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^{27}Al nuclear-spin dephasing in the ruby frozen core and Cr^{3+} spin-flip-time measurements

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Nuclear-spin-echo decay has been measured in the ^{27}Al frozen core surrounding Cr^{3+} in ruby using optical Raman heterodyne detection. Bloembergen's frozen-core model was directly verified by the observation of ~ 1 -msec dephasing times in the core compared with $60 \mu\text{sec}$ in the bulk. Observation of echoes in the ground and optically excited states of ^{52}Cr and ^{53}Cr allowed separation of direct and indirect Cr^{3+} spin-flip contributions to dephasing and hence measurement of the Cr-Cr spin-flip time. The direct dephasing time follows a square-law dependence on concentration, in accord with theory. Indirect dephasing has a square-root dependence on concentration, similar to that observed for optical echoes. Contrary to earlier studies, it is concluded that optical dephasing in ruby, in the concentration range 0.0034 to 0.05 wt % Cr_2O_3 , is primarily due to magnetic fluctuations produced by Cr^{3+} spin flipping; i.e., that indirect rather than direct dephasing is dominant.

I. INTRODUCTION

Raman heterodyne spectroscopy (RHS) has been demonstrated¹ to be a highly sensitive technique for detection of nuclear magnetic resonance (NMR) of hyperfine (hf) transitions in low-temperature solids. Recently RHS has been extended^{2,3} to superhyperfine (shf) transitions in ruby. In the latter case the radiofrequency (rf) and optical photons interact with different atoms (Al and Cr, respectively), whereas in the former, these photons interact with the same atom. In this paper we demonstrate that the ability to observe NMR spin echoes of coupled atoms allows direct measurement of spin-flipping rates along with new insights into the mechanisms of optical dephasing.

One such capability is to perform, for the first time we believe, a direct measurement of the NMR dephasing time for nuclei in the frozen core. The concept of the frozen core (or diffusion barrier⁴) was introduced by Bloembergen⁵ in 1949. In the case of a B spin undergoing dephasing due to magnetic field fluctuations produced by flipping host-lattice A spins, it is evident that an A spin in the immediate vicinity of the B spin cannot flip-flop with those in the bulk because of detuning resulting from, e.g., exchange and dipolar interactions. The region of detuned spins is called "the frozen core." NMR spectra in the frozen core have been measured in ruby using ENDOR (electron-nuclear double resonance) and PENDOR (photon echo nuclear double resonance) techniques.⁶ As discussed by Mims,⁷ the frozen core leads to a substantial reduction of the effects of flipping host spins on the electron paramagnetic resonance (EPR) dephasing time of impurity atoms. Another example of frozen-core effects is evident for optical transition dephasing.^{8,9} Thus, the R_1 transition (693.4 nm) in ^{3+}Cr in dilute ruby (involving an electronic spin) has a similar dephasing time ($\sim 10 \mu\text{sec}$) (Ref. 9) as does the $^3H_4 \rightarrow ^1D_2$ transition (592.5 nm) of ^{3+}Pr in LaF_3 (Ref. 10) involving only a weaker nuclear spin interaction between Pr-F. The explanation is the same as that outlined by Mims⁷ for EPR, i.e., a large

frozen core forms around the Cr^{3+} electronic spin that suppresses magnetic field fluctuations due to nearby host-lattice spin flips. Since the inverse dephasing time⁷ $T_2^{-1} \sim S(\Delta H_0^2)^{1/2}$ (where S , the magnetic splitting rate, $\equiv \partial\nu/\partial H$, ν is the transition frequency, H is the applied magnetic field, and ΔH_0 is the mean-field fluctuation), the corresponding larger S for electronic spins is balanced by the smaller mean field because of the frozen core. This paper describes measurements that directly verify the frozen-core concept by observations of Al nuclear-spin dephasing in the core and comparison of these times with those in the bulk sapphire lattice.

Some time ago,¹¹ it was concluded that optical dephasing of the R_1 line in ruby was produced by direct Cr-Cr spin flips. This paper sheds new light on this question with the realization that the Al nuclear dephasing in the frozen core gives a lower limit on the ^{3+}Cr spin-flip-flop time (Sec. III B). Finally, we show that the Al nuclear and Cr optical dephasing times, at low-Cr concentrations, are both controlled by fluctuating magnetic fields generated by various nuclear and electron spin flips.

II. EXPERIMENT

Figure 1 shows the experimental setup. The echo generation and detection scheme was similar to that described by Mlynek *et al.*¹ A four-turn Helmholtz coil pair allowed the application of strong (~ 1 G rms) rf magnetic field pulses (15–70 μsec width) oriented perpendicular to the ruby C_3 axis. The rf frequency was adjusted to a ground- or excited-state ^{27}Al NMR resonance in the first shell surrounding ^{3+}Cr , i.e., in the frozen core. In all this work, the $^4A_2(-\frac{3}{2}) \rightarrow \bar{E}(-\frac{1}{2})[R_1(-\frac{3}{2})]$ optical transition (at $14\,418.32 \text{ cm}^{-1}$ for the ^{52}Cr isotope) in ^{3+}Cr was excited with a 50-mW single-frequency laser beam from a Coherent 699-21 ring dye laser. The circularly polarized laser beam was propagated parallel to a magnetic field of ~ 3.7 kG applied precisely ($\pm 0.1^\circ$) along the crystal C_3 axis. The beam diameter in the sample was ~ 1.5 mm. The sample temperature was moni-

