Spectral spin diffusion in dilute ruby*

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The broadening of the $+1/2 \leftrightarrow -1/2$ or low-field EPR absorption line of Cr^{3+} in dilute ruby has been studied at 2.7 GHz at liquid-helium temperature. Experimental evidence is given that the line is inhomogeneously broadened when observed with the external magnetic field H_0 parallel to the crystal axis, while it tends to be homogeneously broadened when observed with H_0 perpendicular to the crystal axis. A qualitative model is discussed in which the effect is attributed to the local-field modulation at the Cr^{3+} sites by ^{27}Al nuclei. A new technique of double resonance at microwave and radio-frequency energy has been used in which the phase of the wave at harmonic frequency is detected as a function of the external magnetic field and rf frequency. It is shown that spin transitions induced in the ^{27}Al nuclei create spectral spin diffusion in the electron Cr^{3+} spin system which is seen directly as an increase of the width of the central spin packet of the Cr^{3+} absorption line.

I. INTRODUCTION

The EPR absorption linewidth of dilute ruby (Al_2O_3 with very low concentration of Cr_2O_3) is caused by superhyperfine interaction of the Cr^{3+} paramagnetic ion with the 13 neighboring ^{27}Al nuclei.[1,2] Experimental investigations of this interaction were carried through using electron-nuclear double resonance (ENDOR) technique[3] and, more recently, using the spin-echo modulation effect.[4,5] From ENDOR spectra Laurance *et al.*[3] obtained numerical values of the superhyperfine coupling constants, which well account for the magnitude of the EPR linewidth[2] and the spin-echo modulation envelope.[4] However, an unusual feature was pointed out by these experiments: ENDOR spectra of neighboring ^{27}Al nuclei in ruby were observed only when the external magnetic field was directed along the optic axis of the crystal within a very few degrees. Similarly, the spin-echo modulation pattern disappeared very fast when the magnetic field was tilted from the c axis. Both effects suggest that a spin-packet structure of the EPR absorption line is present only when H_0 is parallel to the c axis and that a basic change of the line structure should occur when H_0 is rotated from the c axis.

In this paper we present measurements of the spin-packet width of the EPR absorption line of Cr^{3+} in ruby at various angles near $\theta = 0°$ ($\vec{H}_0 \parallel \vec{c}$) and at $\theta = 90°$ ($\vec{H}_0 \perp \vec{c}$). In order to get the experimental value of the width of the spin packet, we make use of the so-called "stirring effect," i.e., the dependence of the transverse relaxation time T_{2e} on the saturation degree of the spin system.[6,7] We present here the measurements of T_{2e} as a function of the microwave input power in three different samples of ruby: some peculiarities in this dependence are discussed. By fitting the experimental results with the theory, we are able to obtain the value of the spin-packet width and the correlation time of the random magnetic field at the Cr^{3+} site. The relation with ENDOR and spin-echo measurements is discussed. A qualitative model[4] is discussed that explains the observed dependence of the spin-packet width on the angle θ. As a test for the proposed model, some measurements are made in the presence of a rf field resonating with the ^{27}Al nuclei. This technique, at least in principle, can be proposed as a new ENDOR technique.

II. EXPERIMENTAL PROCEDURE

Let us consider a spin system in a static magnetic field H_0 and a microwave magnetic field H_1 of frequency ω. We have previously shown[6] both experimentally and theoretically that because of its intrinsic nonlinearity such a spin system emits radiation at second-harmonic (SH) frequency 2ω. The SH spectrum consists of two lines resonating at $\omega = \omega_0$ and at $\omega = \frac{1}{2}\omega_0$, respectively, where $\omega_0 = \gamma H_0$ is the resonance frequency of the spin system. The SH signal is phase coherent, the phase angle being a function of the external field H_0. When $\omega \approx \omega_0$, the spin system is strongly perturbed by the microwave input power and it is heavily saturated. In this condition the phase angle of the SH signal is given by

$$\tan\phi_1 = T_{2e}^{-1}/(\omega - \omega_0), \tag{1}$$

where T_{2e} is the effective transverse relaxation time which depends on the microwave input power level. Near $\omega = \frac{1}{2}\omega_0$ the phase angle is given by

$$\tan\phi_2 = T_{20}^{-1}/(2\omega - \omega_0), \tag{2}$$

where T_{20} (power independent) is the same as the one obtained from the EPR spectrum because the spin system, in this case, is very far from saturation. So, from measurements of the phase of

the SH signal, it is possible to deduce the values of T_{20} and T_{2e} at various input power levels.

