Effect of Al^{27} on Electron Cross Relaxation in Ruby*

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Nonexponential electron-spin cross relaxation in dilute ruby provides a measure of the coupling between the Cr^{3+} electron dipole–dipole reservoir and the aluminum nuclear Zeeman reservoir. The electron dipole–dipole reservoir is more closely coupled to the nuclei than to the remainder of the electron-spin system. A relation is obtained between electron spin-lattice relaxation and nuclear spin-lattice relaxation in ruby.

THE customary discussion of spin cross relaxation sets up rate equations for the populations of the spin energy levels of the general form, for example,

$$dn_i/dt=\sum W_{ij}(n_in_k-n_jn_l), \qquad (1)$$

in terms of transition probabilities W_{ij} for the mechanisms involved. In the high-temperature approximation $kT\gg h\nu_{ij}$, the equations are linear and the solutions give linear combinations of exponentials for the decay curves. Many measurements of the corresponding time constants T_{12} have been reported, especially for ruby, and theoretical analyses have been made predicting the behavior of T_{12} as a function of the energy discrepancy ΔE which represents the departure from exact integral relationships among the transition frequencies.[1–4] It was therefore somewhat surprising when, in some circumstances, our measurements of the electron cross relaxation in dilute ruby showed a large deviation from exponential decay, and it was also surprising that there was very little published comment on this result.

Specifically, the time dependence of the transient susceptibility for two-quantum cross relaxation with ΔE greater than the paramagnetic resonance linewidth was observed to be of the form

$$\Delta\chi''\sim t^{-1/2}, \qquad (2)$$

where t is time, while three-quantum cross relaxation showed normal exponential behavior. This paper reports on the measurements and shows that the results are consistent with cross-relaxation theories if one includes energy transfer between the electron spins and the Al^{27} nuclear Zeeman reservoir by a mechanism closely related to dynamic polarization. The discussion also clarifies some results of earlier paramagnetic-resonance experiments on ruby, and provides a relationship between nuclear and electron spin-lattice relaxation.

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[1] N. Bloembergen, S. Shapiro, P. S. Pershan, and J. O. Artman, Phys. Rev. **114**, 445 (1959).
[2] M. Hirono, J. Phys. Soc. Japan **16**, 766 (1961); **17**, 788 (1962).
[3] W. J. C. Grant, J. Phys. Chem. Solids **25**, 751 (1964).
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EXPERIMENT

Figure 1 shows the familiar energy-level diagram of the ground-state configuration of Cr^{3+} in Al_2O_3 with a typical two-quantum and a three-quantum cross-relaxation process. The pulse-saturation and recovery method was used to observe the cross-relaxation decay. All measurements were made at 4.2°K and at 9 GHz. The saturating pulses were $\frac{1}{2}$ μsec long and were also at 9 GHz. A broadband TR cavity isolated the detector from the pulses. The observing EPR

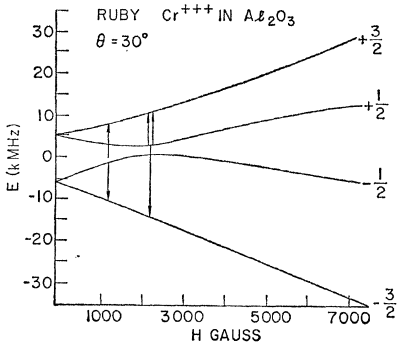

FIG. 1. Ruby ground-state Zeeman levels and cross-relaxation transitions.

spectrometer used heterodyne detection with an i.f. bandwidth≈3 MHz and also incorporated an electronic Smith Chart plotter. This feature permitted the display of complex susceptibility on an oscilloscope. Of course, reflection coefficient is not strictly proportional to susceptibility, but in our experiments the change in reflection coefficient was small and closely approximated the change in susceptibility. Smith Chart corrections were made in some cases.[5]

By proper selection of magnetic field and of ruby crystal orientation in the field, it was possible to observe approximately 7 two-quantum and 9 three-quantum cross-relaxation processes. Figure 2 shows typical oscilloscope traces of a two-quantum and a three-quantum cross relaxation. Figures 3 and 4 show the corresponding log–log plots of $d\chi''/dt$ versus t. The slope $d\chi''/dt$ was read directly from the photographs with a protractor. This proved to be the most useful way of analyzing the data.

[5] M. W. P. Strandberg, Proc. IRE **48**, 1307 (1960).

