number 36% of the maximum wavenumber in the (1,0,0) direction. This places the conduction minima at 82% of the way from the center to the edge of the Brillouin zone. The 0.046-ev phonon corresponds to umklapp scattering between valleys on different axes using a phonon with wave number q given by $(1,0.18,0.18)2\pi/a$. Since the longitudinal acoustic and optical modes are degenerate at $q=(1,0,0)2\pi/a$ and, according to Brockhouse,[2] have phonon energies of 0.049 ev, the 0.046-ev intervalley phonon is probably a longitudinal acoustic mode.

The intensity maximum 0.063 ev below the main intensity maximum in Si corresponds in energy to a two-phonon process in which, in addition to the 0.058-ev phonon, an optical mode phonon is emitted during virtual scattering in the valence band. Although the virtual scattering may occur in a conduction valley, it seems unlikely that optical mode scattering in the conduction band is very significant. If we calculate the matrix element for optical mode scattering in the valence band from the experimental ratio R for the 0.063-ev intensity maximum, this matrix element squared is approximately 76% that which is required to explain the anomalous temperature dependence of the hole mobility in Si[5,6] on the basis of mixed acoustic and optical mode scattering with parabolic valence bands. Because of the small spin orbit splitting between the valence bands in Si it seems likely that the non-parabolic nature of these bands[8] would also contribute to the deviation of the temperature dependence of the hole mobility from a $T^{-\frac{3}{2}}$ law.

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[8] E. O. Kane, J. Phys. Chem. Solids **1**, 82 (1956).

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Cross Relaxation Studies in Diamond*

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A microwave double resonance experiment performed on the paramagnetic nitrogen centers in diamond shows that in this system cross relaxation occurs via a four spin flip mechanism which exactly conserves Zeeman energy. In this process, which was first postulated by Bloembergen and co-workers in their paper on cross relaxation, two spins of the center line make a downward transition while a spin belonging to each satellite makes an upward transition. Simple rate considerations for this process indicate that if a saturating microwave field is suddenly applied to one of the three lines of the nitrogen spectrum, a weak probing microwave signal at either of the two other lines should register a definite change in absorption in a time T_{21}. Specifically, if T_{21} is much less than other relaxation times of the system, then setting the pump upon the center line should force the absorption at either satellite to drop to zero. Setting the pump at the position of one of the satellites, on the other hand, should reduce the center line absorption to $\frac{3}{5}$ its thermal equilibrium value but should increase the absorption measured at the other satellite by the factor 6/5. This behavior was precisely observed at 1.6°K, using a bi-modal cavity.

By resolving the rate at which a satellite decays to zero when the pump is set on the center line, T_{21} is measured for all five satellites in the three principal orientations: $H_0\|[100]$, $H_0\|[110]$, and $H_0\|[111]$. The measured anisotropy is discussed.

It is shown that the four spin flip transition may be used in special cases to establish continuous wave maser operation by inverting the population of one of the satellite lines. Steady state inversion of one of the nitrogen satellites is incidentally observed in a number of diamonds.

1. INTRODUCTION

RECENTLY Bloembergen and co-workers[1] have analyzed the processes of energy transfer between adjacent resonances in both nuclear and electronic spin systems. These authors consider that multiple spin reversals of neighboring spins which are induced by the dipolar and exchange interactions between the ions are primarily responsible for the transfer of energy between resonances. For a given multiple spin flip process to be important in the establishment of spin-spin equilibrium a necessary requirement is that the total Zeeman energy be nearly or exactly conserved by the process. This led Bloembergen et al. to suggest that in certain instances a relatively high-order process which conserves Zeeman energy may be more probable than a simple flip-flop between two spins whose resonance frequencies are sufficiently different that there is no appreciable overlap between the lines.

It occurred to us that the paramagnetic resonance of nitrogen centers in diamond[2] could be used to verify quantitatively the occurrence of a higher order spin flip process, the reason being that the characteristic resonance spectrum of three narrow, equally spaced hyperfine lines is compatible with only one multiple spin reversal process which exactly conserves Zeeman energy. This process (Fig. 1) consists of simultaneous double flip-flops and was invoked by Bloembergen and co-workers to explain qualitatively the cross saturation

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[*] A preliminary account of this work was given at the International Conference on Quantum Electronics, held at High View, New York, September 14–16, 1959 (proceedings to be published).

[1] N. Bloembergen, S. Shapiro, P. S. Pershan, and J. O. Artman, Phys. Rev. **114**, 445 (1959).

[2] W. V. Smith, P. P. Sorokin, I. L. Gelles, and G. J. Lasher, Phys. Rev. **115**, 1546 (1959).