The experimental values of T_{2e} and T_{20} are obtained by measuring the magnetic fields H_{01} and H_{02}, at which the phase of the SH signal is $\pm 45°$. According to Eqs. (1) and (2),

$$T_2 = 2/\gamma(H_{02} - H_{01}). \tag{3}$$

This relation applies to both the SH lines resonating at $\omega = \omega_0$ and $\omega = \frac{1}{2}\omega_0$ with T_2 equal to T_{2e} and T_{20}, respectively. We recall that Eqs. (1) and (2) have been inferred and are strictly valid for homogeneously broadened lines. In this case no question arises about the meaning of T_2 in Eq. (3). Since an inhomogeneous line is the envelope of many homogeneous lines (spin packets), questions arise as to whether T_2, as obtained from Eq. (3), refers to the total line or to the spin packet. In the Appendix we show that near the center of the $\omega = \omega_0$ line, destructive interference effects cancel out the contributions of symmetrical spin packets, with the result that the value of T_{2e}^{-1} which one gets from Eq. (3) is equal to the half-width of the central spin packet, eventually narrowed by the microwave power. Instead, for the SH line at $\omega = \frac{1}{2}\omega_0$ no interference effect occurs and the value of T_{20}^{-1} is equal to the half-width of the total line.

The dependence of T_{2e} on the input power level has been theoretically[8,9] and experimentally[7] investigated. According to Tomita[8] and Strandberg,[9] T_{2e} varies linearly with the input power, at high power levels (i.e., $H_1^2/H_{\text{eff}}^2 \gg 1$):

$$1/T_{2e} = (1/T_{20})H_{\text{eff}}^2/H_1^2, \tag{4}$$

where H_{eff}^2 is the mean-square width of the spin packet and H_1 is the microwave field amplitude. The increase of T_{2e} should be limited by the spin-lattice relaxation time T_1.[10] However, we remember that Eq. (4) is carried out under the hypothesis that the whole spin system is embedded in a time-independent environment (rigid lattice). The hypothesis is appropriate when the sources of the random local fields are internal to the spin system (this is the case, for instance, of dipolar interaction between similar spins). But, if the local fields are due to sources external to the electron spin system and have a finite correlation time τ_c, they are responsible of a broadening of the spin packets which only partially can be shrunk by a microwave field. The microwave field cannot lessen the dephasing effect owing to abrupt changes in the local fields; so such a correlation time would appear as a limiting value in the increase of T_{2e}.[8] In this case, if $\tau_c \ll T_1$, the appropriate relation is

$$1/T_{2e} = (1/T_{20})H_{\text{eff}}^2/H_1^2 + 1/\tau_c. \tag{5}$$

By fitting the experimental results with Eqs. (4) and (5) we are able to get the values of H_{eff} and τ_c. In the following, Eqs. (4) and (5) will be applied to the experimental values of T_{2e} obtained at $\omega = \omega_0$, while T_{20} is measured at $\omega = \frac{1}{2}\omega_0$, i.e., at a higher static magnetic field. In spite of this fact, the procedure is correct, since the condition $\Delta H \ll H_0$ is always fully satisfied in our experimental situations and no dependence of ΔH on the magnitude of H_0 is to be expected where ΔH is the EPR linewidth.

The experimental apparatus used for the present measurements is shown in Fig. 1. The bimodal rectangular cavity is resonating at 2.7 and 5.4 GHz. The sample is located in a point of the cavity where both the microwave fields H_1 (ω) and H_2 (2ω) are maxima. The microwave pulse oscillator is working at 2.7 GHz and it gives a maximum peak power of 5 kW lasting for 1 μsec with a repetition rate of about 200 pulses/sec. The SH signal present at the output of the pulse oscillator is used as a reference signal in the phase measurements: after passing an attenuator and a variable phase shifter, it is mixed with the SH signal generated by the spin system. The mixed signal is then detected with a conventional superheterodyne receiver. By varying the position of the phase shifter, it is possible to measure the relative phase of the SH signal radiated in the cavity by the spin system.

Some measurements are made in the presence of rf power, at frequencies ranging from 0.5 to 2.0 MHz, in resonance with the ^{27}Al nuclei. A five-turn coil is wound around the sample in such a way that its plane contains the c axis and the rf magnetic field is orthogonal to the external field H_0. The rf oscillator is a General Radio model 1211C which gives a cw output power of about 1.0 W in the range of our interest.