Figure 4 (three-quantum cross relaxation) shows three well-resolved processes. The fastest, in the microsecond range, is spectral spin diffusion. This is confirmed by the Smith Chart display of χ' and χ''. When the saturating pulse is detuned to "burn a hole" in one side of the paramagnetic resonance, the appropriate χ' behavior is observed. The exact time dependence of the spin diffusion is not important, only the fact that it is fast. The intermediate process is cross relaxation, and in the case illustrated, in a 0.05% ruby, $T_{12}=3$ msec. The slowest rate is spin-lattice relaxation, and we have at 4.2°K a value $T_1=125$ msec. These results are not unusual.

Figure 3 (two-quantum cross relaxation) again shows the spin-lattice relaxation, and the spin diffusion could be seen on the Smith Chart display. In contrast, the cross relaxation shows no time constant, but a long

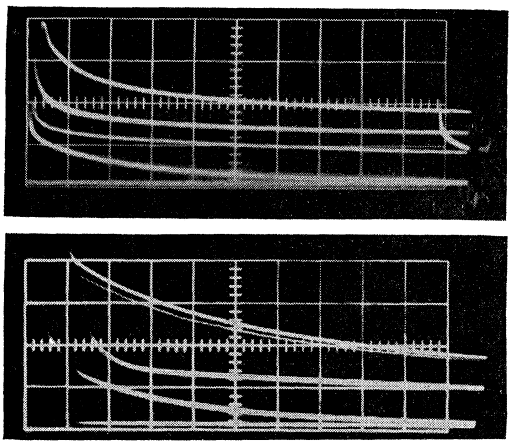

FIG. 2. (a) Two-spin cross relaxation. Sweep speeds: 50 μsec/cm, 500 μsec/cm, 5 msec/cm, 50 msec/cm. $H=3291$ G, $\theta=66°$. (b) Three-spin cross relaxation. The 50-μsec/cm sweep is omitted. $H=3145$ G, $\theta=33°$.

tail, and follows a power law with time as reported in Eq. (2). In the example shown the two transitions involved were detuned by approximately two linewidths. (When the transition frequencies were identical, good two-quantum cross-relaxation measurements could not be obtained. In order to avoid saturating both transitions at once, it was necessary to apply the saturating pulse across a transition to the fourth energy level. The cross relaxation was then very rapid and occurred in part during the saturating pulse.)

Some of the cross-relaxation orientations and magnetic fields were measured in detail. Figure 5 shows some of the three-quantum results for three different Cr^{3+} concentrations. The concentrations are from the manufacturers's specifications (the 0.1 and 0.02% from Adolf Meller Company, the 0.05% from Linde Company). All were laser-quality rubies.

Much of the early work on ruby cross relaxation was done before the development of laser-quality rubies. The early rubies had inhomogeneous broadening

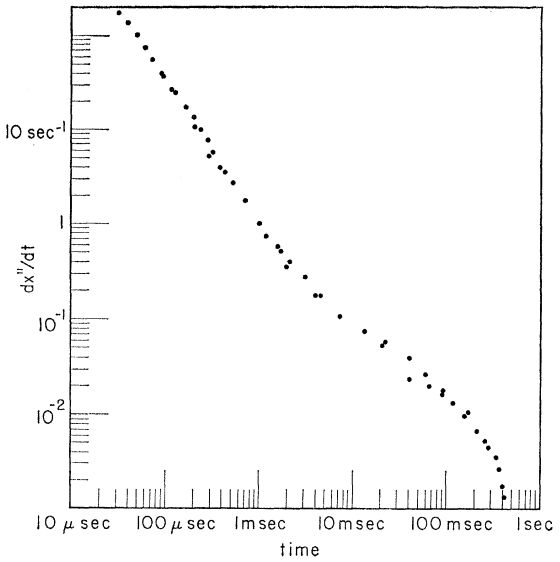

FIG. 3. Spin relaxation at 1:1 cross-relaxation orientation.

resulting from c-axis wander which could have masked the nonexponential nature of two-quantum cross relaxation. With the Smith Chart display, inhomogeneous broadening effects are clearly recognizable.

