the degeneracy of the manifolds of the eigenstates of H_0 and it causes CR transitions. These two parts can be separated by introducing

$$H=\sum_{\Gamma} P_\Gamma H_{\text{dip}} P_\Gamma \tag{24}$$

and

$$\hat{O}=\sum_{\Gamma\neq\Lambda} P_\Gamma H_{\text{dip}} P_\Lambda (=H_{\text{dip}}{}^{NS}).$$

P_Γ and P_Λ are projectors on the manifolds of degenerate states of H_0. The manifolds are defined by prescribing the population distributions $\{n^\Gamma\}$ and $\{n^\Lambda\}$. If $\{n^\Gamma\}\neq\{n^\Lambda\}$ but the energies E_Γ and E_Λ are equal, the spins can flip, conserving energy. The CR processes can also occur in the vicinity of the coincidence of energies. The excess, $h\Delta\nu=E_\Gamma-E_\Lambda$, is then absorbed in the energy rearrangement of the entire spin system.

Equations (23) and (24) are appropriate for first-order perturbation theory, which can only account for two-spin processes. More generally, for m-spin processes we should use

$$\hat{O}=\sum_{\Gamma\neq\Lambda} P_\Gamma \Big(\sum_{i_1}\cdots\sum_{i_m} O_{i_1 i_2\cdots i_m}\Big) P_\Lambda. \tag{25}$$

$O_{i_1 i_2\cdots i_m}$ is an operator of the type introduced for $m=3$ in Eq. (21).

Computation of the moments proceeds from a theorem of Van Vleck,[5] modified for CR shape functions by Bloembergen *et al*,[1] and summarized elegantly by Grant[11d]:

$$h^{2n}\langle\Delta\nu^{2n}\rangle=(-1)^n\,\text{Tr}\,U_{2n}U_{2n}^{+}/\text{Tr}\,\hat{O}\hat{O}^{+}, \tag{26}$$

with

$$U_{2n}=[H, U_{2n-2}], \qquad U_0=\hat{O}.$$

It can be shown[7] that the trace of the numerator is a sum of traces evaluated in configuration spaces of m, $m+1, \cdots$, $m+n$ spins. For the m-spin processes, the numerator of the $2n$th moment can be expressed as a sum of the type

$$\sum_{k=0}^{n}\Big(\sum_{i_1}^{N}\sum_{i_2}^{N}\cdots\sum_{i_{m+k}}^{N}\Big). \tag{27}$$

The denominator of the moment formula is of the form $\sum_{i_1}\sum_{i_2}\cdots\sum_{i_m}$. When we convert spin sums to lattice sums $(\sum^N\rightarrow f\sum^M)$, each summing index introduces one concentration factor f. The leading term of Eq. (27) ($k=0$) has the same number of summation indices as the denominator. The leading term of all moments is concentration-independent. Therefore, according to the method of moments the shape functions are concentration-independent in diluted spin systems. We postpone further discussion of this result until Sec. V.

We have computed the concentration-independent terms of the second moments of the three-spin α and β processes of Fig. 1. They are of the form

$$h^2\langle\Delta\nu^2\rangle=\sum_{j,k\neq}^{M} G_{ijk}\Big/\sum_{j,k\neq}^{M} K_{ijk}. \tag{28}$$

The sums in the denominator are those of Eq. (22). Details of the computation of the lattice sums appearing in the numerator of Eq. (28) can be found in Ref. 7. The pertinent matrix elements of the secular part of the dipolar interaction are given in the Appendix. The numerical values of the numerator of Eq. (28) are

$$\begin{aligned}\sum_{j,k\neq} G_{ijk}{}^{(\alpha)}&=2.012\times10^6\ (\text{MHz})^4,\\ \sum_{j,k\neq} G_{ijk}{}^{(\beta)}&=8.451\times10^7\ (\text{MHz})^4.\end{aligned} \tag{29}$$