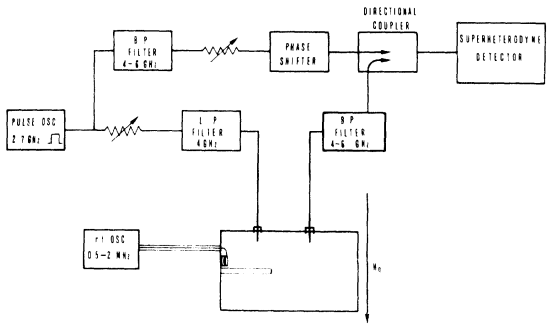

FIG. 1. Block diagram of the apparatus used for transverse relaxation time measurements and double-resonance experiments. All the experiments reported here were carried out at liquid-helium temperature. L. P. and B. P. stand for low pass and band pass, respectively.

The measurements reported here were made at 4.2°K on three single crystals of ruby, supplied by Union Carbide, with nominal Cr^{3+} concentration of 0.050, 0.065, and 0.16% by weight. We call these samples No. 1, No. 2, and No. 3, respectively. These crystals were cut in rectangular parallelepipeds $4\times4\times5$ mm^3 with the c axis parallel to the long axis. The orientation of the external field H_0 along the c axis was accomplished by utilizing the fact that the pronounced dip observed in the SH signal at $\omega=\omega_0$ falls at the highest value of H_0 for H_0 parallel to the c axis. In this way we are able to obtain alignments within ±0.5°.

TABLE I. Characteristic parameters of the investigated ruby crystals. H_{eff}, listed in the last column, is determined by fitting the experimental results with Eqs. (4) and (5).

Ruby sample No.	Conc. (wt%)	θ (deg)	$10^8\,T_{20}$ (sec)	ΔH (G)	$10^7\,T_p$ (sec)	H_{eff} (G)
1	0.050	0	0.80	6.7	4.4	$\lesssim$0.7
1	0.050	90	0.40	6.7	0.42	4.8
2	0.065	0	0.78	7.0	4.4	$\lesssim$0.7
2	0.065	6	0.78	7.0	2.2	$\lesssim$1.2
2	0.065	90	0.39	7.0	0.42	4.8
3	0.16	0	0.60	9.5	···	2.4
3	0.16	90	0.30	9.5	···	2.8

III. EXPERIMENTAL RESULTS AND DISCUSSION

The $+\frac{1}{2}\longleftrightarrow-\frac{1}{2}$ or low-field transition of Cr^{3+}, of which we are interested, is resonant with the input frequency of 2.7 GHz at $H_0=1015$ G when $\theta=0°$ and at $H_0=480$ G when $\theta=90°$. The EPR half-widths of the three ruby samples are reported in Table I. The main contribution to the EPR linewidth in dilute ruby comes from the superhyperfine interaction of the Cr^{3+} ion with its 13 neighboring ^{27}Al nuclei. Near $\theta=0°$ and 90° at the lowest Cr^{3+} concentrations the residual half-width is roughly independent of θ and is equal to 6.6 G.[1,2] The Cr^{3+}-Cr^{3+} dipolar interaction is evaluated[11] to be 0.73, 0.9, and 2.5 G for samples No. 1, No. 2, and No. 3, respectively. So, samples No. 1 and No. 2 show an EPR line half-width essentially equal to the residual one. The half-width of sample No. 3 is the result of the convolution between the superhyperfine and electron dipolar Cr^{3+}-Cr^{3+} interactions.[11] For each sample the linewidth when expressed in gauss, is the same at $\theta=0°$ and 90°, but the values of T_{20} are different because of the different γ_{eff} values: $\gamma_{\text{eff}}\equiv 2\pi\partial\nu/\partial H$ is equal to 1.8×10^7 G^{-1} sec^{-1} at $\theta=0°$ and to 3.6×10^7 G^{-1} sec^{-1} at $\theta=90°$.

Figure 2(a) shows T_{2e} of sample No. 2 of ruby as a function of the microwave input power level at three different orientations $\theta=0°$, 6°, and 90°. Essentially the same figures are obtained with the less concentrated sample No. 1. Figure 2(b) shows T_{2e} of sample No. 3 of ruby as a function of the microwave input power level at $\theta=0°$ and 90°. The continuous lines are the ones which best fit the experimental points. It is worthwhile to note that the power dependence of T_{2e} is qualitatively different for samples No. 2 and No. 3 and, further, T_{2e} of sample No. 2 shows a strong angular dependence.

