Low-Temperature Paramagnetic Relaxation of Color Centers in KCl†

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The spin-lattice relaxation of color centers in KCl was experimentally studied at liquid helium temperatures by following the recovery of the magnetization after saturation of the electron spin resonance. X-irradiated and additively colored crystals were both studied and found to behave in the same manner. For crystals containing only F centers, the recovery rates were roughly proportional to the F-center concentration. A tendency toward concentration independence at the lower concentrations was observed. The most dilute system studied had about 8×10^{16} F centers/cc, and showed a relaxation rate at $2°K$ of 2.2×10^{-3} sec^{-1}. Measurements at $1.4°K$ indicated a linear temperature dependence for the relaxation rate. A crystal containing 3×10^{18} F centers/cc showed an initial recovery rate of about 0.1 sec^{-1}. The recovery was nonexponential, and the terminal recovery rate was about 0.03 sec^{-1}. Measurements at the same temperatures as those used with the dilute system showed the relaxation rate for this concentrated system to be temperature independent. Samples of intermediate concentration gave a smooth transition between these two types of behavior. Measurements in magnetic fields of 3500 gauss and 1750 gauss indicate a field-independent relaxation rate for all samples. After optical bleaching in the F absorption band, with concomitant production of M, R, and N centers, crystals showed an increased recovery rate for both the initial and terminal portions of the recovery. As bleaching progressed, the recovery became more nonexponential and less temperature dependent. Increases in relaxation rates by factors of several hundred were observed with no signs of saturation of the effect. Subsequent thermal bleaching of M, R, and N centers restored the relaxation rate to its value prior to optical bleaching. Details of sample preparation are given, as is a discussion of possible explanations of the results.

I. INTRODUCTION

EITHER heating in the presence of potassium vapor or x irradiation produces in KCl crystals an optical absorption band, the F band, centered at 5600 Å with a room-temperature linewidth of 890 Å. The F centers responsible for this optical absorption also give rise to a 56-gauss wide electron-paramagnetic-resonance (EPR) line, which is only slightly shifted from that which would result from free electrons. Room-temperature bleaching of such colored crystals with light, which is absorbed by the F centers, results in the production of other absorption bands in the near infrared, M, N, and R bands.[1] We shall call the centers which are responsible for these absorption bands, and any other centers which are produced by optical bleaching, the "derived centers." Even after extensive bleaching there remains a large optical absorption band similar to the original F band, though very likely arising in part from certain optical transitions of some of the derived centers.[2] There also remains, after bleaching, an EPR signal which is similar to the original F-band signal.

EPR experiments have contributed significantly to the verification of de Boer's model[3] for the F center.[4] On the other hand, attempts to establish by means of EPR the nature of the atomic defects responsible for the M, R, and N bands have so far met with little success. This lack of success stems perhaps primarily from the inability to produce only one species among these other centers in a given crystal. At least the M center, and probably the others, are formed by coagulation of F centers,[1,2,5,6] and one should expect to have difficulty in freezing in one particular species of coagulate at the expense of the dispersed F centers and the other species of coagulates.

The experiments to be reported here consist of an attempt to use one characteristic of the electron spin system, namely, its relaxation time for energy transfer to the lattice, T_1, to investigate interactions among the F centers and between the F-center system and the systems of derived centers. The measurements of T_1 were made below $4°K$ in KCl crystals containing (1) only F centers and (2) F centers plus the derived centers.

Our work stemmed from attempts to isolate the paramagnetic behavior of the various derived centers by means of selective optical excitation in the optical absorption bands. It became clear quite early in this work that the presence of the derived centers drastically reduced the relaxation time of the F centers. (This fact has also been noted by Noble and Markham.[7]) It seemed likely that a careful study of this reduction in T_1 would yield useful information about the nature of the derived center systems and their distribution in the lattice. The results of such a study are reported here.