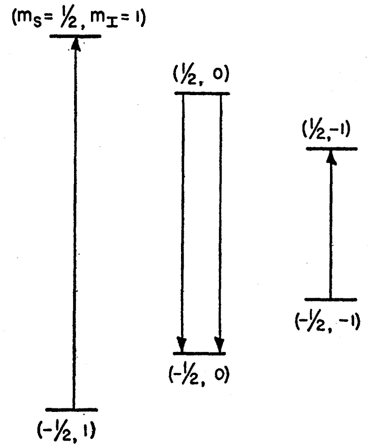

FIG. 1. Electron spin resonance energy level diagram for nitrogen centers in diamond ($H_0 \| [100]$) showing the four spin flip mechanism through which cross-relaxation proceeds. The hyperfine splitting is 94.2 Mc/sec.

results reported by Townes et al.[3] in a copper salt. In the unit forward process two spins of the center line make a downward transition while a spin belonging to each satellite makes an upward transition. Spin-spin equilibrium between the three absorption lines is reached when the number of forward transitions per unit time exactly balances the number of reverse transitions per unit time. If the relative number of spins in the ground and excited states which correspond to one of the three resonance lines is suddenly changed, there will then occur a redistribution of the spins in the ground and excited states corresponding to the two other resonance lines as spin-spin equilibrium is sought via the four spin flip mechanism. The time required to attain this equilibrium would here be what Bloembergen terms the cross relaxation time T_{21}. In our experiments T_{21} is intermediate between the more familiar times T_2 and T_1. T_2 is roughly the time required for equilibrium to be established between all the spins in a given resonance line and T_1 is the spin-lattice relaxation time which becomes increasingly long at low temperatures.

Recently there has begun to appear other evidence[4–6] that cross relaxation does in certain cases proceed via high-order spin flip processes when Zeeman energy can be conserved. The case of nitrogen centers in diamond appears, however, to be uniquely simple to interpret because only one mechanism is involved in bringing about spin-spin equilibrium between the different absorption lines in the spectrum. With the double resonance method described below it is possible in this system to measure T_{21} directly. In addition, by making T_{21} measurements with the dc magnetic field aligned along each one of the principal crystal directions, it is possible to determine the dependence of T_{21} on the value of the splitting of the triplet spectrum.

The four spin flip transition may be used in special cases to establish continuous wave (c.w.) maser operation by inverting the population of one of the satellite lines. This unusual but nevertheless straightforward method of maser pumping is discussed in Sec. 5. Steady-state inversion of a line through this scheme was incidentally observed in a number of diamonds.

2. EXPERIMENTAL TECHNIQUES

A double resonance method was used, with two independent *X*-band microwave sources functioning as pump and probe. The microwave cavity (Fig. 2) used the two orthogonal, degenerate cylindrical TM_{110} modes which could be continuously split in frequency from

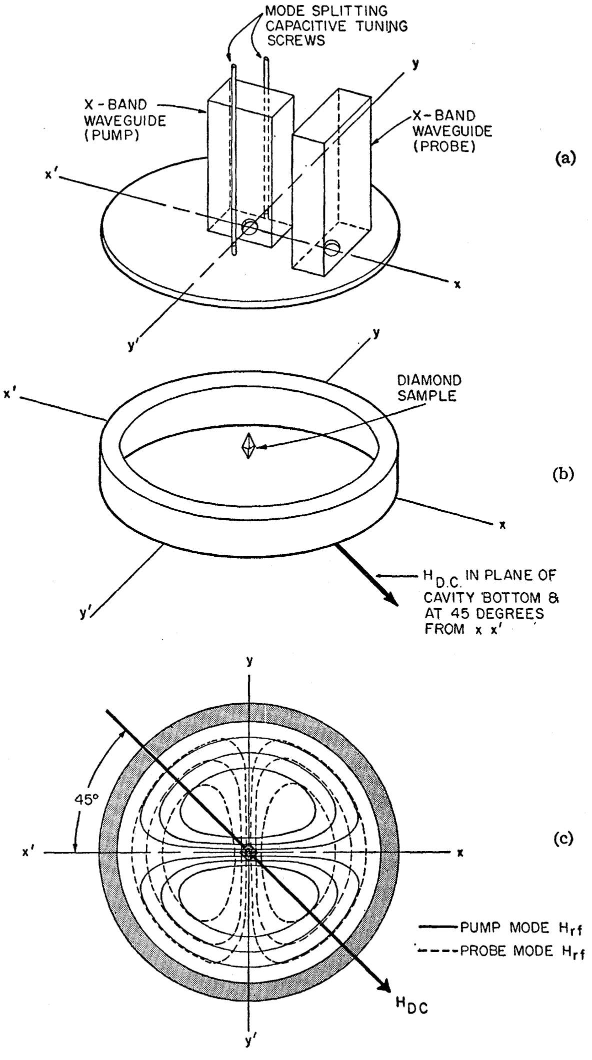

FIG. 2. Sketches showing the dual mode cavity used to measure cross relaxation times. (a) Top plate of cavity showing waveguide couplings and tuning screws. (b) "Pill-box" shaped cavity with sample mounted in position. (c) Plan view showing disposition of rf and dc magnetic fields inside cavity. (The fields are uniform in the *z* direction perpendicular to the plane of the diagram.)

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[3] J. A. Giordmaine, L. E. Alsop, F. R. Nash, and C. H. Townes, Phys. Rev. **109**, 302 (1958).