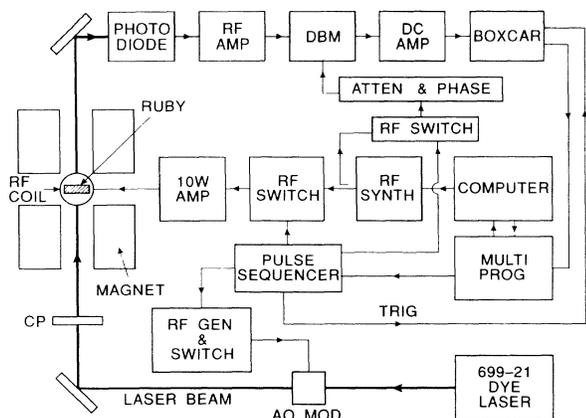


FIG. 1. Schematic of experimental setup used for Raman heterodyne detection of ^{27}Al nuclear-spin echoes in ruby.

tored and maintained by a Lakeshore 93C controller in the range 1.8–2.2 K. The ruby samples ranged in concentration from 0.0034 to 0.1 wt % Cr_2O_3 and were all Czochralski grown.

The coherent optical Raman signal due to an Al nuclear-spin echo was first heterodyned against the excitation laser on the photodiode. The resulting rf signal was then amplified and phase sensitively detected by mixing the signal and rf driving power (with amplitude and phase adjustment) in a double-balanced mixer. Finally, the signal was amplified by a low-noise dc amplifier (Ithaco 1201) and displayed on real-time and averaging oscilloscopes (Fig. 2). The optical pulse sequence, rf pulses, and boxcar trigger were digitally controlled by a computer. The echo signal was measured by a boxcar integrator whose output was digitized and processed giving a plot of the echo amplitude versus rf pulse spacing on the computer graphics screen.

An important feature of the measurement procedure was the gating of the laser relative to the rf pulse sequence. We found that if the laser was left on during the pulse sequence, the observed nuclear dephasing time depended on laser intensity. The reason for this is the interruption of the ^{27}Al nuclear coherence caused by absorp-

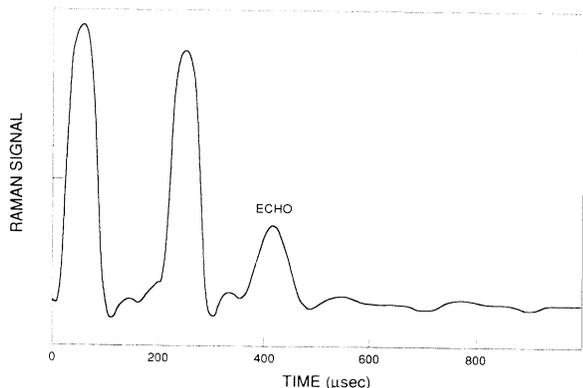


FIG. 2. Averaged echo signal (output from dc amplifier shown in Fig. 1).

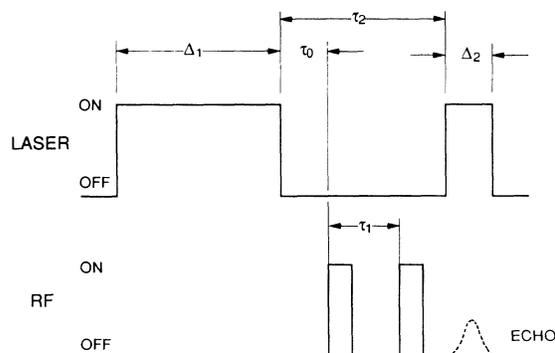


FIG. 3. Laser and rf pulse sequence used in the experiments. Typical pulse values are $\Delta_1=10$ msec, $\tau_0=200$ μsec , and $\Delta_2=40$ μsec .

tion or stimulated emission of optical photons by the ^{3+}Cr . This idea is qualitatively supported by a simple rate equation calculation. The pulsing scheme shown in Fig. 3 avoids these problems and provides large signals at full laser power, however, as will be discussed later, it requires an empirical correction to the dephasing time. Log plots of the echo decays are shown in Fig. 4. The decay curve consists of 100 points which were stored on a floppy disc along with run parameters and later fit to an exponential decay by regression analysis. A pulse repetition rate of 25 Hz with a 1-sec boxcar output time constant and a dwell time of 3 sec gave an average of 75 echo measurements per point.

III. RESULTS

A. Correction time measurements

Referring to the laser and rf pulse sequence shown in Fig. 3, the purpose of the first long laser pulse (width Δ_1) is to create polarized ^{27}Al nuclei in the frozen core of the

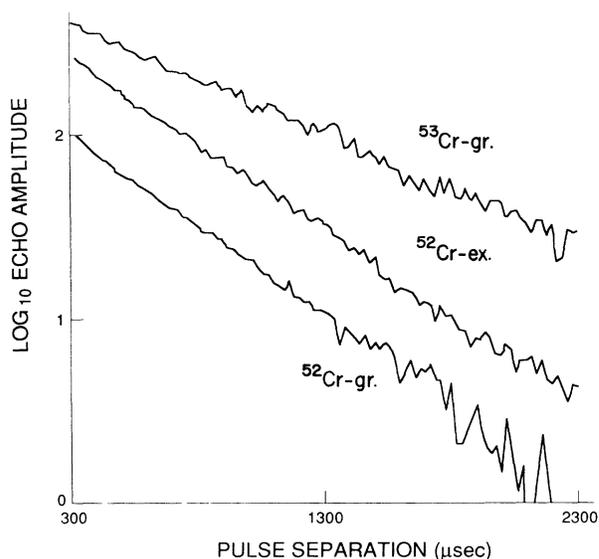


FIG. 4. ^{27}Al nuclear-spin-echo decay associated with ground (gr) and excited (ex) ^{52}Cr and ^{53}Cr ions for 0.0034 wt. % Cr_2O_3 ruby.

ground and excited states of ^{3+}Cr . The details of how this polarization is created and decays remain obscure, however, the effect is probably similar to the dynamic nuclear polarization^{12,13} produced by microwave pumping of EPR transitions. Interestingly, for the ^{53}Cr isotope, echo signals could be seen without a laser polarization pulse (for the most dilute sample).