We assume the shape functions to be Gaussian and obtain for the CR rate

$$\begin{aligned}1/T_{12}=\tfrac{9}{16}W_{\text{CR}}=f^2[&1.046\times10^7\\ &\times\exp\{-\tfrac{1}{2}(\Delta\nu/1.161\times10^8)^2\}\\ &+0.347\times10^7\exp\{-\tfrac{1}{2}(\Delta\nu/5.847\times10^8)^2\}].\end{aligned} \tag{30}$$

D. Comparison with the Experiment

The CR time T_{12} of Eq. (30) has been used to plot the theoretical relative index of absorption $\eta(\Delta\nu, f)$, which is shown in comparison with experimental results for η in Figs. 6 and 7. The inverse of the CR time (normalized by the square of concentration) is shown in Fig. 8 versus the experimental results for five crystals of lower concentrations. The estimated probable error in the experimental points varies linearly from →15% at the harmonic point to ±50% at $|\Delta\nu|=680$ MHz. The agreement with the computed shape is generally good and the main predictions of the hybrid method appear to be confirmed: The shape is concentration-independent and the intensity of the interaction is proportional to f^2. The data are for experiments performed at 4.2°K. We have dispensed with the corresponding presentation of the data collected at 1.6°K; the comparison also shows good agreement of the shape with Eq. (30), but the theoretical intensity of the interaction is uniformly too high by about 10%. We believe it to be the result of a systematic error in the determination of $2U_+$. At both temperatures the results obtained for more concentrated crystals ($f=0.586\times$

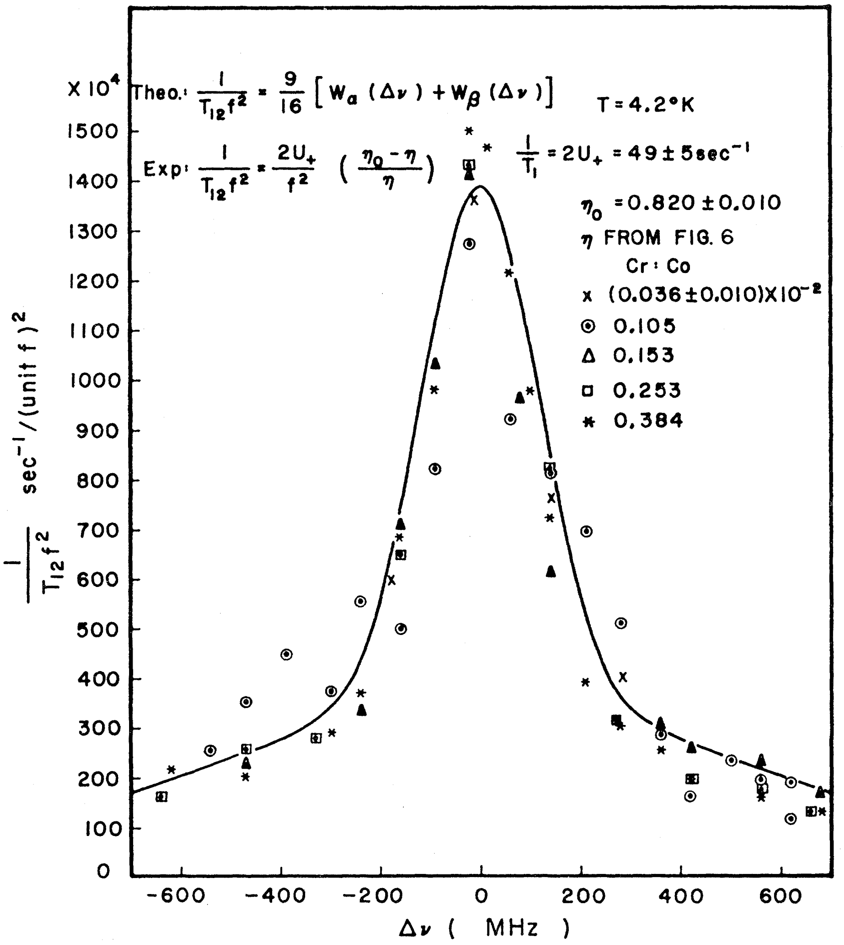

FIG. 8. Comparison of the experimental CR rates in five diluted crystals with the rate determined by the hybrid method ($T=4.2$°K).