For the concentrated sample No. 3, T_{2e} depends linearly on the input power at both orientations $\theta=0°$ and 90°. In the limit of high input power levels at which we are operating we fit the experimental results with the theoretical relation

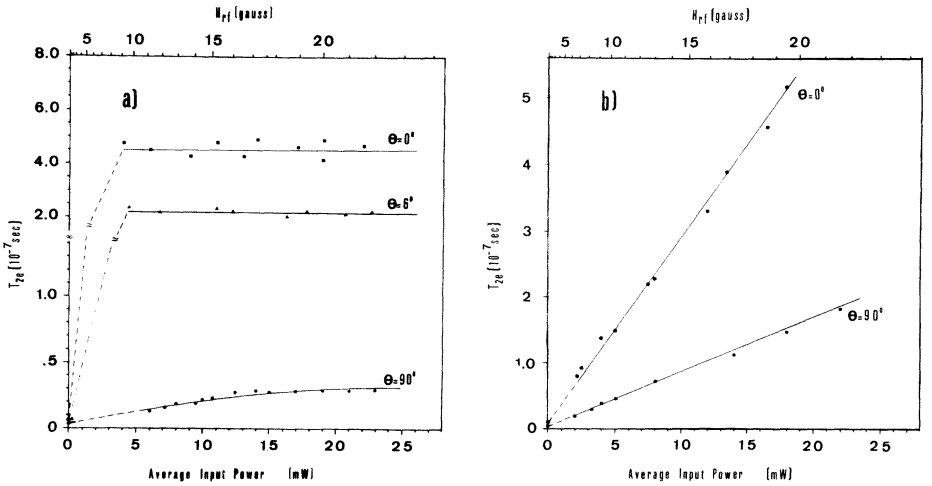

FIG. 2. (a) T_{2e} as a function of the input microwave power or microwave field amplitude of dilute ruby, sample No. 2, at three different orientations. $T=4.2$°K. (b) T_{2e} as a function of the input microwave power or microwave field amplitude of concentrated ruby, sample No. 3, at two different orientations. $T=4.2$°K.

(4). By fitting, we get $H_{eff} = 2.4$ G for $\theta = 0°$ and $H_{eff} = 2.8$ G for $\theta = 90°$. The small difference between the two values at $\theta = 0°$ and $90°$ may be seen as a residue of the effect which we shall discuss later for the more dilute samples. The results are consistent with the fact that the EPR line of our concentrated ruby is inhomogeneously broadened with a spin-packet width of about 2.5 G, which may be ascribed to the homogeneous dipolar Cr^{3+}-Cr^{3+} interaction.

For sample No. 2 at $\theta = 90°$ T_{2e} increases linearly with the power at relatively low input power levels and soon it tends to reach a plateau value. The same behavior can be assumed for $\theta = 0°$ and $6°$, though we are unable to work at low power levels at which T_{2e} is expected to be power dependent and only the constant values are detected. The plateau values are $T_p = 4.4 \times 10^{-7}$ sec at $\theta = 0°$ and $T_p = 2.2 \times 10^{-7}$ sec at $\theta = 6°$, very different from T_{20}, equal to 7.8×10^{-9} sec for both orientations. The experimental results for sample No. 2 of ruby are fitted by Eq. (5). The values of H_{eff} and T_p are reported in Table I. By comparing the spin-packet width (H_{eff}) with the width of the total line (7.0 G), it comes out that the nature of the line broadening is quite different in the two orientations $\theta = 0°$ and $90°$. At $\theta = 0°$ the line shows an inhomogeneous structure with well-defined spin packets, the width of which ($\lesssim 0.7$ G) is at most $\frac{1}{10}$ of the total linewidth. Further, the local field has a long correlation time $T_p = 4.4 \times 10^{-7}$ sec, suggesting a quasistatic environment around the Cr^{3+} ion. The situation is very different at $\theta = 90°$: the line appears to be almost completely homogeneously broadened and the local field is seen rapidly varying in time ($T_p = 0.42 \times 10^{-7}$ sec).

Cross-relaxation and spin-diffusion effects are typical mechanisms responsible of the broadening of the spin packets of an inhomogeneous line. In dilute ruby cross relaxation involving spatial nuclear-spin diffusion is present in the particular directions in which two absorption lines of the Cr^{3+} have near equal energy.[12-14] On the other hand, cross relaxation within a line, as observed by Atsarkin,[14] is effective when the line is saturated with some deviation from the center in order to drastically perturb the temperature of the SS_e (Cr^{3+} dipole-dipole) reservoir. Such effects cannot be invoked for a full account of our results for a variety of reasons. We observe a broadening of the spin packets near the parallel direction in which cross relaxation between two different transitions is not possible at our frequency. Further, we are operating in conditions in which the saturation of the Cr^{3+} line occurs very close to the center peak. Finally, times required for spatial nuclear-spin diffusion are long compared with the plateau values which we are measuring.[12]