As mentioned earlier, to avoid laser intensity effects in the echo decay time, the laser was turned off during the rf pulse sequence and then turned on again briefly to allow RHS detection of the echo. It is clear from Fig. 3 that, as the rf pulse separation is varied, the time $\tau_2 + \Delta_2/2$ between the end of the polarizing pulse and the echo will change. Thus, part of the observed echo decay arises from polarization decay. To correct for this, we obtained a correction time T_c by measuring the echo decay for a fixed rf pulse spacing and varying τ_2 . The true nuclear dephasing time T_{2n} is then given by

$$T_{2n}^{-1} = T_{2nm}^{-1} - T_c^{-1}, \quad (1)$$

where T_{2nm} is the measured dephasing time (i.e., twice the observed decay time in Fig. 4). For ^{27}Al dephasing associated with the ^{3+}Cr excited state [$\bar{E}(-\frac{1}{2})$], the correction arises because of population decay determined by the \bar{E} spontaneous emission lifetime of $T_s = 4$ msec. The observed T_c was 2.0 ± 0.2 msec in good agreement with the expected value of $T_s/2$. This follows from the theoretical¹ echo amplitude decay for a pulse spacing t

$$E(t) \propto (n_1 - n_2)(n_1 + n_2) \exp(-2t/T_{2n}), \quad (2)$$

where n_i are nuclear populations present at the echo time $2t$. Since

$$n_i = n_{i0} \exp(-2t/T_s),$$

where n_{i0} is the population at the start of the echo sequence, then

$$E(t) \propto \exp - [(1/T_{2n} + 2/T_s)2t],$$

giving $T_c = T_s/2$.

For ^{27}Al nuclei associated with ground state ^{52}Cr , T_c was measured to be identical to the excited-state value of 2 msec and independent of concentration over the range studied. For the ground state we expect T_c to be determined by the optical branching rates in the six levels of ^{27}Al and the NMR and EPR relaxation times [several seconds¹² and ~ 0.5 sec (Ref. 14), respectively]. The most important factor, however, appears to be the ^{3+}Cr spin-flip-flop time (μsec to msec as discussed later) that serves to quickly thermalize the polarized ^{27}Al .

For ^{27}Al nuclei associated with ground state ^{53}Cr , T_c decays were nonexponential with the fastest value ranging from 9 to 38 msec depending on concentration and the optical polarization pulse length and intensity. This decay was sufficiently long that it did not significantly affect the ^{27}Al dephasing times. As will be discussed later, the long T_c for ^{27}Al near ^{53}Cr (which has a nuclear spin $\frac{3}{2}$, the other isotopes have zero spin) is due to detuning¹⁵ of the ^{52}Cr and ^{53}Cr ground electronic spin levels which results in suppression of electronic spin flipping.

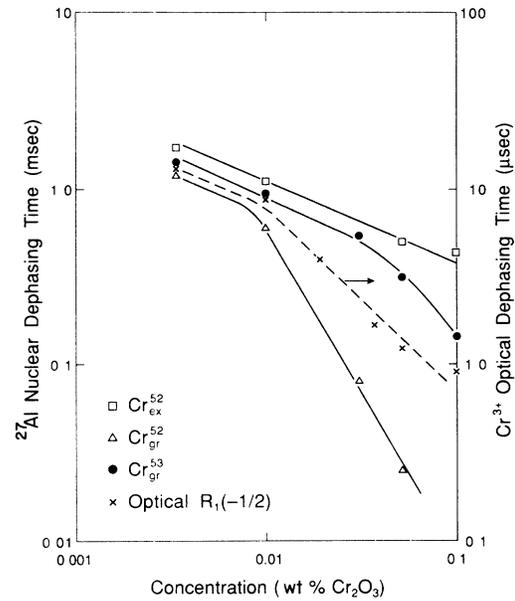


FIG. 5. Measured dependence of ^{27}Al nuclear dephasing time vs $\% \text{Cr}_2\text{O}_3$ concentration for ground (gr) and excited (ex) ^{52}Cr and ^{53}Cr ions. The point for $^{52}\text{Cr}_{\text{gr}}$ at 0.05% is obtained from a linewidth measurement (see text). Also shown is the concentration dependence of optical dephasing time for the $R_1(-\frac{1}{2})$ line for a field of 3.5 kG along the C_3 axis (dashed line).