In Secs. II and III we will describe the resonance techniques and methods of sample preparation used. F centers were produced both by x raying and by addi-

[1] S. Petroff, Z. Physik 127, 443 (1950).
[2] H. Pick, Z. Physik, 159, 69 (1960); F. Okamoto, Phys. Rev. 124, 1090 (1961).
[3] J. H. de Boer, Rec. trav. chim. 56, 301 (1937).
[4] A. F. Kip, C. Kittel, R. A. Levy, and A. M. Portis, Phys. Rev. 91, 1066 (1953); W. C. Holton and H. Blum, *ibid.* 125, 89 (1962). The recent paper by Holton and Blum includes many other references to intervening work.
[5] C. Z. van Doorn, Phys. Rev. Letters 4, 236 (1960).
[6] B. J. Faraday, H. Rabin, and W. D. Compton, Phys. Rev. Letters 7, 57 (1961).
[7] G. A. Noble and J. J. Markham, Bull. Am. Phys. Soc. 5, 419 (1960).

tive coloration in potassium vapor. In Sec. IV, A, we establish the low-temperature relaxation behavior of crystals containing only F centers. Finally, in Sec. IV, B, we describe the effects of the presence of the derived centers on the relaxation processes of the F-center system.

II. EXPERIMENTAL DETAILS

The X-band microwave spectrometer used was of the two-bolometer balanced-mixer type discussed by Feher.[8] The reference cavity of the spectrometer frequency stabilizer was temperature stabilized to within 0.01°C. A glass Dewar system with a helium capacity of about 800 cc was employed, and the helium bath was always pumped to a temperature below the lambda point to eliminate noise caused by boiling of the helium. The only thermal conductor into the helium Dewar was one stainless-steel X-band waveguide of 10-mil wall thickness provided with two copper radiation shields cooled by the evaporating helium. With this arrangement, the capacity of the system was sufficient to supply the losses associated with pumping down to 2°K and maintaining that temperature for longer than 30 hrs. A Cartesian diver type of pressure regulator was used to hold the bath temperature constant to within 0.01°K. Efficient utilization of the pumped liquid helium, and maintenance of the uniformity of sample treatment was made possible by the use of an *in situ* sample changing system.[9]

The spin-lattice relaxation time was studied by the direct method of measuring the recovery of the magnetization as a function of time after saturation of the resonance. The magnetic-field sweep speed dH_0/dt, the modulation frequency f_m, the modulation amplitude H_m, and the microwave magnetic field $2H_1$, used in the measurements of recovery were picked to conform to Weger's[10] prescription for obtaining maximum signals from samples with long relaxation times. The conditions of this prescription are roughly

$$T_1 2\pi f_m \gg 1, \quad \gamma H_1 (T_1 T_2)^{\frac{1}{2}} \gg 1, \quad 3 < 2\pi f_m H_m \gamma^{-1} H_1^{-2} < 10,$$

and

$$10 < 2\pi f_m H_m (dH_0/dt)^{-1} < 100,$$

where γ is the electron gyromagnetic ratio, T_1 is the spin-lattice relaxation time, and $1/\pi T_2$ is the homogeneous spectral width of an individual spin packet.[11]

The first condition is difficult to violate for the systems in question. The second condition is the saturation condition which is also easily satisfied. The third condition dictates that each passage through a hyperfine component of the resonance shall be nonadiabatic but not sudden. In such a passage, the magnetization is tipped away from the direction of H_0 an appreciable

amount but is not inverted. The rapid destruction of the components of magnetization transverse to H_0 results in a loss of net magnetization. The lower bound of the fourth condition guarantees that a hyperfine component is passed through a sufficient number of times to result in essentially complete destruction of its magnetization. The upper bound of this condition guarantees that enough previously untraversed hyperfine components are encountered with each modulation sweep to yield a large signal and avoid spurious line splittings. Sweeping through the resonance under these conditions yields a large dispersion signal of essentially Gaussian shape whose amplitude is proportional to the magnetization. The experimental parameters usually used were $dH_0/dt = 350$ gauss/sec, $f_m = 500$ cps, $H_m = 2$ gauss, $H_1 = 0.01$ gauss, and filter time constant, $\tau = 0.05$ sec.