[4] W. S. C. Chang, paper given at the International Conference on Quantum Electronics held at High View, New York, September 14–16, 1959 (proceedings to be published).

[5] W. Mims (to be published).

[6] J. E. Geusic (to be published).

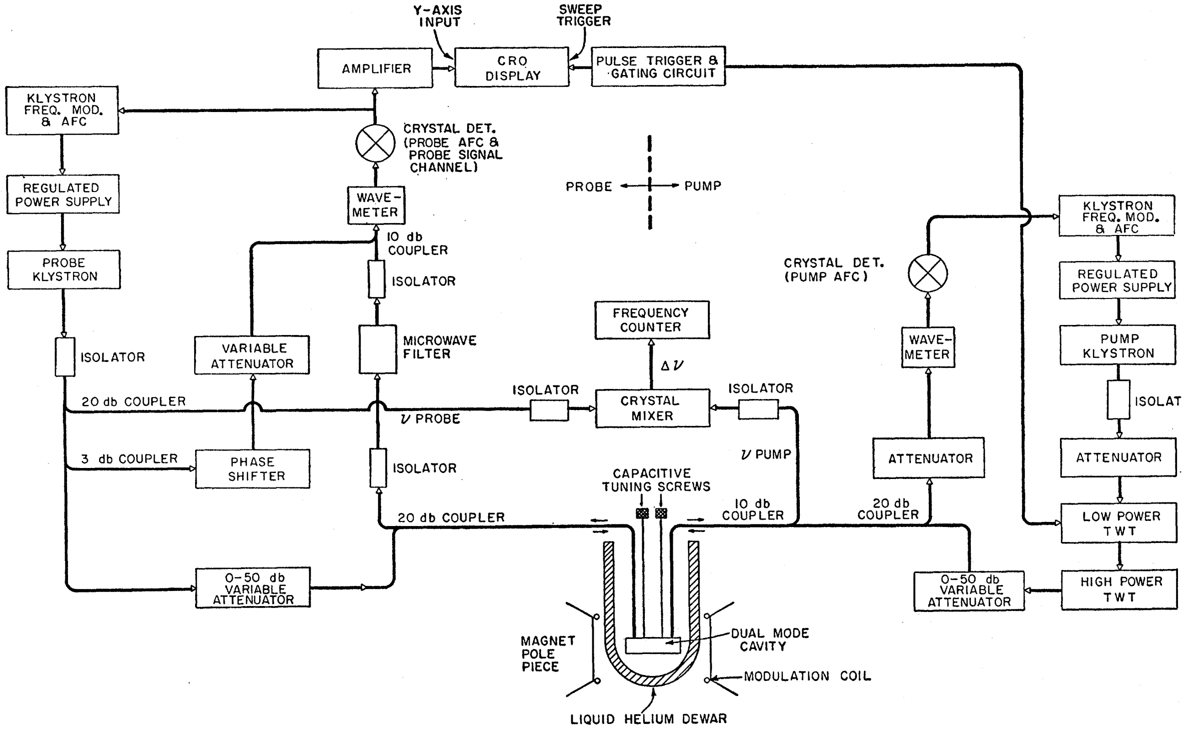

FIG. 3. Block diagram of double resonance system used to measure cross relaxation times.

0 to ~600 Mc/sec by a symmetrically arranged pair of capacitive tuning screws. Both pump and probe klystrons were AFC stabilized on their respective cavity modes. A counter monitoring the difference frequency of the two sources allowed the pump and probe to be set precisely on any two lines. A fast microwave switch in the pump line consisting of a series combination of a low power traveling wave tube (TWT) gate and a high-power TWT amplifier made it possible to turn the pump power on or off rapidly. Most of the measurements were done at liquid helium temperatures so that the field modulated absorption lines as seen by the probe could be displayed on an oscilloscope with good signal-to-noise ratios. A block diagram of the equipment is presented in Fig. 3.

More specifically, we used for the probe a standard Varian Associates V-4500 EPR Spectrometer but changed the form of the microwave circuitry to that shown in Fig. 3. This modification avoids power levels in the cavity which could saturate the resonances and yet enables sufficient microwave energy to be fed to the probe crystal for efficient detection. A Frequency Standards 85BW pass band filter, tunable in the range 8500–9600 kMc/sec, was inserted between the probe cavity and the detecting crystal and tuned to the probe frequency. Although the input ports of the bi-modal cavity are positioned in such a way that power cannot theoretically be coupled from the pump mode into the probe waveguide and vice versa, in practice this isolation is not perfect and with a typical mode frequency splitting of 90 Mc/sec there is observed a 40 db down cross coupling of power into the probe waveguide and vice versa. Once the pump is turned on this residual cross coupling by itself would have no particular effects on the detection and display of the resonance line monitored by the probe. In the process of turning the pump on, however, the slight change in power reaching the probe crystal would be recorded as a transient. Also, as the pump is turned on, there could be developed momentarily a transverse component of magnetization corresponding to the resonance line upon which the pump acts. This transverse magnetization would precess at the pump frequency and couple power into the probe waveguide. Since this coupled power would vary at the field modulation frequency it would distort the display of the line being monitored by the probe. For these reasons the filter was inserted. Its bandwidth, being sharper than the klystron mode and broader than the sample cavity mode, made probe adjustments relatively easy to perform. The symmetric capacitive tuning screws are situated in the two $E_{\max}$ regions for the pump mode and hence when inserted into the cavity they rapidly lower the frequency of the pump mode but leave virtually unchanged the frequency of the probe mode; this feature also, of course, considerably simplified the tuning procedure. For a few measurements the pump and probe mode inputs were reversed.