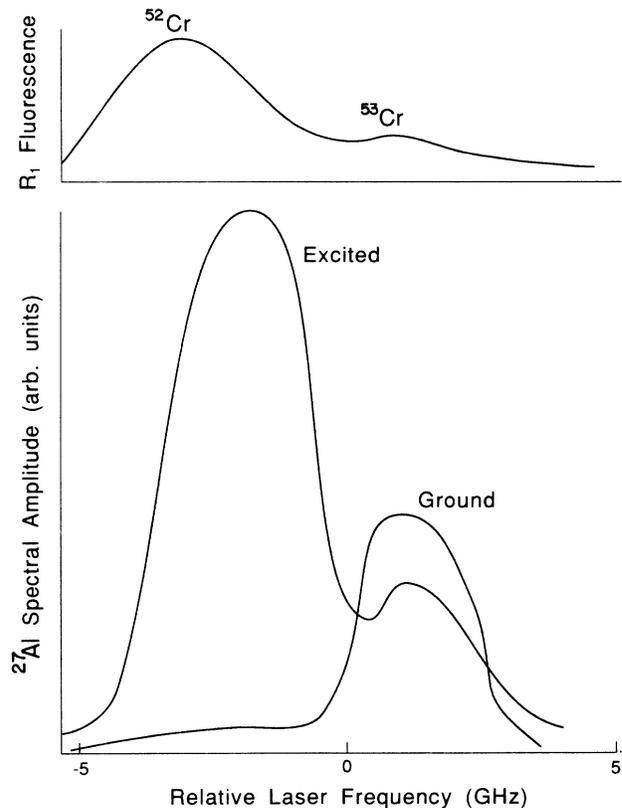


FIG. 6. Dependence of ^{27}Al Raman spectral intensity and R_1 line fluorescence on laser frequency for a 0.03-wt $\% \text{Cr}_2\text{O}_3$ sample. The peak ground-state signal (J line at 7.4 MHz) (Ref. 3) appears at the ^{53}Cr R_1 line which is shifted blue by 3.6 GHz from ^{52}Cr . The excited-state signal (L line at 4.7 MHz) (Ref. 3) peaks near the ^{52}Cr R_1 line.

B. ^{27}Al dephasing times in the frozen core

Figure 5 shows the dependence on concentration of the dephasing time T_{2n} of ^{27}Al nuclei associated with ground-state ^{52}Cr and ^{53}Cr ions and excited-state ^{52}Cr ions. The results for excited-state ^{53}Cr ions were the same as for the ground state (the two highest concentrations were not measured however). The times represent averages of decays taken for various lines³ in the I, J, K, L ^{27}Al sets. We did not exhaustively study all 40 lines,³ however, there was no marked ($< 20\%$) variation of T_{2n} for various lines. For 0.05% ruby, ground-state echoes for ^{27}Al associated with ^{52}Cr could not be observed and a dephasing time was inferred from linewidth measurements discussed in Sec. IV C.

C. Optical spectral dependence of Raman heterodyne signal

Figure 6 shows the optical spectral dependence of the RHS spectra reported earlier.³ The echo intensities follow a similar dependence. Especially noteworthy for this more concentrated sample is that the ^{27}Al NMR signals are $\sim 10\times$ larger for ^{53}Cr than for ^{52}Cr in the ground state (^{53}Cr abundance is 9.65%, ^{52}Cr is 83.8%). It is probable that the ^{27}Al signals reported for the ground state in Ref. 3 are for ^{53}Cr while the excited-state ones are for ^{52}Cr . We also note that the temperature dependence of the spectra reported earlier³ (for 0.05% ruby) becomes less marked for lower concentrations and both ground- and excited-state spectra appear at 2 K.

IV. DISCUSSION

A. Verification of the frozen-core concept

A unique capability of superhyperfine RHS is that it allows NMR echo studies of host (^{27}Al) ions immediately surrounding a paramagnetic (^{3+}Cr) ion in ruby, i.e., in the frozen core as discussed in the Introduction. Earlier ENDOR (Refs. 16 and 17) and PENDOR (Ref. 6) studies have shown that the ^{27}Al ions surrounding ^{3+}Cr in ruby have their NMR frequencies substantially shifted from those in the bulk. Calculations¹⁸ show that the core extends out at least as far as ~ 400 Å for the $S = -\frac{3}{2}$ state of ^{3+}Cr . Since flip-flops are absent in the core, one would expect that the Al dephasing time should be longer in the core than in the bulk. This expectation is indeed verified from the data in Fig. 5 which shows an Al-core dephasing time > 1 msec (for 0.0034% ruby), a value considerably longer than the bulk time¹⁹ of ~ 60 μsec . Thus, the ~ 10 kHz linewidth shown in Fig. 7 is primarily inhomogeneous with a homogeneous width of $1/(\pi T_{2n}) \sim 300$ Hz. The inhomogeneity arises from the slow time varying magnetic field^{8,20} of nearby Cr and Al spins and possibly from static variations in the Al shf parameters^{6,17} (dipolar, exchange, and quadrupole) due to crystal defects. However, theoretical¹⁶ and experimental²¹ studies indicate that dipole interactions account for most of the observed ^{27}Al NMR linewidth (~ 8 kHz) in the bulk. The observation, in this work, of a similar linewidth in the core suggests that dipole interactions also determine this width. Finally, it appears that, even for our most dilute