After each point on the recovery curve was obtained, the resonance was in a saturated condition and the recovery began again from zero magnetization. Since relaxation times approaching 500 seconds were studied and since usually about 12 points were taken, the time required to obtain one curve sometimes exceeded $\frac{1}{2}$ hr. The temperature stabilization mentioned in conjunction with the apparatus was included to insure spectrometer stability over periods of longer than $\frac{1}{2}$ hr. It might be expected that it would have been simpler to retune the spectrometer between points, but this procedure resulted in more scatter in the data. The stability of the
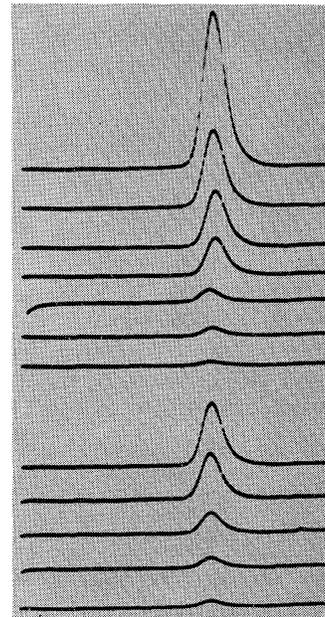

FIG. 1. Electron spin resonance signals obtained for various lengths of the recovery period following the saturation of the resonance. From top to bottom the lengths of the recovery periods in seconds were: 2600, 350, 200, 110, 25, 15, 5, 150, 50, 20, and 10. These data were obtained using an x-irradiated crystal containing 8×10^{16} F centers/cc. The relaxation took place in a field of 3500 gauss at a temperature of 1.4°K.

[8] G. Feher, Phys. Rev. **105**, 1122 (1957).
[9] W. D. Ohlsen, Rev. Sci. Instr. (to be published).
[10] M. Weger, Bell System Tech. J. **39**, 1013 (1960).
[11] A. M. Portis, Phys. Rev. **91**, 1071 (1953).

spectrometer easily exceeded the operator's ability to retune in a consistent manner.

The $\frac{1}{2}$ hr per curve does not include the time required to completely polarize the sample in order to determine its equilibrium magnetization, M_∞. M_∞ was required, since an attempt was made to fit the data to the equation $M_t = M_\infty(1 - e^{-t/T_1})$, where T_1 is the spin-lattice relaxation time, t is the time interval since saturation, and M_t is the value of the magnetization at time t. The slope of a plot of $\ln(M_\infty - M_t)$ as a function of t should equal $1/T_1$, the recovery rate. Actually, this plot, which we shall term a recovery curve, was always found to be nonlinear, so that no unique T_1 existed. In consideration of this nonexponential recovery the symbols $T_1(t)$ and $W(t)$, the recovery rate, will be used in this text instead of T_1 and $1/T_1$. Initial and terminal slopes of the recovery curves were measured. The measured slopes of the tangents to the recovery curve were of necessity much less accurate than the magnetization measurements themselves. The accuracies in the slopes varied from $\pm 10\%$ to as low as $\pm 100\%$. The latter figure only applies to the initial-recovery slopes measured using a few heavily optically bleached crystals.

The following measuring sequence was used:

Time	Action
O	The field sweep and time clock are started together.
a	The resonance is swept through and saturated.
$a+b$	The field sweep is stopped at the H_0 value at which the relaxation is to be studied.
t	Simultaneously, the reverse field sweep is started, the time clock is stopped, and the oscilloscope is triggered.
$t+b$	The resonance is swept through and saturated, and the signal is recorded on the oscilloscope-camera film.

At the end of the measuring sequence, the time clock reads t, while the time between passes through the resonance has been $t+b-a$. Usually a was chosen equal to b, and in those cases where this was not so, a correction to t was made. The a and b values used ranged from 1 to 6 sec., while t ranged from 2 to 600 sec. The values of H_0 chosen for the relaxation field were always more than 300 gauss away from resonance. To obtain M_∞ for each set of data, the first cycle through this sequence was made with a t at least three times the maximum expected value of $T_1(t)$. For this first point in a data set, the final spectrometer alignment was done just before the reverse field sweep.

