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$$\frac{1}{T_{mm}} \cong \frac{\zeta(3/2)}{2}\left(\frac{g\mu_B}{M_s}\right)^2\left(\frac{k_BT}{4\pi D}\right)^{5/2}\frac{Dk^3}{\hbar},$$

which $\approx 5\times 10^3$ sec^{-1} for YIG at 5°K, taking $k \approx 2\times 10^6$ cm^{-1} as a typical magnon produced in the process leading to Eq. (3).

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ELECTRON NUCLEAR DOUBLE RESONANCE EXPERIMENTS WITH RUBY*

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The polarization of nuclear spins throughout a crystal by saturation of an electron spin resonance of paramagnetic ions present as impurities has recently been reported.[1,2] We have observed an apparent inverse of this effect in ruby (Al_2O_3:0.05% Cr^{+++}), i.e., when the induced nuclear polarization is partially removed by saturating an aluminum nuclear spin resonance transition, a large decrease in the power absorbed by the electron spin resonance of the Cr^{+++} ions is observed. We have also observed effects associated with inducing transitions between the hyperfine levels of the chromium-53 ions.

Magnetic field modulation at 5 kc/sec was used to observe the edge of the ($+\frac{1}{2} \rightleftarrows -\frac{1}{2}$) electron spin resonance absorption line of ruby with a microwave power level about 20 db above saturation. The spectrum shown in Fig. 1 was then obtained by scanning the frequency of a low-power rf oscillator connected to a single turn of wire around the ruby sample. The five lines in the 3-Mc/sec region correspond very well with the nuclear magnetic resonance spectrum of the host aluminum nuclei in the crystal. The same dependence of the splitting between lines upon the angle of dc magnetic field and line width were observed both here and in the nuclear magnetic resonance spectra.

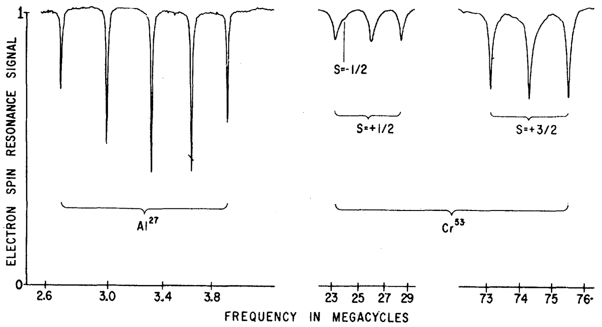

FIG. 1. Spectrum obtained by observing the ($+\frac{1}{2} \rightleftarrows -\frac{1}{2}$) electron spin resonance signal from ruby under saturation conditions and scanning the frequency of an rf generator connected to a coil around the crystal. ($H \cong 3285$ gauss, $\theta = 0°$, $\nu = 9160$ kMc/sec, $T = 4.2$°K.)

The lines near 25 and 75 Mc/sec are associated with the $\vec{I}\cdot\vec{S}$ splitting of the chromium-53 ions[3] which have a nuclear spin of 3/2 and a natural abundance of 9.5%. The other isotopes of chromium all have zero nuclear spin. The +1/2 and +3/2 electron spin states are very close together at our operating point. As a result they interact strongly as the angle of the dc magnetic field is varied, causing large changes in the hyperfine splitting (Fig. 2). Also, the second order correction to their hyperfine splitting is appre-

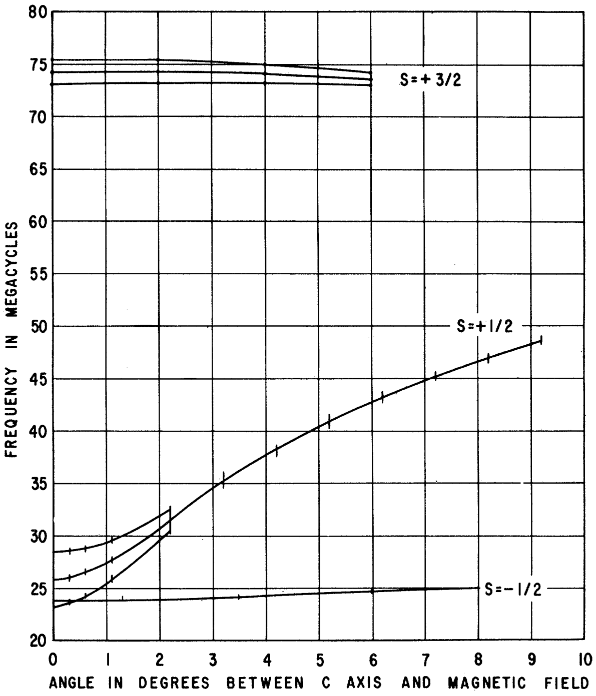

FIG. 2. Experimental data on angular dependence of the hyperfine splittings of the electron spin states of the Cr^{53} ion in ruby. The change in frequency with angle results from the mixing of electron spin states. ($\nu = 9160$ kMc/sec, $T = 4.2$°K.)

ciable, leading to the observed triplets. The strength of the lines reduced very rapidly with departure from zero degrees. A weak triplet associated with $S = -3/2$ was also observed with the lines falling at 71.93, 72.15, and 72.37 Mc/sec at zero degrees. It is interesting to note that while all the Cr^{53} data were taken by observing the $S = -1/2$ to $+1/2$ transition, saturation of the hyperfine levels in the $S = +3/2$ state caused the largest changes in the electron spin resonance signal.