10^{-2} and 1.030×10^{-2}) disagree with the computed CR rate. This is shown in Fig. 9. We might expect such changes of shape and intensity to occur when in the computation of the moments the terms linear in concentration cannot be neglected. For the assumed Gaussian shapes of $W_{\text{CR}}f^{-2}$ an approximate computation which includes terms linear in f in the G_{ijk} sums shows the effect of these terms to be negligible. The hybrid method is thus unable to account for the sudden change of shape and intensity of the CR rate between the group of crystals with lower concentration of chromium (Fig. 8) and the two crystals of Fig. 9. While the probable errors can account for the discrepancy in the wings of the CR rate, it cannot do so for the central peak.

IV. ANALYSIS OF THE CR RATE BY THE THEORY OF GRANT

For single spin CR processes, Grant[11] shows that the CR rate W_{CR} is proportional to the convolution of two functions: $\chi(\omega)$, which is the power spectrum of the dipolar transition operator and $\varphi(\omega)$, the shape function of the paramagnetic line. For two-spin processes, it is still possible to evaluate $\chi(\omega)$ and $\varphi(\omega)$ separately, by including their correlation in the $\varphi(\omega)$ function, and computing $\chi(\omega)$ as the power spectrum of the transition operator. For three-spin (and higher) processes the determination of W_{CR} becomes more complicated, because the three-spin $\chi_3(\omega)$ is not a convolution of two two-spin $\chi_2(\omega)$ functions. The two $\chi_2(\omega)$'s are correlated by the modulation of "the squiggles" of i and j spins from "the squiggles" of the k spin [Grant, Ref. 11(b)]. The CR rate (per spin) then becomes

$$W_{\text{CR}}^{(3)}(\omega)=\frac{2\pi}{\hbar}\frac{f^3}{v^2}\frac{1}{(2S+1)^3}\int\chi_3(\omega-\omega')\varphi_3(\omega')d\omega',\tag{31}$$

where f is the concentration, v is the lattice volume per paramagnetic site, and $(2S+1)$ is the number of energy levels. We have used for $\varphi_3(\omega)$ the convolution of the three line shapes of the paramagnetic transitions at the frequencies ν_{23}, ν_{12}, ν_{34}. These shapes are nearly Lorentzian with half-power half-widths $\Delta\nu_{23}$, $\Delta\nu_{12}$, and $\Delta\nu_{34}$, dependent on concentration as given in Table V.