A qualitative account of the observed behavior can be given in the framework of the model developed for the spin-echo modulation effect.[4] Let us look at the Cr^{3+} ion and its 13 neighboring ^{27}Al nuclei. When the magnetic field is directed along the c axis, the ^{27}Al nuclei can be grouped into four sets of three magnetically equivalent nuclei. The remaining nucleus is located along the c axis above the Cr^{3+} ion. The four sets of nuclei precess about a direction close to the c axis, the small angle φ being due to the fact that they also experience, in addition to the H_0 field, the dipolar magnetic field of the Cr^{3+} spin owing to the fact that the field gradient is a little tilted from the c axis.[5] This statement is strictly valid only at high external magnetic fields. However, for our qualitative discussion it can be assumed to be valid also at our fields. The assumption is partially justified by the fact that the Cr^{3+} dipolar field is less effective because of very quick transitions of the Cr^{3+} spin: this point is evident in the ENDOR experiments which we shall discuss later. For each one of these sets of nuclei, the projection of the nuclear magnetic moment $\vec{I}$ over the direction of the electronic magnetic moment $\vec{S}$ is quasistatic, with a small time-dependent component. In this condition, the EPR absorption line of ruby is expectedly inhomogeneously broadened. The spin-packet width is caused by the amplitude of the modulation of the hyperfine field and by the residual Cr^{3+}-Cr^{3+} dipolar interaction. At high input power levels the Cr^{3+}-Cr^{3+} dipolar interaction fades out because of a "stirring effect." However, the microwave field cannot shrink the contribution of the Cr^{3+}-^{27}Al superhyperfine interaction to the spin-packet width below $1/\tau_c$. τ_c is the correlation time of the hyperfine field which is essentially fixed by the Larmor frequencies of the four sets of nuclei and is equal to the plateau value T_p which we observe in Fig. 2. One may wonder that at $\theta = 0°$ we find a spin-packet width less than the theoretical width owing to the Cr^{3+}-Cr^{3+} dipolar interaction. We remember that rough experimental measurements of the spin-packet width of dilute ruby by different authors[15,16] have proved that these calculations overestimate the dipolar contribution.

The situation described above is peculiar to the $\theta = 0°$ orientation. In fact, because of the trigonal crystalline electric field at the Cr^{3+} site, when H_0 is rotated an angle θ from the c direction, the electron-spin precession axis is no longer along H_0.[4] The angle φ, between the precession axes of $\vec{I}$ and $\vec{S}$, increases and the projection of each nuclear spin $\vec{I}$ over the $\vec{S}$ direction has now a greater time-dependent component which causes an increase of the amplitude of modulation of the hyper-

fine field at the Cr^{3+} site. A spectral spin diffusion within the EPR line takes place because of the mixing of adjacent spin packets. On the other hand, when $\theta \neq 0°$, all the 13 neighboring nuclei become magnetically inequivalent and each one contributes with a different frequency to the modulation field, thus shortening the correlation time τ_c of the resultant local field. On increasing θ the plateau value T_p is expected to decrease. We have measured the dependence of T_p on the angle near $\theta = 0°$. The results are reported in Fig. 3. As expected, T_p is maximum at $\theta = 0°$ and rapidly decreases on increasing θ. Calculations show that at $\theta = 90°$ the angle φ is much greater than at $\theta = 0°$. At $\theta = 90°$ orientation the local field at the Cr^{3+} site has a greater time-dependent component with a shorter correlation time, the spectral spin diffusion within the line is expected to be enhanced. Each Cr^{3+} practically experiences many of the possible orientations of the nuclear spins. Therefore, all the Cr^{3+} ions of the ruby crystal tend to be magnetically equivalent and give rise to a homogeneously broadened EPR line.