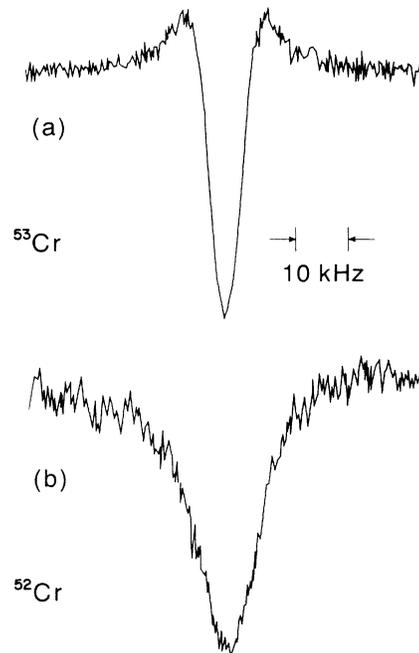


FIG. 7. ^{27}Al NMR line shapes (L line at 6.4 MHz) (Ref. 3) associated with ground-state (a) ^{53}Cr and (b) ^{52}Cr ions for a 0.03-wt % Cr_2O_3 ruby. For the most dilute crystal (0.0034%), ^{27}Al linewidths associated with ^{52}Cr equaled the ^{53}Cr value of 6 kHz shown here.

concentration of 0.0034%, the ^{27}Al dephasing time is still being determined by Cr-Cr spin flips. Presumably, at sufficiently low concentration, the ^{27}Al dephasing time will be determined by Al-Al spin flips outside the core and remaining Cr dephasing processes.

B. Dephasing due to direct and indirect spin flipping

The ^{27}Al dephasing in Fig. 5 shows an interesting variation with concentration. We attempt to analyze these results using a model of host or dopant spin-flip-induced dephasing used previously for nuclear- and electron-spin resonance^{7,22} and optical transitions.^{11,20} In this model, dephasing can occur by a *direct spin flip* between a B atom in a coherent superposition state (henceforth called a “coherent atom”) and other incoherent B atoms. For optical dephasing of the inhomogeneous R_1 line in ruby, this process (in the ground-state 4A_2 spin levels) removes the B atom (Cr) from the coherent system similar to a spontaneous emission event. For the NMR dephasing of Al in the frozen core, a $\text{Cr}(-\frac{3}{2}) \leftrightarrow \text{Cr}(-\frac{1}{2})$, (where the bracketed numbers indicate the electronic-spin state) spin flip, involving a coherent Al attached to the $\text{Cr}(-\frac{3}{2})$, will dephase the NMR coherence because of the large change in NMR frequency that occurs when the Cr changes spin state. For the field used in this work, this change is³ $\Delta f_n \sim 1-3$ MHz when the Cr spin changes from $S = -\frac{3}{2}$ to $-\frac{1}{2}$, an amount well outside the NMR linewidth of ~ 10 kHz. We note that even if the Cr flips back to its original state after a time Δt , the associated Al will be de-

phased by a (random) amount $\Delta f_n \Delta t$. There are, of course, other processes that dephase frozen-core Al nuclei, in particular, *indirect spin flips*, as will be discussed further below. However, an important conclusion is that the observed Al dephasing time gives a lower limit to the Cr-Cr spin-flip time.

Indirect spin flips create a fluctuating magnetic field that produces random frequency shifts and hence dephasing. For Al dephasing in the frozen core there are at least two contributions. One is due to Cr-Cr spin flips involving Cr's not participating in the Raman detection process (because of optical inhomogeneous broadening) or in electronic spin states other than $S = -\frac{3}{2}$. The former will be predominant since the ratio of the R_1 optical inhomogeneous to homogeneous width is $\sim 10^5$. Another source of *indirect spin flip* dephasing of the Al NMR will be Al-Al flips outside the frozen core. This contribution is expected to be small and is apparently not significant in this work since T_{2n} , the nuclear dephasing time, was found to be Cr concentration dependent over the entire range studied.

Consider now the Al dephasing associated with ^{52}Cr in the ground [$(^4A_2(-\frac{3}{2}))$] or optically excited [$(\bar{E}(-\frac{1}{2}))$] state. In the excited state only indirect Cr-Cr and Al-Al spin flipping is important. Direct Cr flips are negligible because the number of Cr in the excited state will be much smaller, because of hole burning, than the ground-state population by about a factor equal to the ratio of optical inhomogeneous to homogeneous widths. Also, we note that the level spacings are different in the ground and excited states, so that excited-state ions cannot flip with those in ground state. These arguments allow a deconvolution of the direct and indirect spin-flip-induced dephasing. Since all decays are exponential, we write for the ^{27}Al dephasing time $T_{2n}(-\frac{3}{2})$ associated with a ground-state $^4A_2(-\frac{3}{2})^{3+}\text{Cr}$ spin,

$$T_{2n}^{-1}(-\frac{3}{2}) = T_D^{-1}(-\frac{3}{2}) + T_I^{-1}(-\frac{3}{2}), \quad (3)$$

where D and I stand for direct and indirect. For the excited state,

$$T_{2n}(-\frac{1}{2}) = T_I(-\frac{1}{2}) \quad (4)$$

since $T_D(-\frac{1}{2})$ is very long. Also, we have $T_I(-\frac{1}{2}) = T_I(-\frac{3}{2})$ since T_I is proportional⁷ to the magnetic splitting rate of ^{27}Al which is independent of the ^{3+}Cr spin state. Finally, we assume (1) that the fluctuating magnetic field generated by Cr-Cr spin flips at a particular ^{3+}Cr site are independent of the spin state of that site and (2) that the field due to Al-Al flips are much smaller than that due to Cr-Cr flips. Equations (3) and (4) then allow calculation of the direct and indirect dephasing times from the observed T_{2n} values in Fig. 5. These times are shown plotted in Fig. 8. We see that the indirect dephasing time varies with concentration c as $c^{1/2}$ while the direct time varies as c^2 . The direct and indirect times are equal for $c \sim 0.01\%$ and for concentrations above this value, ^{27}Al nuclear dephasing is predominantly determined by direct Cr-Cr spin flips. The square-law concentration dependence of $T_D = T_f$ (the Cr-Cr spin-flip