An example of the data which were obtained is reproduced in Fig. 1. The dotted appearance of the large signals is a result of using a filter time constant τ such that the condition $\tau \gg 1/(2\pi f_m)$ was not satisfied.

Immediately before loading the samples into the cryostat for relaxation time measurements, their optical absorption spectra were measured using a Model 14 Cary spectrophotometer. (To avoid excessive sample bleaching during infrared measurements, this instrument has been modified by P. L. Hartman of this laboratory. The light passes through the monochromator *before* passing through the sample rather than after

passing through the sample as is the case for the unmodified instrument when used in the infrared range.) When the highest resolution was desired, the samples were cooled by contact with a copper block maintained at 77°K. The resulting crystal equilibrium temperature was not determined.

Most of the crystals used had F absorption-band optical densities greater than 2. To measure the optical density in these crystals, it was necessary to use neutral density filters in the reference beam of the spectrophotometer and, for the most heavily colored crystals, to infer peak values of optical density by extrapolation from values closer to the tails. For use in this extrapolation, full widths at $\frac{1}{2}$, $\frac{1}{3}$, and $\frac{1}{4}$ maximum absorption were measured at room temperature and found to be 890, 1100, and 1240 Å, respectively.

The F-center concentration was calculated from the optical density using Smakula's equation and an F-center oscillator strength of 0.8.

Since the ratio of R_1 to R_2 peak optical density is nearly a constant, the optical absorption of only the better resolved of these bands was measured. At room temperature, the R_2 is better resolved, while near 77°K the R_1 is preferable. Near 77°K, the absorption spectrum of the N band is composed of three or more unresolved lines. The peak absorption of this complex was measured.

III. SAMPLE PREPARATION

All samples used in this work were prepared from KCl crystals grown by the Harshaw Chemical Company. At 2°K these crystals, as received, show a weak and complex paramagnetic-resonance spectrum at H_0 values of a few hundred gauss. At H_0 values near 3000 gauss there is a strong spectrum which has been identified by Känzig and Cohen[12] as being associated with O_2^-. In the orientation used, with H_0 along a [100] axis, part of this oxygen spectrum overlaps the region of the F-center resonance. For this reason, special precautions were taken to eliminate the O_2^-.

Both x-irradiated and additively colored crystals were studied. The additive coloring was done in Pyrex bombs using doubly distilled potassium. The crystals were maintained at 560°C, while the potassium temperature was set, using the potassium solubility data of Rögener[13] and the vapor pressure data of Honig,[14] to yield the desired density. Before being sealed in the bomb, the crystals were baked in a vacuum of about 10^{-6} torr at 500°C for 1 hr to remove the O_2^-. It is not known if this treatment in itself is sufficient to eliminate the O_2^-, but after coloring no trace of the undesired resonance could be found. The coloring temperatures were maintained for 8 hrs to ensure uniform coloration, and then the bomb was cooled to room temperature in a few minutes time. Under the red illumination from a Wratten No. 1

[12] W. Känzig and M. H. Cohen, Phys. Rev. Letters **3**, 509 (1959).
[13] H. Rögener, Ann. Physik **29**, 386 (1937).
[14] R. E. Honig, RCA Rev. **18**, 195 (1957).

safe light, the crystals were removed from the bomb and cleaved to dimensions of about $2\times5\times25$ mm.

The relatively slow cooling the samples received results in the formation of M centers. To obtain, for a starting point, a sample containing only F centers, it is necessary to heat the crystal to over 500°C and then quench it to a low temperature. In this work the crystal was heated to about 620°C and quenched to room temperature. Ideally, the crystals should be quenched to liquid nitrogen temperature and studied without warmup.[15] Use of such an ideal quench was not feasible with the existing equipment. Although, for completeness, an investigation using such an ideal procedure would be desirable, it is predicted that the results would not differ from those obtained in this work. The basis for this prediction is the observed insensitivity of the "pure F center" $T_1(t)$ to the method of preparation. Samples which were cooled to 4°K shortly after they were quenched showed the same relaxation time as those cooled four days after quenching.