The low power TWT in the pump line was a Hewlett-

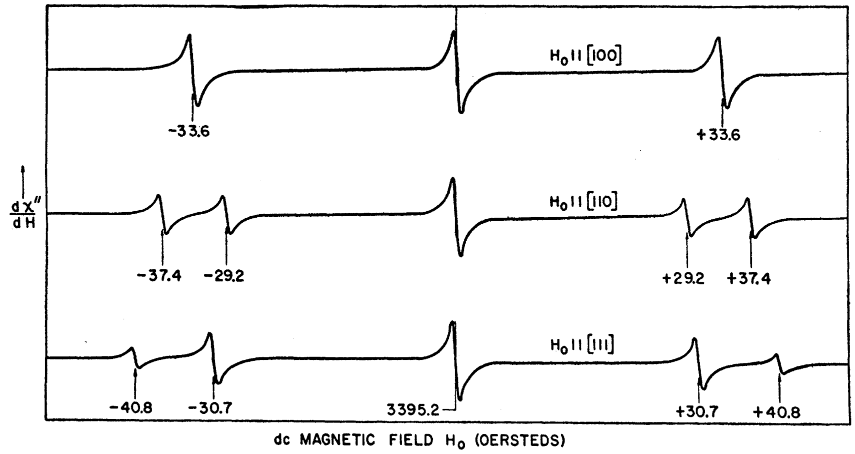

FIG. 4. Electron spin resonance spectrum of nitrogen in diamond at approximately 9500 Mc/sec ($T=295°$K). The dc magnetic field is parallel to the crystal axis indicated.

Packard 494A which conveniently served as a gate for microwave power. The high power TWT was a Federal F-6996 amplifier with a 10 watt maximum output. The availability of high power is desirable to insure that the resonance line on which the pump is set can be saturated in a time short compared to cross relaxation times.

In the experiments reported here sine wave field modulation was used, the depth of modulation being adjusted to allow the probe to sweep back and forth through the line it monitors. The cross relaxation times which can be measured using this type of probe display can obviously be no shorter than the inverse of the field modulation frequency which in our case could be raised to 500 cycles per second. Fortunately, the average of the T_{21} values we measured was about 30 milliseconds.

3. DEMONSTRATION OF CROSS RELAXATION VIA THE FOUR SPIN FLIP PROCESS

Figure 4 shows the nitrogen center paramagnetic resonance spectrum for the three principal orientations of the magnetic field H_0 relative to the crystal axes. Consider the case $H_0 \| [100]$ for which the energy level diagram of Fig. 1 is directly applicable. The net rate of the four spin flip process is proportional to $[(n_0^-)^2 n_{-1}^+ n_{+1}^+ - (n_0^+)^2 n_{-1}^- n_{+1}^-]$, where the n's are level populations, subscripts referring to nuclear spin quantum numbers and superscripts to electron spin quantum numbers. As shown in the Appendix, in the linear approximation of small population differences the rate becomes:

$$R=(1/2T_{21}) \times[2(n_0^- - n_0^+)-(n_1^- - n_1^+)-(n_{-1}^- - n_{-1}^+)]. \quad (1)$$

If a saturating microwave field is suddenly applied to one of the three lines of the nitrogen spectrum, a weak probing microwave signal at either of the two other lines should register a change in absorption in a time T_{21}. Specifically, if T_{21} is much less than other relaxation times of the system, then making the pump incident upon the center line should force the absorption at either satellite to drop to zero. Setting the pump at the position of one of the satellites, on the other hand, should reduce the center line absorption to $\frac{3}{5}$ its thermal equilibrium value but should increase the absorption measured at the other satellite by the factor 6/5. One arrives at these simple ratios by considering the population readjustments necessary to make the net rate R of the four spin flip process equal to zero. For example, when the pump acts on the $m_I=-1$ satellite, $(n_{-1}^- - n_{-1}^+)$ must equal zero. Let $(n_{+1}^- - n_{+1}^+)$, $(n_0^- - n_0^+)$ be written as $(n_{+1}^- - n_{+1}^+)_0 + \Delta(n_{+1}^- - n_{+1}^+)$, $(n_0^- - n_0^+)_0$