The strong effect of nuclear polarization on the electron spin resonance can easily be observed in ruby without applying rf. At microwave power level well above saturation, if one rapidly moves from one part of the resonance line to another a large transient with a decay time of about 5 seconds is observed. The same decay time is observed for the transient following removal of rf power sufficient to saturate one of the aluminum nuclear transitions. Further, the observed decay time of the aluminum nuclear polarization is also 5 seconds while T_1 for the electron spin resonance transition is approximately 0.2 second. The decay time of the effects associated with the chromium-53 nuclei was also near 5 seconds.

The effects of nuclear polarization upon the electron spin resonance signal were only observable when microwave power levels of the order of or greater than that needed to saturate the electron spin transition were used. When the electron spin resonance signal was observed at low microwave powers, the application of rf had no effect upon the signal. Further, when the signal was observed during the nuclear polarization relaxation time following a quick reduction in the microwave power level from above to well below saturation, only a 0.2-second time constant transient was observed. The application of rf power had no effect upon the transient, indicating that T_1 is independent of the nuclear polarization.

A decrease in microwave power absorption with the application of rf power was always observed. As a check, some observations were made using amplitude modulation of the microwaves rather than magnetic field modulation. Also, the amplitude of the magnetic field modulation was varied over a wide range with no significant effects being observed.

It does not seem that the effects reported here can be explained by any of the mechanisms proposed by Feher[4] to explain his observations in doped silicon. The slow relaxation after the removal of rf power would seem to indicate that the host nuclei play an important role in either the induced transition probabilities or relaxation mechanisms between electron spin states. If such were the case, in order to get an appreciable percentage effect in the electron system by saturating the nuclei, one would have to reduce the relative electronic polarization (N_i/N_j) to the same order as the nuclear polarization (n_k/n_l), i.e., $N_i/N_j \cong n_k/n_l$. This idea is consistent with our experimental results as the nuclear polarizations are increased by about a factor of[1] 40 and the electronic polarizations are decreased by about a factor of 100 under our experimental conditions, making the two comparable.

We have also studied the effect of rf upon maser action in ruby,[5] and have observed a number of additional very weak lines.

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THERMAL EQUILIBRIUM BETWEEN *F* AND *M* CENTERS IN POTASSIUM CHLORIDE

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Various models have been proposed for the M centers in alkali halides. According to Seitz[1] an M center consists of an F center associated with a neutral vacancy pair. A modification, having inversion symmetry, was put forward by Knox.[2] Van Doorn and Haven[3] have proposed a model consisting of a pair of associated F centers (F_2 model). From these models it is clear that the formation of M centers from F centers requires one F center for each M center formed in the case of the Seitz-Knox model and two in the case of the F_2 model.

It might be possible to distinguish between these cases by investigating (a) the kinetics of the reaction $F \rightarrow M$ and (b) the thermal equilibrium $F \rightleftharpoons M$. For the Seitz-Knox center the equilibrium can be written as

$$F + \text{vacancy pair} \rightleftharpoons M,$$

$$K = [M]/[F][\text{vac. pairs}];$$

and for the F_2 center as

$$2F \rightleftharpoons M, \qquad K' = [M]/[F]^2.$$

In the first case the M concentration will be proportional to the F concentration at a fixed temperature (the concentration of vacancy pairs being constant), whereas in the second case the M concentration will vary quadratically with the F concentration.

Theisen and Scott[4] found the thermal bleaching of F centers at about 300°C to be a second-order reaction, indicating that two F centers combine to form a new center. The thermal equilibrium between F and M centers was studied by Smith and Scott.[5] They colored a KCl crystal inhomogeneously by heating for a short time in potassium vapor in order to obtain a range of F concentrations. It was assumed that the attainment of the equilibrium between F and M centers is rapid compared with the diffusion of the centers in the crystal. The F and M concentrations in different regions of the crystal were measured optically, using a thin beam of monochromatic light. A linear dependence between F and M centers was found up to a concentration of 10^{17} F centers/cm^3. This experiment is, however, not conclusive because (a) no true equilibrium existed and (b) the high M/F ratio found indicates that the crystals were not properly quenched. Therefore, the following experiment was performed. KCl was purified by crystallizing it twice according to the Kyropoulos method. From the single crystal thus obtained, plates were cut having the dimensions $4 \times 5 \times 1.3$ mm^3. These were colored by heating to 697°C in potassium vapor of various pressures in a nickel tube. A heating time of 10 minutes was found to be sufficient to obtain equilibrium, as no further increase in optical absorption was observed with longer heating times. After quenching in carbon tetrachloride to room temperature, which was done in the dark to avoid photochemical reactions, the relative F and M concentrations were determined by measuring the extinction of the absorption bands at 77°K. With the apparatus used for coloring (to be described in a forthcoming publication) it took less than one second to transfer the crystal from the furnace to the quenching bath, thus ensuring freezing-in of the high-temperature equilibrium. All crystals had the same dimensions in order to obtain equal quenching rates.

The results are shown in Fig. 1. It is seen that the M concentration varies quadratically with the F concentration, which is inconsistent with the Seitz-Knox model but agrees well with the F_2 picture.