To avoid introducing oxygen into the crystal during the process of heating to 620°C, the cycle was carried out entirely in a helium atmosphere. The crystal was placed in a Pyrex tube through which there was a slow flow of helium. The tube was inserted into a hot oven for heat treatment and then, simultaneously, the crystal was dropped into a cold portion of the tub and the helium flow rate was greatly increased. This flowing-gas quench resulted in F/M peak-optical-density ratios ranging from 50 to 100.

While studying the concentration dependence of the relaxation rate $W(t)$ of F centers alone in additively colored crystals, one set of crystals was encountered which had an abnormally large $W(t)$. Also, the room-temperature optical F-band width in these crystals was about 40% larger than normal. Since, as far as was known, there was nothing unusual in the preparation of these crystals, suspicions were raised concerning reproducibility of characteristics of the additively colored crystals.

To check the results obtained with additively colored crystals, x-irradiated crystals were studied. The advantage of avoiding the possible introduction of impurity atoms during coloring with x-irradiation is somewhat offset by the fact that V centers are introduced. However, no paramagnetic resonance has been reported for any V center which is stable at room temperature. Such a resonance, if hidden under the F-center resonance, should have been detected by Silsbee[16] as a difference between x-irradiated and additively colored crystals in the F-center oscillator strength.

The x-irradiation was carried out in the dark with a tungsten-anode tube operating at 130 kv. The crystal temperature was about 40°C as determined by the temperature of the x-ray tube envelope.

Two procedures for eliminating O_2^- from the crystals before irradiation were tried. If the crystals were heated for $\frac{3}{4}$ hr at 600°C in a helium atmosphere, the freshly irradiated crystals showed no sign of the O_2^- resonance. However, after heat treatment, as discussed in the last paragraph of this section, the O_2^- resonance reappeared and with further heat treatment, grew. Heating the crystals for 18 hr at 600°C in a chlorine atmosphere successfully eliminated all traces of O_2^- resonance in the irradiated crystals. For neither of these treatments was a check made for the O_2^- resonance in the uncolored crystals.

Freshly x-irradiated crystals contain M centers. These centers cannot be dispersed by using a high-temperature thermal bleach since, in the case of x-irradiated crystals, this procedure also completely bleaches the F centers. Instead, the crystals were heated to 150°C and then quenched. This procedure was found to restore the "pure F center" $W(t)$ to crystals which had been optically bleached.

$W(t)$ as a function of the concentration of the various centers which result from optical bleaching was studied using two methods of sample preparation. Variation in the amount of F-band optical bleaching results not only in a variation in the number of these centers, but also in a variation in the ratios of their concentrations. In particular, as shown by Petroff,[1] the concentration of M centers reaches a peak value and then decreases as as the bleaching progresses. $W(t)$ and optical-absorption spectra were measured on sets of crystals which differed from one another only in the amount of optical bleaching in the F band each received.

To obtain uniform bleaching in samples with optical densities of 2 to 4, it was necessary to bleach in a tail of the F absorption band. Blue light was used, rather than red light, to avoid affecting those centers which have appreciable absorption in the spectral region of the red side of the F absorption band. The blue light was furnished by a 100-w tungsten projection lamp and a Corning 5-61 filter. This filter has a peak transmission of about 77% at 4200 Å and passes only about 5% at 5200 Å. The light intensity was of the order of 4×10^{15} photons/cm^2 sec. The sample absorption for this blue light was about 30 to 50%.

For the sake of reproducibility, all optical bleaching was done with the crystals in good thermal contact with an ice bath.

The second means of varying the concentrations of the M, R, and N centers is based on the work of Tomiki.[17] This work found the M center to be more thermally stable than the N center which, in turn, is more stable than the R centers. $W(t)$ and optical absorption spectra were measured on a set of crystals which had identical optical bleaches in the F band and differed only in the temperature at which they had been thermally bleached. All thermal bleaches were of 15-min duration and were done in the dark.

[15] P. J. Botden, C. Z. van Doorn, and Y. Haven, Philips Research Repts. **9**, 469 (1954).
[16] R. H. Silsbee, Phys. Rev. **103**, 1675 (1956).
[17] T. Tomiki, J. Phys. Soc. Japan **15**, 488 (1960).