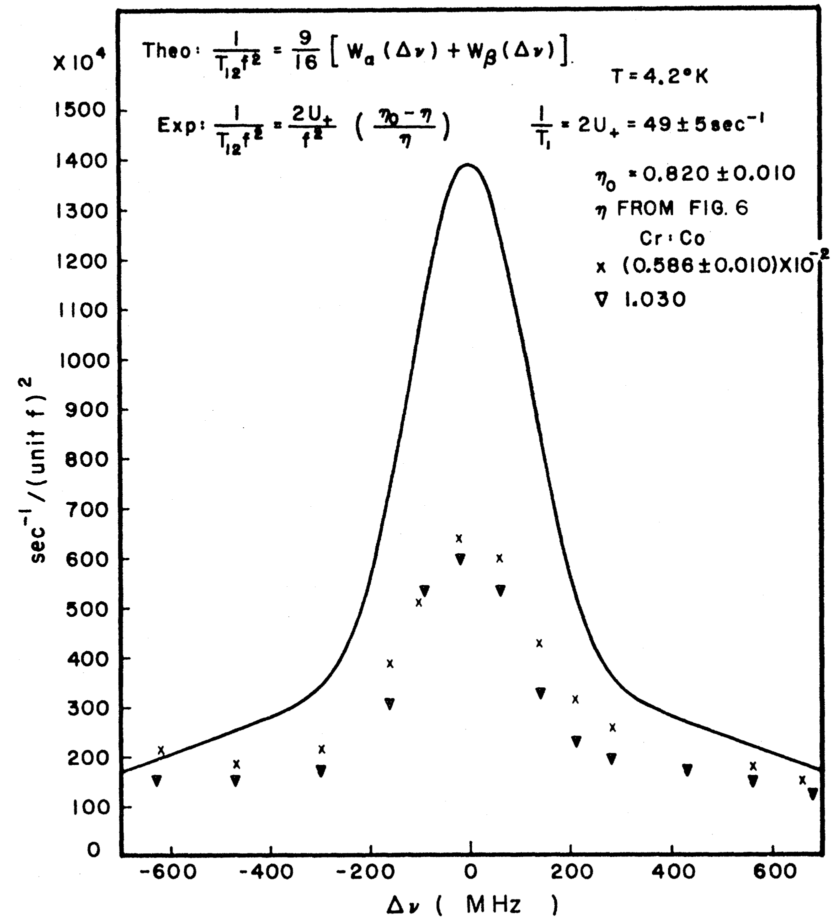

FIG. 9. Experimental CR rates in two more concentrated crystals, and the rate determined by hybrid method (T = 4.2°K).

The convolution of Lorentzians is a Lorentzian with width equal to the sum of the widths of the convolution factors. We have used a Lorentzian $\varphi_3(\nu)$ with half-width $3a = 2\Delta\nu_{23} + \frac{1}{2}(\Delta\nu_{12} + \Delta\nu_{34})$. The determination of $\chi_3(\omega)$ can be performed in two ways. If near neighbors dominate the interaction, a "discrete" method of summation over the first few neighbor shells is directly possible from the definition of $\chi_3(\omega)$ [Grant, Ref. 11(c), Eq. (9)]. This method includes the "squiggle" correlations explicitly and is useful when the near shells contain small number of atoms, and differ appreciably in radii. This is the way in which Grant treated three-spin CR processes of nuclear spins[8] of LiF. The domination of the interaction by near neighbors is due to the absence of exchange and the relatively small radii of the near shells. There are six F atoms and 12 Li atoms in the first shell, and eight F atoms and six Li atoms in the second shell. The number of terms for the determination of $\chi_3(\omega)$ is then 72 and 252 for first shell and first-and-second shell approximation. In orthorhombic $K_3Co(CN)_6$ the shells contain the numbers of paramagnetic sites shown in Table VI. The nearest-neighbor distance is large and the first few shells do not differ significantly in radii. Because all spins belong to the same species, the number of terms in the summation over first and second shells is 8!,

TABLE V. Linewidths of the paramagnetic transitions and the width ($3a$) of the Lorentzian convolution versus concentration.

Crystal No.	Cr:Co	$\Delta\nu_{23}$ (MHz)	$\Delta\nu_{12}$ (MHz)	$\Delta\nu_{34}$ (MHz)	$3a$ (MHz)
1	0.036×10^{-2}	25±3	24±3	20±3	72±5
2	0.105×10^{-2}	27	24	22	77
3	0.153×10^{-2}	27	24	22	77
4	0.253×10^{-2}	27	24	22	77
5	0.384×10^{-2}	27	24	22	77
6	0.586×10^{-2}	24	30	28	97
7	1.030×10^{-2}	36	32	30	103

TABLE VI. Number of neighbors and their distance from the reference site in the $2Or$ type of $K_3Co(CN)_6$.