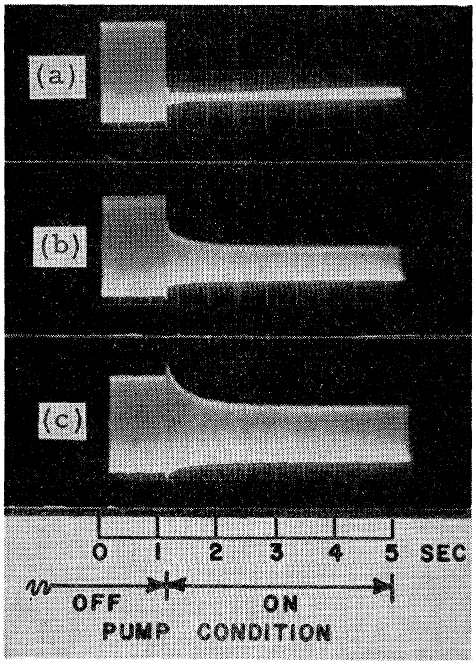

FIG. 5. Probe absorption in sample W-2 versus time showing effect of turning on the pump; (a) probe on low field satellite, pump on center line; (b) probe on centerline, pump on high field satellite; (c) probe on low field satellite, pump on high field satellite. The sweep speed is 0.5 sec/cm. The modulation frequency is 100 cycles per second. ($T=1.6°$K.)

$+\Delta(n_0^- - n_0^+)$, respectively, where the first terms are the population differences in thermal equilibrium and the Δ's refer to changes in the population differences as a result of four spin flip transitions when the pump is set on the $m_I = -1$ satellite. Clearly, $\Delta(n_0^- - n_0^+) = -2\Delta(n_{+1}^- - n_{+1}^+)$. Let s denote $(n_{+1}^- - n_{+1}^+)_0 \cong (n_0^- - n_0^+)_0$. Then the condition $R=0$ requires that $\Delta(n_{+1}^- - n_{+1}^+) = (s/5)$, $\Delta(n_0^- - n_0^+) = -\frac{2}{5}s$. Similar considerations apply in the case where the pump is set on the center line.

We observed precisely this behavior at liquid helium temperatures in a number of diamonds with relatively strong nitrogen center concentrations. Figure 5 shows oscilloscope traces whose rapidly oscillating vertical component represents the detected signal at the probe crystal as the magnetic field is modulated an amount sufficient to traverse the resonance. When the pump is turned on the absorption jumps to a new value and then relaxes slowly to the equilibrium pump-on value. The jump in absorption is interpreted as the change in spin population caused by the four spin flip mechanism. The magnitude of the jump in all three cases agrees with the predicted value. The slow change in absorption which follows the jump is probably caused by spin lattice relaxation mechanisms[7] T_s, T_x, $T_{x'}$, T_N working under the constraint that R of Eq. (1) equals zero. For the case of the sample (W-2) in Fig. 5, these other relaxation times are actually 2 orders of magnitude greater than the cross relaxation time T_{21} so that the rapid establishment of spin-spin equilibrium via the four spin flip mechanism can be easily seen in the time domain.

4. MEASUREMENT OF CROSS RELAXATION TIMES

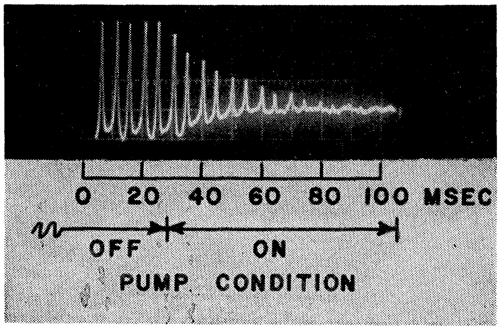

FIG. 6. Typical decay of absorption of low field satellite when the pump is applied to the center line. The sweep speed is 10 milliseconds/cm. The modulation frequency is 100 cycles per second. ($T=1.6$°K.)

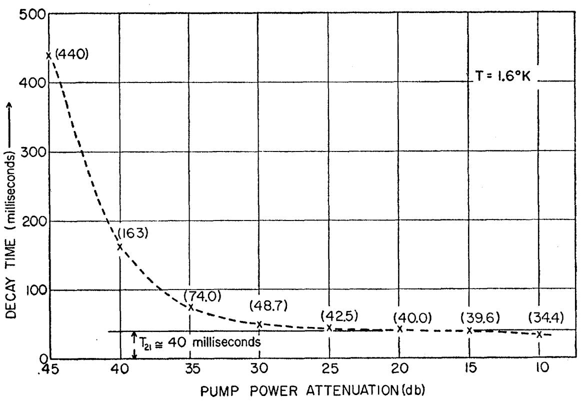

FIG. 7. Decay time for outer satellite in sample W-2 ($H_0 \| [111]$) versus pump power attenuation.

Since in the sample of Fig. 5 T_{21} is much shorter than the other relaxation times, it can be directly measured. Accordingly the pump was set on the central line and the rate at which a satellite dropped to zero was measured. Figure 6 shows a typical decay well resolved. Similar measurements were done for the two other principal orientations, the pump being always applied on the central line with the probe arranged as a monitor on each of the satellite lines. An accurate analysis of these orientation studies could determine how T_{21} varies with the magnitude of the hyperfine splitting. In either case $H_0 \| [111]$ or $H_0 \| [110]$, one has two types of centers, distinguishable by the angle made between the hyperfine axis (the N-C bond direction) and the dc magnetic field H_0. The spectrum of each center is a perfect triplet and the hyperfine splittings of the centers are known from Fig. 4. In the $H_0 \| [110]$ case the two centers have equal concentrations; for $H_0 \| [111]$ the concentrations are in the ratio 3:1. Some complexity is introduced by the fact that the g values of all the centers are precisely the same. In the rough comparison made at the end of this section it is assumed that all the spins belonging to the central line ($m_I=0$) are equivalent. The proper weighting factors for this situation are derived in the Appendix.