Our results are consistent with the angular dependence of the spin-echo modulation experiments.[4,5] In fact, in the parallel direction, in which we find a long correlation time and narrow spin packets, a maxium echo signal is observed, the modulation pattern being due to the small time-dependent component of the local field. The disappearing of the spin-echo signal when $\theta \gtrsim 3°$ can be ascribed to the broadening of the spin packets and to the shortening of the correlation time. Similarly, double-resonance experiments require an inhomogeneous EPR line; in dilute ruby ENDOR signals are to be expected only near $\theta = 0°$, as observed by Laurance *et al.*[3]

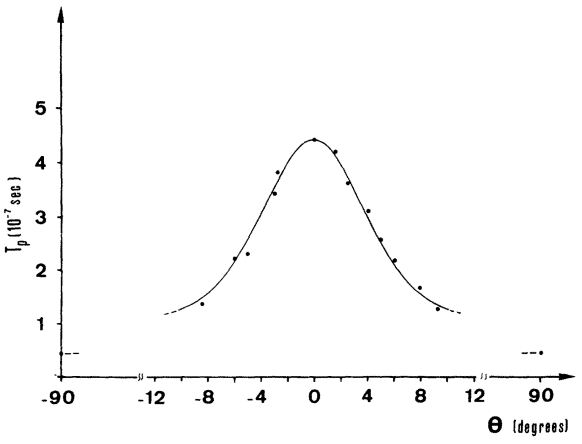

FIG. 3. T_p of dilute ruby, sample No. 2, as a function of θ, the angle between H_0 and c axis, for small θ. Value of T_p at $\theta = 90°$ is also displayed.

We wish to point out that the observed inhomogeneous-homogeneous transition is not peculiar of the $+\frac{1}{2} \rightarrow -\frac{1}{2}$ magnetic resonance, but should be observed also at the higher-field resonances, perhaps in a less pronounced way. On increasing H_0, the precession axes of the electron and nuclear spins both tend to the direction of H_0 even for for $\theta \neq 0°$, the angle φ is expected to decrease. Kopvillem *et al.*[17] have shown that the three-four resonance of Cr^{3+} in a field of 5430 G at $\theta = 90°$ is inhomogeneously broadened, the angle φ being equal to zero at this orientation. Even for the $+\frac{1}{2} \rightarrow -\frac{1}{2}$ magnetic resonance line at higher frequencies (and therefore higher fields H_0) one should expect that the inhomogeneous-homogeneous transition should be less pronounced and eventually disappear. In fact, one can easily show that the angle φ, at a given orientation of H_0 from the c axis, decreases on increasing the external magnetic field.

According to this simple model the modulation of the z component of the local field at the Cr^{3+} site owing to the precession of the nuclear spins about an axis different from $\langle \vec{S} \rangle$ is responsible for the inhomogeneous-homogeneous transition of the EPR absorption line of ruby. Nuclear transitions induced in the nuclear-spin system of ^{27}Al change the z component of the local field. Therefore, one expects that at $\theta = 0°$ externally induced nuclear transitions should make the absorption line of Cr^{3+} more homogeneous, playing the same role as a rotation of H_0 from the c axis.

With the above statement in mind, we have made double-resonance experiments in our dilute ruby, sample No. 2, in which the electron spins are resonating with the strong microwave field near $\omega = \omega_0$ and nuclear transitions in the spin system of ^{27}Al are induced by a cw radio-frequency field. In these experiments the external magnetic field H_0 ($H_0 \approx 1000$ G) was aligned along the c axis and we were measuring T_p at different values of ω_{rf}, the frequency of the rf field. As expected, we found that T_p is strongly dependent on ω_{rf}, it decreases by as much as a factor 5 when the rf field is resonating with one of the ^{27}Al nuclear transitions. A plot of T_p as a function of ω_{rf} shows five groups of resonance lines near the values 0.41, 0.77, 1.13, 1.49, and 1.84 MHz. Each group has a hyperfine structure which we have not yet well resolved and it seems that its resolution depends on the microwave input power.

According to the model discussed above, one should expect to detect the resonance lines of the 13 neighboring ^{27}Al nuclei which strongly interact with the Cr^{3+} ion. Instead, the values of ω_{rf} at which the resonances occur and their separation of 0.36 MHz correspond to the values reported in

literature for distant ^{27}Al nuclei. An accurate check of our experimental procedure will make this point clearer. In the present double-resonance experiments the $+\frac{1}{2} \rightleftharpoons -\frac{1}{2}$ line of Cr^{3+} is heavily saturated very close to the resonance by the strong microwave field, the electron spin turns over very fast so that the dipolar field $\pm\vec{h}_n$ that it produces at the ^{27}Al sites changes within a time which, depending on the microwave power, can be much shorter than $(2\pi/\gamma_n|\vec{H}_0 \pm \vec{h}_n|)$. The nuclear spins cannot follow such field changes, practically they experience only the external field H_0 and therefore the resonance values will be the same as those of distant nuclei as long as the strong microwave field is on. This hypothesis is supported by the fact that in our preliminary results the hyperfine structure in each one of the quadrupole transitions of ^{27}Al seems to be directly dependent on the microwave power, being better resolved at lower microwave power levels.