Shell	No. of atoms	Distance (Å)
1	4	6.68
2	4	7.02
3	2	8.35
4	8	8.70
5	2	10.45
6	2	13.38
7	4	13.58
8	4	16.20

while for first, second, and third shells it is 10!. The discrete distribution of $\chi_3(\omega)$ becomes very dense, suggesting the use of Grant's "continuous" method of the determination of $\chi(\omega)$. The "continuous" method has been applied by Grant[11c] and Weissfloch.[13] to two-spin CR processes of Cr^{3+} in ruby and $K_3Co(CN)_6$, respectively. It is useful whenever exchange coupling eliminates near neighbors from contributing to CR. The strong coupling creates pairs whose paramagnetic spectrum is not, in general, harmonically related to the spectrum of a single atom. Only atoms outside of the exchange radius participate in the CR process. Grant determined the exchange radius in ruby to be 6.15 Å, in good agreement with the independent work of Statz *et al.*[29] Weissfloch determined the exchange radius of Cr^{3+} atoms (in nonequivalent sites) in $K_3Co(CN)_6$ as 10.1 Å. This is unusually large. In experiments with $K_3Co(CN)_6$ crystals of large Cr^{3+} concentrations (2–3%) we have not observed any pair spectra. In view of the lack of direct evidence of exchange coupling in $K_3Co(CN)_6$ and because of the large distance of the nearest neighbors, we have used Grant's "continuous" approximation to the $\chi_3(\omega)$ function, neglecting exchange. $\chi_3(\omega)$ was determined by folding Grant's approximate two-spin function $\chi_2(\omega)$ with itself. In Grant's notation [Grant, Refs. 11(a) and 11(b)]

$$\begin{aligned}\chi_2(\omega) &= \tfrac{8}{3}\pi^2(\langle m^2\rangle/2L)\ln(L\epsilon/|\omega|), && 0\leq|\omega|\leq L\epsilon\\ \chi_2(\omega) &= 0, && |\omega|>L\epsilon.\end{aligned} \tag{32}$$

In this expression $\langle m^2\rangle$ is the square of the matrix element of the two-spin transition operator averaged over a sphere of unit radius, L the change in dipole energy between the flipping spins, maximized with respect to the angular position of the two atoms for unit radius, and $\epsilon=1/r_0^3$, with r_0 either the distance of the nearest neighbors or the exchange radius. With the dipolar interaction of Eq. (14) and the wave functions of Eq. (13) we obtain

$$\begin{aligned}\langle m^2\rangle &= 1.07g^4\beta^4,\\ L &= 2.17g^2\beta^2.\end{aligned} \tag{33}$$

The function $\chi_3(\omega)$ is then determined from

$$\chi_3(\omega)=(\tfrac{4}{3}\pi\langle m\rangle^2)^2\frac{\epsilon}{(\Delta E_{23})^2L}\int_{x-1}^{1}\ln|x'|\ln|x-x'|\,dx', \tag{34}$$

with $x=\omega/L\epsilon$ and $\Delta E_{23}=h\nu_{23}$. The convolution appearing in Eq. (34) extends from $x=-2$ to $x=2$, its shape is nearly triangular, and its value at $x=0$ is 4. The smoothing of the sharp peak of $\ln|x|$ at $x=0$ is characteristic of the convolution operation. The convolution does not take into account the correlations of $\chi_2(\omega)$ functions. However, according to Grant, an approximation to $\chi_3(\omega)$ which includes the correlation can be obtained from $\chi_3(\omega)$ of Eq. (34) by increasing its width by a factor of 1.5, while preserving its shape.

For the three-spin CR rate we have, according to Eq. (32),

$$\begin{aligned}W_{\mathrm{CR}}^{(3)}(\omega) &= (2\pi/h)[f^3/(2S+1)^3](4\pi\langle m^2\rangle/3v)^2\\ &\quad\times[2\pi\epsilon/(\Delta E_{23})^2L]\Psi(\omega/L\epsilon,3a/L\epsilon),\end{aligned} \tag{35}$$

where

$$\Psi\left(x,\frac{3a}{L\epsilon}\right)=\int\chi_3(x')\,L_3\left(x-x',\frac{3a}{L\epsilon}\right)dx'.$$