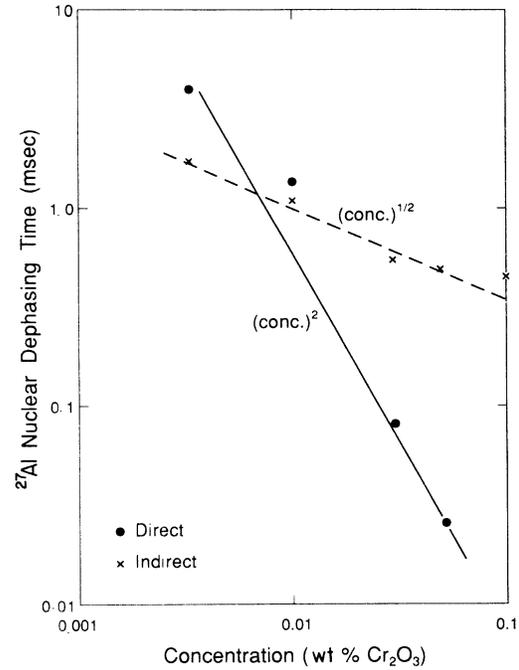


FIG. 8. Deconvoluted (from Fig. 5, see text) direct and indirect spin-induced ^{27}Al NMR dephasing time dependence on $\% \text{Cr}_2\text{O}_3$ concentration. Lines showing a square-law and square-root dependence on concentration are fit to the direct and indirect data points.

time) may be compared with standard theories of spin flipping.^{7,23} For dipolar broadening by randomly positioned like spins in a solid, a statistical theory gives

$$\Delta\omega_{1/2} = 3.8\pi\gamma^2n, \quad (5)$$

where $\Delta\omega_{1/2}$ is the ^{3+}Cr (HWHM) EPR linewidth, $\gamma = g_{11}\beta$, and n is the impurity density. Part of this linewidth is quasistatic (inhomogeneous²⁰ or alternatively called heterogeneous²⁴) and part is dynamic (homogeneous) arising from S^+S^- spin-flip terms in the dipolar interaction Hamiltonian. One-third of $\Delta\omega_{1/2}$ is estimated to be homogeneous,^{7,23} yielding a spin-flip time¹¹ (in sec^{-1})

$$T_f^{-1} = \frac{1}{3}(2\Delta\omega_{1/2}) = 2 \times 10^{10}f, \quad (6)$$

where f is the fraction of ^{3+}Cr in ^{27}Al sites (for $W = \text{wt } \% \text{Cr}_2\text{O}_3$, then $W = 149f$). Equation (6) predicts a spin-flip time much shorter than observed and also a linear dependence on concentration, contrary to experiment. This estimate for T_f is incorrect, however, since it assumes that the only source of broadening is due to Cr-Cr interactions. In fact, the ruby EPR linewidth only varies a small amount (36–40 MHz FWHM) in the concentration range 0–0.05% and is mainly due to Cr-Al superhyperfine interactions.^{25,26} Most of this broadening is inhomogeneous and hence T_f will lengthen because of a decrease of line overlap. For an inhomogeneous half-width $\Delta\omega_{\text{inh}} \gg \Delta\omega_{1/2}$, Mims estimates a flip time (with a numerical error correction here)⁷

$$T_f^{-1} = \Delta\omega_{1/2} \left[\frac{\pi\Delta\omega_{1/2}}{2\Delta\omega_{\text{inh}}} \right], \quad (7)$$

where $\Delta\omega_{\text{inh}}$ is the HWHM ^{3+}Cr EPR linewidth due to the Al-Cr interaction. The physical basis of Eq. (7) is clear, two ^{3+}Cr ions can only flip if they are “dressed” with energetically equivalent Al spin orientations. Equation (7) predicts a square-law dependence for T_f^{-1} on concentration in accord with our observations. Taking $\Delta\omega_{\text{inh}} = (2\pi)18 \times 10^6$ and calculating $\Delta\omega_{1/2} = 1.34 \times 10^6$, we obtain $T_f = 40 \mu\text{sec}$ for 0.0034% ruby which is somewhat faster than the observed value of $\sim 5 \text{ msec}$. If we use, more properly, the homogeneous part of $\Delta\omega_{1/2}$ in Eq. (7), i.e., $\frac{1}{3}\Delta\omega_{1/2}$, then $T_f \sim 0.4 \text{ msec}$. This is still an order of magnitude faster than our observation. A plausible argument is that it is incorrect to assume that all of the homogeneous linewidth, $\frac{1}{3}\Delta\omega_{1/2}$, is due to direct spin flipping, part of it is certainly due to indirect flips. To agree with experiment, the direct-spin flipping part should be $\sim \frac{1}{3}$ of the total homogeneous width. Thus, the spin-flip time is determined by $\sim \frac{1}{9}$ of the dipolar width in agreement with the $\frac{1}{10}$ factor estimated by Bloembergen⁵ and used in the Monte Carlo dephasing calculations of DeVoe *et al.*²⁰

The $c^{1/2}$ variation of nuclear dephasing time is not explained by theory. A basic difficulty is that all theories predict a nonexponential decay contrary to experiment. For an echo intensity decay $I(t) \propto \exp(-kt)^n$, the various theories gave $n = \frac{1}{2}, \frac{3}{2}, 2$, or 3 depending on how the dipolar-induced frequency fluctuations are modeled. We refer to the excellent article by Mims⁷ for a discussion of these theories. It is interesting to note that a square-root dependence on concentration has also been observed²⁷ for photon echo dephasing times in ruby suggesting a connection between nuclear and optical dephasing as will be discussed later.