Finally, we wish to make a few comments about the more concentrated ruby, sample No. 3. Our results show that the EPR absorption line of this sample is inhomogeneously broadened even at $\theta = 90°$, though the spin-packet width ($H_{eff} = 2.8$ G) is an appreciable fraction of the total width (9.5 G). Further, the characteristic plateau is not observed at both orientations $\theta = 0°$ and $\theta = 90°$ in all the range of input power investigated. The lower limit of τ_c, as deduced from the data of Fig. 2(b), should be at least 20×10^{-7} and 10×10^{-7} sec for the parallel and the perpendicular directions, respectively. This suggests that the mechanism which gives rise to the inhomogeneous-homogeneous transition is not only concealed by the Cr^{3+}–Cr^{3+} interaction, but it is by itself less effective in the concentrated samples. We have not yet found a satisfactory explanation of this effect; we suspect that it is related to the rapid decrease of the nuclear spin-lattice relaxation time of ^{27}Al in ruby, which has been observed[18] at the concentration $c = 0.08$ wt% intermediate between the concentrations of our samples No. 2 and No. 3. Further experiments are in progress.

ACKNOWLEDGMENT

The authors wish to thank Professor M. W. P. Strandberg for his continuous interest and helpful stimulating suggestions.

APPENDIX

Let us consider a Gaussian inhomogeneous line, which is the envelope of a continuous distribution of Lorentzian spin packets. From Eqs. (9), (12), and (13) of Ref. 6, by integrating the contributions of the single spin packets, one gets

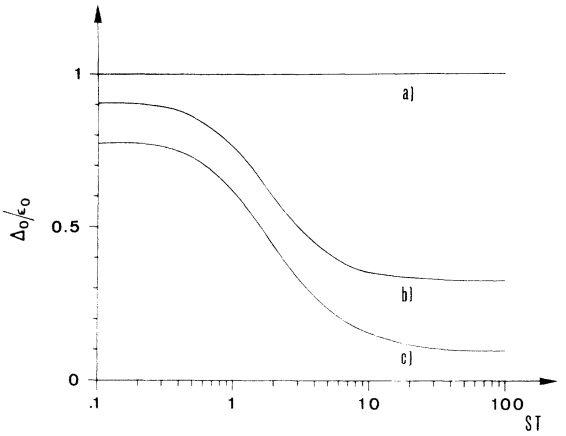

FIG. 4. Δ_0/ϵ_0 as a function of ST; (a) $\epsilon_0 T = 1$; (b) $\epsilon_0 T = 3$, Δ_0/ϵ_0 tends to $(\epsilon_0 T)^{-1} = 0.33$; (c) $\epsilon_0 T = 10$, Δ_0/ϵ_0 tends to $(\epsilon_0 T)^{-1} = 0.1$.

$$\tan\phi = \int_{-\infty}^{+\infty} \exp\left(-\frac{\epsilon^2}{\epsilon_0^2}\right) \frac{d\epsilon}{(\Delta-\epsilon)^2T^2 + S^2T^2 + 1} \Bigg/ \int_{-\infty}^{+\infty} \exp\left(-\frac{\epsilon^2}{\epsilon_0^2}\right) \frac{(\Delta-\epsilon)T\,d\epsilon}{(\Delta-\epsilon)^2T^2 + S^2T^2 + 1}, \quad (6)$$

where ϵ_0 is the half-width of the total line, T^{-1} is the half-width of a single spin packet, both expressed in frequency units, $S = \gamma H_1 (T_1/T)^{1/2}$ is the saturation factor for a spin packet. Equation (6) applies to both the harmonic line resonating at $\omega = \omega_0$ (in this case $S \neq 0$, $\Delta = \omega - \omega_0$) and the harmonic line resonating at $\omega = \frac{1}{2}\omega_0$ with $S = 0$ and $\Delta = 2\omega - \omega_0$. For both the lines the value Δ_0 of Δ at which $\tan\phi = 1$ may be obtained by solving the equation

$$\int_{-\infty}^{+\infty} \exp\left(-\frac{\epsilon^2}{\epsilon_0^2}\right) \frac{d\epsilon}{(\Delta-\epsilon)^2T^2 + S^2T^2 + 1} = \int_{-\infty}^{+\infty} \exp\left(-\frac{\epsilon^2}{\epsilon_0^2}\right) \frac{(\Delta-\epsilon)T\,d\epsilon}{(\Delta-\epsilon)T^2 + S^2T^2 + 1}.$$