$W_{\mathrm{CR}}^{(3)}$ depends on concentration through the factor f^3 and through the half-width $3a$ given in Table V. Because of the inhomogeneous broadening of the paramagnetic lines this latter dependence is weak. The experimental data presented in Sec. II obey reasonably well the f^2 dependence. Table VII shows a comparison of the experimental values of $W_{\mathrm{CR}}^{(3)}(0)$ with the values computed from Eq. (35). Columns 3 and 4 were computed with $r_0=6.68$ Å (nearest-neighbor distance) and

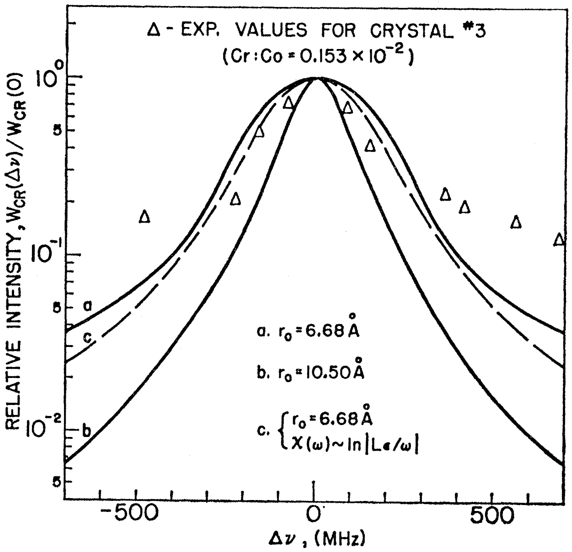

FIG. 10. Relative intensity of the three-spin CR rate. The curves a, b, c are determined by the theory of Grant. Experimental points are for the crystal with Cr:Co$=0.153\times10^{-2}$.

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[29] H. Statz, L. Rimai, M. J. Weber, G. A. DeMars, and G. F. Koster, J. Appl. Phys. **32**, 2185 (1961).

TABLE VII. CR rates at harmonic point. Third and fourth columns determined from theory of Grant with $r_0=6.68$ Å (nearest-neighbor distance) and exchange radius $r_0=10.50$ Å, respectively.

Concentration (Cr:Co)	Effective Lorentzian width ($3a$) (MHz)	$W_{CR}(0)$ (theory) $r_0=6.68$ Å (sec^{-1})	$W_{CR}(0)$ (theory) $r_0=10.50$ Å (sec^{-1})	$W_{CR}(0)$ experiments (sec^{-1})
0.036×10^{-2}	72	6.62×10^{-3}	1.01×10^{-3}	2.52
0.105×10^{-2}	77	1.68×10^{-1}	2.56×10^{-2}	2.54×10
0.153×10^{-2}	77	5.23×10^{-1}	7.95×10^{-2}	5.85×10
0.256×10^{-2}	77	2.44	3.69×10^{-1}	1.65×10^{2}
0.384×10^{-2}	77	8.21	1.27	3.83×10^{2}
0.586×10^{-2}	97	2.68×10	3.78	4.07×10^{2}
1.030×10^{-2}	103	1.40×10^{2}	1.91×10	1.09×10^{3}

$r_0=10.50$ Å (exchange radius), respectively. The disagreement by several orders of magnitude is apparent.

The description of the shape by Eq. (35) is not good either. Figure 10 shows the data for the crystal with $Cr:Co=0.153\times10^{-2}$ compared to the shapes of $\Psi(\omega/L\epsilon, 3a/L\epsilon)$ for $r_0=6.68$ and 10.50 Å. Experimental values have been normalized to agree with the two computed shapes at $\omega=0$. Computations of the shapes for other values of ϵ and $a/L\epsilon$ have also been performed and have not improved the situation. The function $\chi_3(\omega)$ falls off too rapidly in the wings and lacks the sharp center peak.