DISCUSSION

Anderson and Hartmann,[6] Provotoroff,[7] Philippot,[8] and Jeener *et al.*[9] show that one must specify the

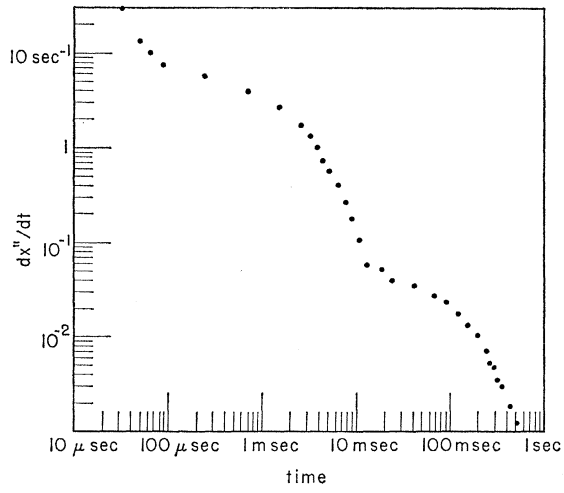

FIG. 4. Spin relaxation near 2:1 cross-relaxation orientation.

[6] A. G. Anderson and S. R. Hartmann, in *Magnetic and Electric Resonance and Relaxation*, edited by J. Smidt (North-Holland Publishing Company, Amsterdam, 1963); A. G. Anderson and S. R. Hartmann, Phys. Rev. **128**, 2023 (1962).
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[8] J. Philippot, Phys. Rev. **133**, A471 (1964).
[9] J. Jeener, H. Eisendrath, and R. Van Steenwinkel, Phys. Rev. **133**, A478 (1964).

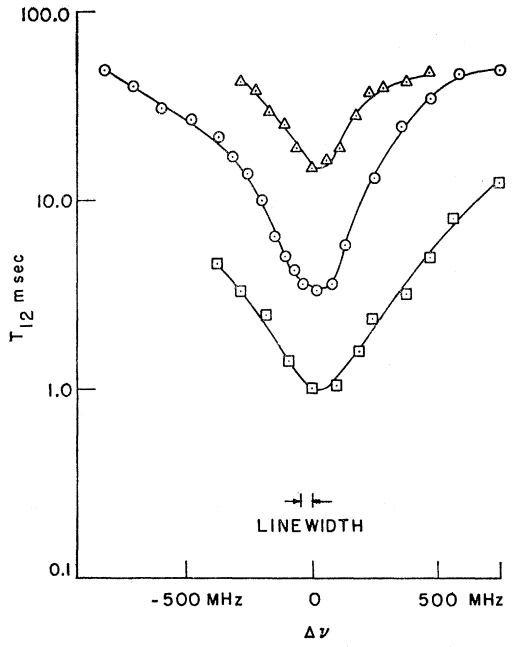


FIG. 5. 2:1 cross relaxation versus detuning at concentrations of 0.02, 0.05, and 0.1%. $H=3150$ G, $\theta=33°$.

populations of the several levels and a dipole–dipole temperature in order to describe adequately the state of a spin system for cross-relaxation analysis. Since spectral spin diffusion is observed to be fast in pink ruby ($\sim 10^{-6}$ sec), a dipole–dipole temperature is rapidly established, and it is not necessary to consider hole-burning phenomena.

We follow the thermodynamic argument of Philippot and Jeener. Under the two-quantum cross-relaxation constraint

$$\Delta n_1=\Delta n_3=-\tfrac{1}{2}\Delta n_2, \tag{3}$$

the maximum entropy of the electron Zeeman subsystem occurs when

$$n_1/n_2=n_2/n_3. \tag{4}$$

Since $\nu_{12}\cong\nu_{23}$, this corresponds approximately to a common Zeeman-spin temperature.

For the electron dipole-dipole subsystem at 4.2°K, the entropy is near its maximum value ($T\cong\infty$). When the ruby orientation and field are adjusted for the linewidth $\Delta\nu\gg|\nu_{12}-\nu_{23}|$, so that the energy discrepancy ΔE to be taken up by the dipole reservoir is small, there is little change in dipole–dipole entropy and the system will cross relax to a common Zeeman-spin temperature (which need not be the same as the dipole–dipole temperature). When $|\nu_{12}-\nu_{23}|>\Delta\nu$, the energy transfer to or from the dipole–dipole reservoir causes a drop in dipole–dipole entropy corresponding to a low (positive or negative) dipole–dipole temperature. An equilibrium results[9] when the sum of the entropies is maximum. The cross relaxation is arrested before a common Zeeman temperature is established. When $|\nu_{12}-\nu_{23}|\gg\Delta\nu$, little cross relaxation can take place. In ruby this equilibrium would be permanent [with spin-lattice coupling or higher-order processes violating (3) neglected], except for the thermal contact between the dipole–dipole reservoir and the much larger Al^{27} nuclear Zeeman reservoir. The Al^{27} NMR frequency ($\sim$3 MHz) is lower than the Cr^{3+} paramagnetic resonance linewidth, so that the frequency spectrum of the dipole–dipole reservoir induces nuclear transitions. The dipole–dipole temperature is restored to approximately its original value (when the Al^{27} reservoir was initially at 4.2°K) and the cross relaxation goes to completion. The cross-relaxation rate is thus determined by the heat flow between the nuclear and dipole reservoirs. Since there is a wide variation in coupling between the Cr spins and different parts of the Al^{27} reservoir, the observed decay is no longer exponential. The $t^{-1/2}$ law is consistent with nuclear spin diffusion between the portion of the nuclei most strongly coupled to the Cr^{3+} and the remainder of the nuclei.[10]