Putting

$$t = \epsilon/\epsilon_0, \quad x = \Delta/\epsilon_0, \quad y = (S^2T^2 + 1)^{1/2}/\epsilon_0 T$$

one gets

$$\frac{1}{(S^2T^2+1)^{1/2}} \int_{-\infty}^{+\infty} \frac{y e^{-t^2} dt}{(x-t)^2 + y^2} = \int_{-\infty}^{+\infty} \frac{e^{-t^2}(x-t)\,dt}{(x-t)^2 + y^2}. \quad (7)$$

The integrals involved in Eq. (7), are, respectively, the real part and the imaginary part of the well-known error function $w(z)$ with complex argument. Using the tabulation and the rational approximations of $w(z)$, it is possible to obtain

a plot of Δ_0 as a function of ST, for a given line, i.e., for a given $\epsilon_0 T$. The results, shown in Fig. 4 for $\epsilon_0 T$ equal to 1, 3, and 10, indicate that, depending on the value of the saturation factor S, Δ_0 has a different meaning. When $ST \gg 1$, Δ_0 tends to T^{-1}, i.e., the half-width of the central spin packet; since ST is generally greater than 100 in our measurements on the $\omega = \omega_0$ line, the value of T_{2e} which one gets from Eq. (3) represents the effective transverse relaxation time of a single spin packet. When $S = 0$ (this is the case of the line resonating at $\omega = \frac{1}{2}\omega_0$), $\Delta_0 \simeq \epsilon_0$ and the value of T_{20} which one gets from Eq. (3) is ϵ_0^{-1}, the inverse of the half-width of the total line. Obviously, no stirring effect is taken into account in deriving Eq. (7): since our measurements of T_{2e} are made on the line at $\omega = \omega_0$, where the condition $ST \gg 1$ is amply satisfied, any observed power dependence of T_{2e} has to be ascribed to a stirring effect on the central spin packet.

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[1]W. J. C. Grant and M. W. P. Strandberg, Phys. Rev. A 135, 727 (1964).
[2]R. F. Wenzel, Phys. Rev. B 1, 3109 (1970).
[3]N. Laurance, F. C. McIrvine, and J. Lambe, J. Phys. Chem. Solids 23, 515 (1962).
[4]D. Grischkowsky and S. R. Hartmann, Phys. Rev. Lett. 20, 41 (1968); Phys. Rev. B 2, 60 (1970).
[5]P. F. Liao and S. R. Hartmann, Phys. Rev. B 8, 69 (1973).
[6]R. Boscaino, I. Ciccarello, C. Cusumano, and M. W. P. Strandberg, Phys. Lett. A 33, 10 (1970); Phys. Rev. B 3, 2673 (1971).
[7]R. Boscaino, M. Brai, I. Ciccarello, and M. W. P. Strandberg, Phys. Rev. B 7, 50 (1973).
[8]K. Tomita, Prog. Theor. Phys. 19, 541 (1958).
[9]M. W. P. Strandberg, Phys. Rev. B 6, 747 (1972).
[10]A. G. Redfield, Phys. Rev. 98, 1787 (1955).
[11]J. P. Gayda and C. Blanchard, J. Phys. 30, 827 (1969).
[12]G. R. Khutsishvili, Usp. Fiz. Nauk 87, 211 (1965) [Sov. Phys. Usp. 8, 743 (1966)].
[13]R. L. Kyhl and B. D. Nageswara-Rao, Phys. Rev. 158, 284 (1967).
[14]V. A. Atsarkin, A. E. Mefeod, and M. I. Rodak, Phys. Lett. A 27, 57 (1968); Zh. Eksp. Teor. Fiz. 55, 1671 (1968) [Sov. Phys.—JETP 28, 877 (1969)]; V. A. Atsarkin, Sov. Phys. Solid State 12, 1405 (1970); V. A. Atsarkin and M. I. Rodak, Usp. Fiz. Nauk 107, 1 (1972) [Sov. Phys.—Usp. 15, 251 (1972)].
[15]J. Lambe, N. Laurance, E. C. McIrvine, and R. W. Terhune, Phys. Rev. 122, 1161 (1961).
[16]D. N. Klyshko, Fiz. Tverd. Tela. 5, 2825 (1963) [Sov. Phys.-Solid State 5, 2066 (1964)].
[17]U. K. Kopvillem, B. P. Smoliakov, and R. Z. Sharipov, Fiz. Tverd. Tela. 14, 1444 (1972) [Sov. Phys.-Solid State 14, 1239 (1972)].
[18]H. H. Niebuhr, E. E. Hundt, and E. Brun, Helv. Phys. Acta 43, 777 (1970).