C. Comparison with other work on Cr-Cr spin-flip times

The subject of spin-flip time arises in many contexts, e.g., calculation of photon echo²² and optical free-

induction decay,^{20,22} optical hole-burning experiments,^{28,29} as well as in EPR studies³⁰⁻³³ which refer to the process as “resonant cross relaxation” (RCR). While harmonic cross-relaxation times involving multiple spin flips have been measured in detail (e.g., in ruby³⁴), direct RCR measurements have remained experimentally elusive because of the resonant nature of the process.

A unique aspect of RHS shf nuclear echoes is that we now have a sensitive probe for detection of spin flipping of the coupled ^{3+}Cr ion. Apart from the interpretation given in the previous section, we may firmly conclude that the Cr-Cr spin-flip time cannot be shorter than the observed ^{27}Al dephasing time. It is of interest to compare our spin-flip data with those estimated using other techniques as shown in Table I. The comparison is for $\sim 0.05\%$ concentration, a popular value because of its use in maser and laser devices. Unfortunately for this concentration, we were unable to see echoes and we estimated the spin-flip time from the increase in NMR linewidth from 6 to 15 kHz as the ^{3+}Cr concentration is increased from 0.0034 to 0.05% (Fig. 7). A Voigt deconvolution procedure was used taking a 6-kHz Gaussian shape [due to ^{27}Al interaction broadening—the calculated value is 6.6 kHz (Ref. 16)] broadened by a Lorentzian contribution $\Delta\nu_L$ (due to lifetime broadening by Cr-Cr flips) to a total width of 15 kHz and setting $\Delta\nu_L = 1/(\pi T_f)$.

We note good agreement between this work and most other data taken at high fields. The faster cross relaxation at low fields (Ref. 29 is an exception, however) is consistent with the known²⁷ decrease in optical dephasing time with decreasing field. This decrease may be due to an increase in the ^{3+}Cr spin-flip rate because of the smaller shf splitting and corresponding ease in conserving energy in a Cr-Cr flip. Earlier studies in this laboratory (Table I, Ref. 36), however, disagree with the current work. This disagreement is ultimately due to the fact that our current conclusion that optical dephasing of 0.05% ruby is mainly due to indirect spin flipping is inconsistent with the observed³⁶ ratio of dephasing times for the $R_1(-\frac{1}{2})$ and $R_1(-\frac{3}{2})$ transitions,

$$T_{2o}(-\frac{1}{2})/T_{2o}(-\frac{3}{2}) = 1.23 \mu\text{sec}/0.45 \mu\text{sec} = 2.73.$$

TABLE I. Summary of Cr-Cr spin-flip times in the ground state of ruby obtained in this work and elsewhere using other techniques.

Conc. Cr_2O_3 (wt %)	Cr-Cr spin-flip time	Field (kG)	Angle (deg)	Technique
0.05	25 μsec	3.5	0	This work
0.068	10	2.1	0	Susceptibility ^a
0.05	30–50	3.3	0	EPR ^b
0.05	20–30	0.35	0	Optical hole recovery ^c
0.05	10	3.0	0	Optical hole recovery ^c
0.052	~ 1	1.3	25.5	Susceptibility ^d
0.073	1	0.2	0	Perturbed photon echo ^e
0.068	< 5	0		Susceptibility ^a
0.05	2–4	3.0	0	Photon echo ^f

^aReference 32.

^bReference 31.

^cReference 29.

^dReference 33.

^eReference 35.

^fReference 36.

For indirect decay this ratio should be equal to the ratio of $R_1(-\frac{3}{2})$ to $R_1(-\frac{1}{2})$ magnetic splitting rates,⁹ i.e., 7.6. A possible explanation for this disagreement is that the field fluctuations due to spin flipping are not the same at spin $-\frac{1}{2}$ and $-\frac{3}{2}$ ³⁺Cr sites, i.e., that spin correlations exist. This could be a consequence of the fact that the ²⁷Al frozen core surrounding a ³⁺Cr is larger at spin $-\frac{3}{2}$ sites than at $-\frac{1}{2}$ sites.^{7,9} This would tend to inhibit $\pm\frac{3}{2} \leftrightarrow \pm\frac{1}{2}$ spin flips compared to $\pm\frac{1}{2} \leftrightarrow \pm\frac{1}{2}$ flips. Since a $\pm\frac{3}{2}$ spin would have a tendency to have close to it a $\mp\frac{3}{2}$ spin (to preserve local magnetic neutrality), then it follows that the magnetic field fluctuation would be slower for $\pm\frac{3}{2}$ spins than for $\pm\frac{1}{2}$ spins. This would tend to push $T_{2o}(-\frac{1}{2})/T_{2o}(-\frac{3}{2})$ to smaller values consistent with experiment.