V. DISCUSSION

The "hybrid" method utilizing an exact computation of the transition operators and of the second moments of the three-spin processes gives reasonable account of the concentration dependence of the magnitude and shape of the interaction at low-spin concentrations ($f<0.5\%$). In accordance with the hybrid method the magnitude is proportional to f^2 and the shape is concentration-independent. The theory does not explain the change of shape and magnitude for concentrations larger than 0.5%. The splitting of the two three-spin interactions into independent processes (α and β) and the resulting addition of the two Gaussian shapes is rather arbitrary. The resulting shape and magnitude depend critically on the exact values of the second moments and, considering the approximate character of the wave functions used, the good quantitative agreement (for $f<0.5\%$) of the experimental and computed shapes has to be considered fortuitous.

Grant's theory provides for the concentration dependence in a dual way. For three-spin processes the magnitude is proportional to f^3, but the power of this dependence can be lowered by the dependence of the paramagnetic linewidths on concentration. This latter dependence can also modify the shape. It was therefore expected that this theory could account for the experimental results at all the concentrations studied. Instead, we have to conclude that it cannot explain the present experiment. The f^3 dependence of the theory could be lowered to f^2 if the linewidths depended linearly on concentration. Because of the inhomogeneous broadening they are very weakly concentration-dependent. Therefore the theory predicts essentially an f^3 relation, which is not confirmed. The theoretical shapes cannot be fitted even approximately, whether one uses the three-spin $\chi_3(\omega)$ folded with either a Lorentzian or Gaussian $\varphi(\omega)$, or the two-spin $\chi_2(\omega)$ of Eq. (32). An approximate evaluation of $\chi_3(\omega)$ by the "discrete" method did not improve the agreement. The experimental shape is characterized by the central ("resonant") peak and large wings and is not reproduced by the theory. The variation of the effective-interaction radius from the distance of the nearest neighbors $r_0=6.68$ Å (no exchange) to $r_0=10.50$ Å (an exchange radius which excludes 20 near neighbors from contributing to CR) does not improve the agreement.

The sharpness of the central peak has been demonstrated previously by Feng and Bloembergen[9] for a five-spin process in ruby. For such higher-order processes, Grant's theory, because of the use of multiple convolutions of two-spin $\chi(\omega)$ functions and the associated $\varphi(\omega)$ functions, results in smoothed-out shapes for $W_{CR}(\omega)$. The magnitude of the interaction at the harmonic point of the Feng and Bloembergen experiment varied as $f^{2.6}$ instead of f^5. At $f=0.04\%$, $W_{CR}(0)$ was determined to be approximately 50 sec^{-1}. The ratio of the CR rates for the two subsequent-order CR processes is approximately[7,30]

$$K=W_{CR}^{(n+1)}(0)/W_{CR}^{(n)}(0)=f(g^2\beta^2\epsilon/h\bar{\nu}),$$

where $h\bar{\nu}$ is a measure of the average Zeeman energy. For the case of ruby with $f=0.04\%$ and $\epsilon=1/(235\text{ Å}^3)$, as determined by Grant, $K\simeq1.5\times10^{-5}$. If one uses Grant's value for the Mims experiment, $W_{CR}^{(2)}(0)=2.59\times10^4\ sec^{-1}$, then Feng and Bloembergen rate should have been $W_{CR}^{(5)}(0)\simeq10^{-10}\ sec^{-1}$ and would have hardly been observable.

In higher-order CR processes, described here and by Feng and Bloembergen, groups of spins undergo the same transitions. In the latter, three spins flip up and two flip down $[|33333\rangle\rightleftarrows|11144\rangle]$ while in our experi-

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[30] In this respect, the hybrid method does not differ from Grant's.

ment two spins flip together [$|222\rangle \rightleftarrows |311\rangle$, and $|333\rangle \rightleftarrows |422\rangle$]. In both cases all spins have a common energy level. Grant's ensemble model does not distinguish between degenerate and nondegenerate cases in which each spin flips through a different transition. The experiments presented here suggest a need for reexamination of Grant's statistical model when applied to higher-order CR processes in diluted paramagnetic salts.