For three-quantum cross relaxation, the constraint is, for example,

$$\Delta n_1=\tfrac{1}{2}\Delta n_3=-\tfrac{1}{3}\Delta n_2. \tag{5}$$

In other respects the previous remarks apply. Since the three-quantum cross relaxation is a higher-order process, however, it is slower than the heat transfer with the Al^{27} nuclei. The electron dipole–dipole temperature remains approximately constant, and the observed decay is exponential.

The general coupling scheme is diagrammed in Fig. 6. The nuclear dipole–dipole reservoir is very small and is not shown.

In ruby there is a large Cr^{3+} exchange interaction. Of course, nearest-neighbor exchange pairs have an entirely different frequency spectrum and, presumably, do not take part in the processes under consideration. Distant exchange can probably be lumped with the dipole–dipole interaction as a source of line broadening

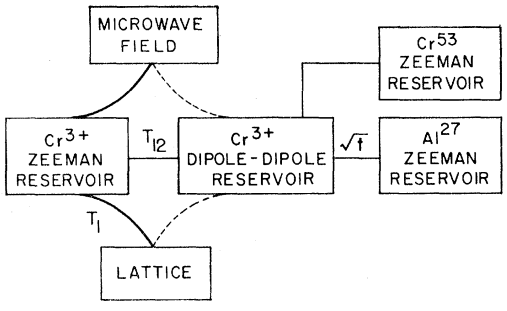


FIG. 6. Electron and nuclear spin-coupling scheme in dilute ruby.

[10] A. Abragam, *Principles of Nuclear Magnetism* (Oxford University Press, London, 1961), p. 380.

and as a contribution to the dipole–dipole thermal reservoir. Rodak[11] also concluded that another thermal reservoir was necessary, but suggested that electron exchange takes up the extra energy. Such a hypothesis is not necessary for dilute ruby, since there is ample evidence for the role of the Al^{27} reservoir.

Finally, we observe that the electromagnetic-field perturbation and the lattice perturbation couple the electron Zeeman and electron dipole reservoirs together, although in different ways. A monochromatic microwave field can give rise to dynamic polarization. The lattice vibrations, on the other hand, have a broad spectrum and will bring both the electron Zeeman and the electron dipole–dipole reservoirs to lattice temperature. A simple qualitative argument suggests that the spin-lattice mechanisms will primarily cause electron spin flips between Zeeman levels, but at the same time they must destroy coherence in the dipole–dipole system at substantially the same rate. If there were no nuclear reservoirs, one would expect the same order of T_1 for both reservoirs. The presence of the Al^{27} reservoir will change the relaxation time of the combined electron dipole–dipole and nuclear Zeeman system by the ratio of the thermal capacity of the Al^{27} reservoir to that of the electrons; that is,

$$\frac{T_1(\text{nuclear})}{T_1(\text{electron})} = \frac{\text{thermal capacity } Al^{27}}{\text{thermal capacity electron dipole–dipole}} \cong \frac{\frac{1}{3}I(I+1)(h\nu_{\text{nucl}})^2N}{\frac{1}{8}(h\Delta\nu_{\text{elec}})^2n}. \quad (6)$$

For 0.05% ruby at 4.2°K and $H_0=3000$ G, $N/n=2000$, $\nu_{\text{nucl}}\cong 3$ MHz, $\Delta\nu_{\text{elec}}\cong 60$ MHz, $T_1(\text{electron})\cong 125$ msec, and $T_1(\text{nuclear})\cong 10$ sec, which gives good qualitative agreement, in correspondence with the belief that nuclear spin-lattice relaxation is primarily via the paramagnetic electrons.