D. ⁵³Cr results

Figure 5 shows that the dephasing time of ²⁷Al nuclei near ground state ⁵³Cr has a square-root dependence on a concentration over most of the range studied similar to the excited-state ⁵²Cr results. This indicates that the (ground-state) spin-flip time T_f for ⁵³Cr \leftrightarrow ⁵³Cr and ⁵³Cr \leftrightarrow ⁵²Cr is much longer than for ⁵²Cr \leftrightarrow ⁵²Cr. The ⁵³Cr \leftrightarrow ⁵³Cr flip time is longer because of the relative isotope populations which lengthen T_f by ~ 100 (assuming a square-law dependence for T_f as established earlier). The ⁵³Cr \leftrightarrow ⁵²Cr flip time is longer essentially because ⁵³Cr has a nuclear spin $I = \frac{3}{2}$. This splits the electronic spin levels into four levels as described by the Hamiltonian¹⁵

$$H_n = A_{\parallel} I_z S_z + A_{\perp} (I_x S_x + I_y S_y), \quad (8)$$

where $A_{\parallel} = A = 50.4$ MHz for the ground state and < 6 MHz for the excited state. Thus, the EPR lines of ⁵³Cr are detuned from ⁵²Cr by $\pm A/2(m_I = \pm\frac{1}{2})$ and $\pm 3A/2(m_I = \pm\frac{3}{2})$ resulting in a longer flip time. T_f varies with line overlap as³⁰

$$T_f^{-1} \propto \exp - \left[2 \ln 2 \left[\frac{\nu_1 - \nu_2}{\Delta\nu} \right]^2 \right], \quad (9)$$

where $\Delta\nu$ is the FWHM EPR linewidth (Gaussian line shape assumed) and $\nu_1 - \nu_2$ is the line separation. For electronic spin flipping between ⁵²Cr and the $m_I = \pm\frac{1}{2}$ lines of ⁵³Cr [⁵²Cr($m_s = -\frac{3}{2} \leftrightarrow -\frac{1}{2}$) and ⁵³Cr($m_s = -\frac{1}{2} \leftrightarrow -\frac{3}{2}, m_I = \pm\frac{1}{2}$)], T_f is lengthened by a factor 2 and by a factor 600 for $m_I = \pm\frac{3}{2}$, assuming $\Delta\nu = 36$ MHz. Thus, it appears that the echoes observed at higher concentration arise from ²⁷Al associated with $m_I = \pm\frac{3}{2}$ ⁵³Cr ions.

Finally, the effect of the slower spin-flip rate for ⁵³Cr on the optically induced nuclear polarization is clearly evident in Fig. 6. Although ⁵³Cr is $\sim 10\times$ less abundant than ⁵²Cr, the ⁵³Cr Raman NMR signal is $\sim 10\times$ larger than for ⁵²Cr (0.03% ruby). For 0.1% ruby, the latter ratio is much larger and the ⁵²Cr signal is completely swamped by the tail of the ⁵³Cr signal.

E. Relation between Al nuclear and Cr optical dephasing times

Figure 5 shows the concentration dependence of the optical dephasing time T_{2o} of the $R_1(-\frac{1}{2})$ transition obtained from measurements in our laboratory and elsewhere.²⁷ It is clear that both optical and nuclear dephasing times are still controlled by Cr concentration effects even for our most dilute sample of 0.0034 wt% Cr₂O₃. While earlier we concluded that the Al nuclear dephasing time T_{2n} was determined by direct Cr spin flips for concentrations $> 0.01\%$, we conclude from Fig. 5 that T_{2o} is determined by indirect spin flipping for concentrations as high as 0.05%. This conclusion is based on the fact that $T_{2o} \sim 1$ μ sec for 0.05% ruby³⁶ compared with the spin-flip time $T_f \sim 25$ μ sec and disagrees with Compaan's¹¹ conclusion that optical dephasing is caused primarily by direct Cr spin flips.

For the most dilute crystal, if the Al nuclear and Cr optical dephasing are due to a common fluctuating magnetic field (a reasonable assumption since they are adjacent) produced by flipping Cr spins, then the two dephasing times should be related⁷ by their magnetic splitting rates S . For the $R_1(-\frac{1}{2})$ optical transition $S_o = (g_e - g_g)\beta_e/2$, while for the nuclear transition $S_n = g_n\beta_n$, where for Cr, $g_e = 2.445$, $g_g = 1.984$, and $\beta_e = 1400$ kHz/G and for Al, $g_n\beta_n = 1.1$ kHz/G. The ratio of these splitting factors is $S_o/S_e = 290$ compared with the observed⁹ dephasing times ratio

$$T_{2n}/T_{2o} = (1.2 \times 10^{-3}) / (1 \times 10^{-5}) = 120.$$

We believe that this approximate correspondence provides support for the indirect spin-flipping model. However, additional complexities need to be considered, in particular, Al-Al spin flips, frozen-core effects, and possible spin correlations as discussed earlier.

V. CONCLUSIONS

Raman heterodyne NMR echoes of superhyperfine spectra allows measurement of the spin-flip time of the coupled ion. Bloembergen's frozen-core model was directly verified by observation of dephasing times in the core. Optical dephasing ion ruby in the concentration range 0.0034–0.05 wt% Cr₂O₃ is due to indirect ³⁺Cr spin flipping. ²⁷Al nuclear and ³⁺Cr optical dephasing times are approximately related by the magnetic splitting rates of the transitions. The deviation suggests the presence of spin correlations for which different ³⁺Cr spin states see different magnetic fluctuations.

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