In each of the five cases the pump attenuator was set at maximum and was then reduced in 5-db steps, the satellite decay time being measured each time. The measured decays initially vary rapidly as a function of pump power. This corresponds to the time required for the pump to saturate the center line. As the pump power is raised this time becomes shorter than T_{21} and the satellite decay versus pump power curves display plateaus lasting over a wide range of pump power. These plateaus give the value of T_{21} directly. At very high powers the satellite decay times again start to get shorter due perhaps to multiple quantum transitions. Figure 7 shows a curve of measured decay times plotted versus pump power attenuation for a particular orientation and a particular satellite. The value of T_{21} is easily obtained by inspection in this particular case. For orientations in which T_{21} is short the plateaus in curves similar to Fig. 7 may be hard to distinguish since the power levels required to saturate the center line in a time short compared to T_{21} may be sufficiently high to cause spurious effects like multiple quantum transitions. This was, in fact, true for the sample W-2 so that we could only get accurate measurements of T_{21} for the outer satellites in each of the principal orientations. These values are

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[7] See, for example, F. M. Pipkin, Phys. Rev. **112**, 935 (1958).

TABLE I. Cross relaxation times for various orientations and satellites in two diamond samples.

Orientation	Satellite	Sample	T_{21} (milli-seconds)	$\frac{T_{21}(\Delta\nu)^4{}_{100}}{(T_{21})_{100}(\Delta\nu)^4}\left(\frac{I}{I_{100}}\right)$
$H_0\|[111]$	Inner	W-3	19.5±2	0.92
$H_0\|[111]$	Outer	W-3	135.0±15	0.68
$H_0\|[110]$	Inner	W-3	12.5±1	0.48
$H_0\|[110]$	Outer	W-3	62.5±3	0.89
$H_0\|[100]$	···	W-3	23.0±2	1.00
$H_0\|[100]$	···	W-2	7.0±0.5	1.00
$H_0\|[111]$	Outer	W-2	40.0±1	0.67
$H_0\|[110]$	Outer	W-2	20.0±1	0.92

recorded in Table I. To complete the table of relative values it was necessary to select another slightly less concentrated stone, T_{21} being a strong function of concentration. Accordingly, a number of diamonds containing nitrogen centers were tried. The more heavily concentrated stones all showed strongly the effects of the four spin flip transition. There were no effects of this kind in the stones with weak nitrogen concentrations. A number of stones appeared to display two or more exponentials in the decay curves, and these stones invariably were characterized by the nitrogen centers being roughly divided between a densely concentrated surface "skin" region and the remaining weakly concentrated interior portion of the crystal. A homogeneous sample (W-3) having a suitably weaker concentration was finally picked and T_{21} was measured for the various orientations and satellites. For W-3 the T_{21} values are about 3 times longer than the corresponding ones of W-2. Actually, in W-3 there was another spin-spin interaction which was stronger than the four spin flip transition. There was evidently present an unusual background line with a very fast relaxation time which just overlapped the central nitrogen line. On setting the pump on the high field satellite the central line, instead of dropping to three fifths of the normal intensity, remained constant, being effectively relaxed by the overlapping line.[8] The low field satellite, on the other hand, increased to twice the normal intensity when the pump was turned on. This is just what must be expected in this case and the growth time constant is shown in the Appendix to equal $2T_{21}$. The values of T_{21} for W-3 were measured in this way and are recorded in Table I.

Most of the measurements were performed with the sample at 1.6°K. A few runs were also made at 4.2°K and 77°K in order to check the temperature independence of T_{21}. No measurable variation with temperature was found. Mention should also be made of the fact that even at room temperature it was possible to produce a noticeable decrease in intensity of the low field satellite when the pump was set on the central line.

The orientation dependence of T_{21} is explained within a factor of two, after reducing the experimental data by two factors. One of these factors, (I/I_{100}), is the relative intensity of the satellite in question. The other factor is the dependence upon the frequency splitting $\Delta\nu$ of the triplet. Both are discussed in the Appendix. The data thus reduced appear in the last column of Table I. The deviation from unity is a measure of the anisotropy of the matrix elements and the anisotropy of the homogeneous line width.