APPLICATION TO PREVIOUS EXPERIMENTS

The concept of an independent electron dipole–dipole temperature in closer contact with the nuclear spins than with the rest of the electron-spin system adds clarity to the interpretation of a number of previous experiments on ruby.

Experiment of Cowen, Schafer, and Spence

As early as 1959, Cowen, Schafer, and Spence[12] observed dynamic nuclear polarization in ruby when the electron-spin resonance was saturated by a detuned microwave signal. Since hyperfine structure is not resolved, the process is appropriately discussed[9] in terms of the electron dipole–dipole temperature. Cowen *et al.* reported a time constant for generation of the enhanced NMR signal from a fraction of a second to a few seconds. We believe this time constant represents energy transfer from the electron dipole–dipole reservoir to the nuclear Zeeman reservoir. Equilibrium between the electron dipole–dipole reservoir and the electron Zeeman reservoir under the influence of the applied rf field would be established in a much shorter time. In our cross-relaxation experiments we observe primarily the coupling to those Al^{27} nuclei that are nearer to the Cr^{3+} ions, so that our faster coupling is to be expected.

Experiments of Armstrong and Szabo

The experiments of Armstrong and Szabo[13] were essentially the same as those reported in this paper. They did not report the nonexponential behavior of the two-quantum cross relaxation. They did observe time constants as long as 10 sec, and they correctly interpreted this as indicating an influence of nuclear spins on the electron-relaxation phenomena. Since the independent role played by dipole–dipole temperature had not been emphasized at that time, they did not give a description of the interaction mechanism.

Experiments of Lambe and Co-Workers

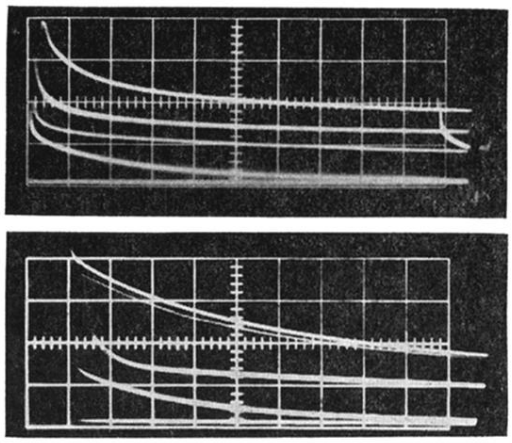
In reporting "distant ENDOR" in ruby, Lambe *et al.*[14] correctly ascribe the interaction to dynamic polarization. They also saw that the Cr^{53} nuclei showed the same relaxation time as the Al^{27}, but the mechanism of coupling between the two kinds of nuclei was not clear because the NMR frequencies were entirely different. It is evident now that the coupling is by means of the electron dipole–dipole reservoir which is more closely coupled to both nuclear species than they are to each other.

Experiments of Yoshioka

Yoshioka[15] observed the interaction between nuclear spins and electron cross relaxation in ruby in a purely nuclear experiment. While making nuclear double-resonance experiments in ruby he observed a drop in Al^{27} spin-lattice relaxation time from 80 to 55 sec when the Cr^{3+} electronic levels satisfied the cross-relaxation condition. He correctly concludes that the mechanism of coupling between the Cr^{53} and Al^{27} is by means of the electron spins.

We would interpret the drop in nuclear T_1 as the result of providing an additional path (see Fig. 6) from the nuclear spins to the lattice through the electron Zeeman reservoir. From our discussion of cross relaxation, we would expect this path to be effective when the cross relaxation is slightly detuned, and to vanish for exact cross-relaxation conditions. Yoshioka's published data do not exclude this possibility.

[11] I. D. Mash and M. I. Rodak, Fiz. Tverd. Tela **7**, 717 (1965) [English transl.: Soviet Phys.—Solid State **7**, 576 (1965)].
[12] J. A. Cowen, W. R. Schafer, and R. D. Spence, Phys. Rev. Letters **3**, 13 (1959).
[13] R. A. Armstrong and A. Szabo, Can. J. Phys. **38**, 1304 (1960).
[14] J. Lambe, N. Laurance, E. C. McIrvine, and R. W. Terhune, Phys. Rev. **122**, 1161 (1961).
[15] H. Yoshioka, J. Phys. Soc. Japan **20**, 623 (1965).



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