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APPENDIX: MATRIX ELEMENTS OF O_{ljk} AND H_{lj}

Explicit expressions for the matrix elements necessary to determine the lattice sums of the transition operator O_{ijk} of Eqs. (11), (20), and (21) are given below.

α=Processes

$$\langle 331 | O_{ijk} | 222\rangle = [3i/(\epsilon_3-\epsilon_2)][(b_{jk}+f_{jk}+\tfrac{1}{2}id_{jk}) \times(b_{ij}+id_{ij}+b_{ik}-f_{ik})+(b_{ik}+f_{ik}+\tfrac{1}{2}d_{ik}) \times(b_{ik}+d_{ij}+b_{ik}-f_{jk})]. \quad \text{(A1)}$$

β=Processes

$$\langle 224 | O_{ijk} | 333\rangle = i(9/8)[\epsilon_3-\epsilon_2]^{-1}e_{ik}e_{kj}. \quad \text{(A2)}$$

The coefficients b_{jk}, f_{jk}, etc., are those given in terms of the dipolar interaction, Eq. (14). The pertinent matrix elements of the secular part of the dipolar interaction which appear in the computation of the moments, Eq. (26), are

$$\begin{aligned}
\langle 22 | H_{ij} | 22\rangle &= -2\,\mathrm{Re}e_{ij}+2b_{ij},\\
\langle 33 | H_{ij} | 33\rangle &= (9/4)a_{ij},\\
\langle 24 | H_{ij} | 24\rangle &= 3\,\mathrm{Im}d_{ij},\\
\langle 24 | H_{ij} | 42\rangle &= \tfrac{3}{2}b_{ij}, \qquad \text{(A3)}\\
\langle 31 | H_{ij} | 31\rangle &= -3\,\mathrm{Im}d_{ij},\\
\langle 31 | H_{ij} | 13\rangle &= \tfrac{3}{2}b_{ij}.
\end{aligned}$$

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Some Calculations on the Jahn-Teller Effect in Octahedral Systems

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Numerical calculations for a soluble one-parameter dynamic Jahn-Teller effect in a system of octahedral symmetry are presented (vibronic coupling of a τ_{2g} vibrational mode in a Γ_8 electronic state, linear approximation). A computer subprogram for computing eigenvectors and eigenvalues is described.

INTRODUCTION

NUMERICAL solutions of the vibronic energy eigenvalue problem were presented by Moffitt and Thorson[1] and by Longuet-Higgins, Öpik, Pryce, and Sack[2] for the dynamic Jahn-Teller interaction of a doubly degenerate vibration with a doubly degenerate electronic state, as may, for example, occur in a system with a single n-fold axis, $n \geq 3$. The tractability of the problem depended upon the fact that a "vibronic angular momentum" emerged in that case as a constant of the motion. The identical dynamical problem occurs in doubly degenerate states of systems with higher symmetry (O_h). The analysis of vibronic coupling in triply degenerate states (T_1, T_2) of such systems, however, proves to be essentially more complicated.[3] Both ϵ_g (doubly degenerate) and τ_{2g} (triply degenerate) vibrational modes may interact with the triply degenerate states. The coupling of the ϵ_g modes alone is very simple, leading only to a uniform shift of all levels. On the other hand, coupling of a single τ_{2g} mode alone is not characterized by a "vibronic angular momentum"; the potential-energy hypersurfaces for nuclear motion have octahedral rather than spherical symmetry; only

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* Deceased.

[1] W. Moffitt and W. Thorson, Colloq. Intern. Centre Natl. Rech. Sci. (Paris) **82**, 141 (1958). Also printed in book entitled *Calcul des Fonctions d'Onde Moleculaire*, edited by R. Daudel (Centre National de la Recherche Scientifique, Paris, 1958), Reprints of French text are available from W. Thorson.

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