5. MASER PUMPING BY THE FOUR SPIN FLIP MECHANISM

In connection with this experiment one of us (G. L.) has noted that the four spin flip transition may be used in special cases to establish c.w. maser operation by inverting the population of one of the satellite lines. For simplicity, consider a spin system of three equally spaced resonances for which the direct ($\Delta m_s=\pm 1$) spin lattice relaxation is the only contact with the lattice. This spin lattice relaxation is represented by rate equations of the form:

$$\left(\frac{dn_{a,b}{}^{+}}{dt}\right)_{SL}=-\left(\frac{dn_{a,b}{}^{-}}{dt}\right)_{SL}$$
$$=-W_{a,b}(e^{h\nu/kT}n_{a,b}{}^{+}-n_{a,b}{}^{-}),$$

where the subscripts a and b refer to the two satellite lines which do not necessarily arise from the nuclear states of the same electronic spin system. If one assumes that the four spin flip probability is much greater than the spin lattice relaxation probability $W_{a,b}$ and that the center line of the triplet is completely saturated by a microwave field, then in the steady state:

$$(n_a{}^{-}-n_a{}^{+})=N_a\left(\frac{e^{h\nu/kT}-1}{e^{h\nu/kT}+1}\right)\left(\frac{W_aN_a-W_bN_b}{W_aN_a+W_bN_b}\right), \quad (2)$$

where

$$N_{a,b}=n_{a,b}{}^{-}+n_{a,b}{}^{+}.$$

Equation (2) holds also when the subscripts a and b are interchanged and therefore shows that if an asymmetry exists in the NW product of the two satellite lines, the one with the smaller NW product will have its spin population inverted. If the system is chosen so that the low field satellite is inverted, then a maser could be built with a pump frequency lower than the amplifying frequency. The pump power levels required should not in principle be higher than those encountered in the usual method of three level maser excitation.

This scheme is applicable to a number of systems. Phosphorus in silicon has a spectrum consisting of two narrow lines spaced by approximately 42 gauss. The iron resonance that Feher[9] has observed in silicon is a single line with a g value of 2.0702±0.0001. Since the g value of the phosphorus resonance is 1.999 one would

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[8] G. Feher and H. E. D. Scovil, Phys. Rev. **105**, 760 (1957).

[9] G. Feher, Phys. Rev. **114**, 1219 (1959).

find in a silicon crystal doped with roughly equal amounts of iron and phosphorus a resonance spectrum of three equally spaced lines at a field $\simeq 1780$ gauss (5000 Mc/sec). Since the relaxation time of the iron[10] is much shorter than that of the phosphorus, saturation of the central line should cause the other phosphorus line to invert at concentrations $\sim 5\times 10^{16}$ P/cm^3, $\sim 5\times 10^{16}$ Fe/cm^3. With a high Q cavity and with a sample of isotopically purified silicon[11] the condition for oscillation can be met with these concentrations.

The effect of other impurity lines on the nitrogen spectrum in diamond is in certain samples strong enough to produce a large c.w. inversion of the low field satellite when the center line is saturated. That is, in contradistinction to the ideal case, represented by sample W-2, in which both satellites drop to zero when the center line is saturated, in roughly half of the more concentrated stones the low field line displays a negative absorption when the pump is set on the center line. The amount of inversion varies from stone to stone; in one sample it was as high as 92%. As is required by the four spin flip mechanism, the high field satellite in these stones displays a positive absorption equal in magnitude to the negative absorption of the low field satellite. This was checked by reversing the pump and probe cavity couplings. The exact cause of the observed asymmetry is unknown to us. Since it varies markedly from sample to sample we are inclined to think that other impurities are affecting the nitrogen spectrum. A broad background line with $g<2.0024$ would shorten the relaxation time of the high field satellite thus providing favorable conditions for the mechanism of maser pumping here being discussed. The more concentrated stones examined have $\sim 10^{16}-10^{17}$ nitrogen resonance centers per cc and as the line width of the resonance lines is only $\simeq 0.3$ gauss, the diamonds which display the above mentioned asymmetry would be suitable candidates for a narrow band maser at K-band or even higher frequencies.

The copper Tutton salt maser action observed at Columbia by Nash and Rosenvasser[12] is apparently explained by the above scheme. In this case the requisite asymmetry is furnished by spin-spin interaction of one satellite with very close neighbors.

6. ACKNOWLEDGMENTS

Our thanks are due J. P. Anderson for building much of the double resonance equipment, M. Okrasinski for fabricating the double resonance cavity, and N. Stemple for x-ray orienting a large number of samples. We would like to thank Dr. W. V. Smith for helpful conversations. Samples were obtained from the Rough Diamond Company and H. Wachsberg, New York City, New York.

APPENDIX

The intensity of the low field satelitte is proportional to $(n_{+1}{}^{-}-n_{+1}{}^{+})$. The rate of change of $(n_{+1}{}^{-}-n_{+1}{}^{+})$ due to four spin flip transitions is given by:

$$d(n_{+1}{}^{-}-n_{+1}{}^{+})/dt = P[n_0{}^{-}(n_0{}^{-}-1)n_1{}^{+}n_{-1}{}^{+}-n_0{}^{+}(n_0{}^{+}-1)n_1{}^{-}n_{-1}{}^{-}]. \quad \text{(A1)}$$

Here P is the *a priori* probability per second that given four spins in the appropriate initial spin states, a four spin flip transition will occur. P contains the factor $1/N^3$ where N is the number of lattice sites per cc. The factor $1/N^3$ results from assuming that a four spin flip process can occur only when all four spins are contained within a sphere of some maximum radius r_0. As Bloembergen and co-workers have shown, the magnitude of P should be computed by treating the dipole-dipole interaction in second order perturbation theory. This results in an inverse fourth power dependence of P on the triplet spacing. There will also be a concentration dependence of P stemming from the density-of-states factor $g(\nu)$ which characterizes the line width of the resonances.

Let $n_i{}^{-}=n_i{}^{+}+\Delta_i$; $i=0,\ \pm 1$. Since $\Delta_i \ll n_i$ one can write:

$$\frac{d\Delta_1}{dt} \cong P(n_0{}^{+})\{2\Delta_0 n_1{}^{+}n_{-1}{}^{+}-\Delta_1 n_0{}^{+}n_{-1}{}^{+}-\Delta_{-1}n_1{}^{+}n_0{}^{+}\}. \quad \text{(A2)}$$

For $H_0\|[100]$ one has $n_0{}^{+}\cong n_{-1}{}^{+}\cong n_{+1}{}^{+}$. Then $d\Delta_1/dt = P(n_0{}^{+})^3\{2\Delta_0-\Delta_1-\Delta_{-1}\}$. In the usual case $\Delta_1=(\Delta_1)_0$, the thermal equilibrium value, at $t=0$; and $\Delta_0=0$, $\Delta_1=\Delta_{-1}$ for $t\geq 0$. Then $\Delta_1=(\Delta_1)_0 e^{-t/T_{21}}$ with

$$T_{21}=1/2P(n_0{}^{+})^3.$$

Consider next the case represented by sample W-3 (see text). Here $\Delta_{-1}=0$ and $\Delta_0=(\Delta_0)_0$ for $t\geq 0$. At $t=0$, $\Delta_1=(\Delta_0)_0$. The solution is: $\Delta_1=(\Delta_0)_0(2-e^{-t/2T_{21}})$, that is, the rise time is twice the decay time as measured for a "pure" nitrogen spectrum as in W-2.

Consider finally a case in an orientation other than $H_0\|[100]$, for example, the $H_0\|[111]$ outer satellite. Using Eq. (A2) with $n_1{}^{+}\cong n_{-1}{}^{+}\cong n_0{}^{+}/4$,

$$\frac{d\Delta_1}{dt}=\frac{P}{4}(n_0{}^{+})^3\left\{\frac{\Delta_0}{2}-\Delta_1-\Delta_{-1}\right\}.$$

The low field satellite decay occurs with a time constant $T_{21}=[2/P(n_0{}^{+})^3]$. This is four times longer than the value of T_{21} for $H_0\|[100]$. Angular variations of P are neglected as are differences in line widths of the various resonances. In a similar manner one multiplies $(T_{21})_{100}$ by a factor of $\frac{4}{3}$ for the inner satellite of [111], and by a factor of 2 for both satellites of [110].

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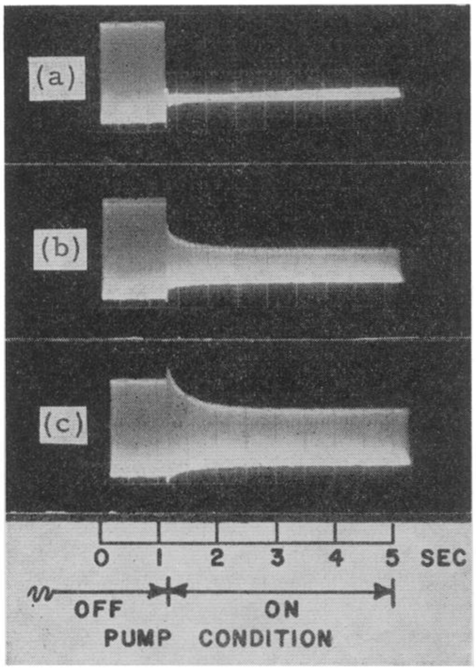

FIG. 5. Probe absorption in sample W-2 versus time showing effect of turning on the pump; (a) probe on low field satellite, pump on center line; (b) probe on centerline, pump on high field satellite; (c) probe on low field satellite, pump on high field satellite. The sweep speed is 0.5 sec/cm. The modulation frequency is 100 cycles per second. ($T=1.6$°K.)

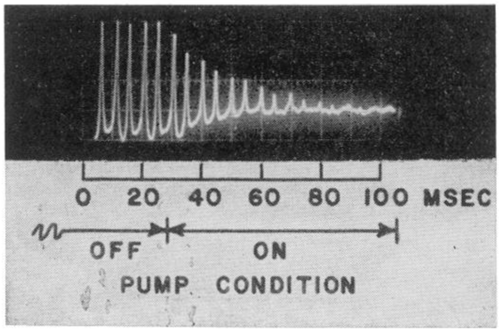

FIG. 6. Typical decay of absorption of low field satellite when the pump is applied to the center line. The sweep speed is 10 milliseconds/cm. The modulation frequency is 100 cycles per second. ($T=1.6$°K.)