IV. RESULTS AND DISCUSSION

A. Crystals Containing Only F Centers

Figure 2 is a plot of terminal recovery rates as a function of the F-center concentration for crystals which contain essentially only F centers. The terminal rates were measured for this plot in order to suppress the effects of any localized rapid relaxation caused by undesired impurities. The terminal rate is probably the rate most characteristic of F centers in a pure crystal.

The point at about $10^{17}/cc$ and about 10^{-2} sec was obtained from the anomalous crystal mentioned in the section concerning the preparation of crystals. The point at $3\times10^{18}/cc$ was obtained from a crystal colored by R. H. Silsbee. For this coloring the same procedure, equipment, and shipment of Harshaw crystals were used as for the other samples. The approximate concentration determination was done by Silsbee through a comparison of the paramagnetic resonance intensities of this crystal and of an optically measurable crystal.

Figure 2 shows that the recovery rate for F centers alone is approximately proportional to the concentration. It was mentioned in the section on crystal preparation that the x-irradiated crystals should show the more reliable concentration dependence. If only points obtained from x-irradiated crystals are considered, a tendency toward concentration independence at lower concentrations becomes apparent.

Figures 3 and 4 illustrate further evidence of a change in behavior of $W(t)$ as a function of concentration. Figure 3 shows recovery curves for the most densely colored crystals of Fig. 2. The recovery curves at these two temperatures show no temperature dependence. Figure 4 shows recovery curves for the least densely colored crystal. In this case a clear temperature dependence exists. The ratio of the temperatures is 0.70, while the ratio of the terminal recovery rates is 0.76. The additively colored crystal, represented by the point in Fig. 2 at 0.0040 sec^{-1} recovery rate at 2°K, has an intermediate ratio of terminal recovery rates of 0.85 for the same two temperatures recorded in Figs. 3 and 4.
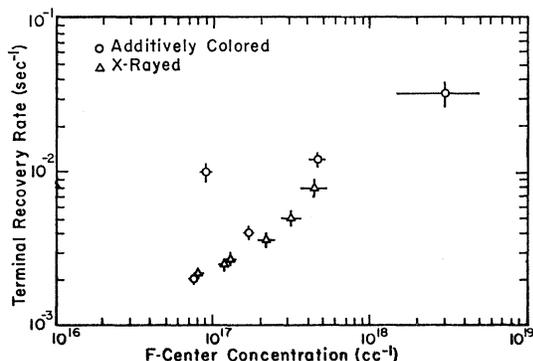

FIG. 2. Terminal recovery rates as a function of F-center concentration for crystals containing only F centers. All data for this figure were obtained at 2.0°K in a magnetic field of 3500 gauss.
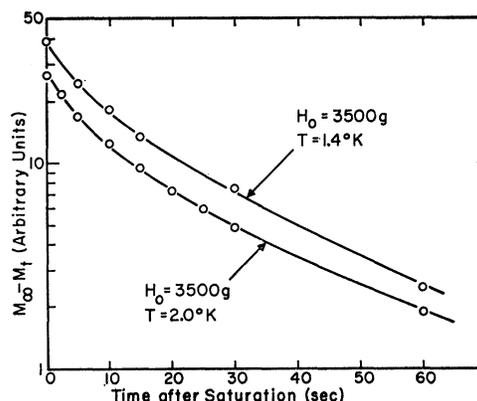

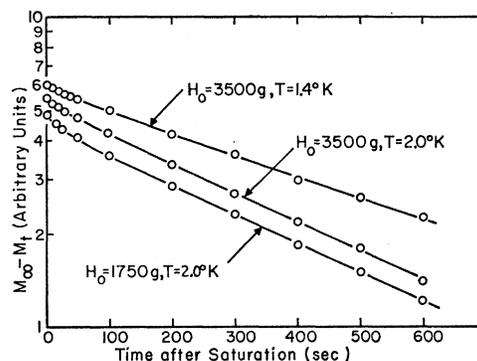FIG. 3. Recovery curves for an additively colored sample containing 3×10^{18} F centers/cc.

FIG. 4. Recovery curves for an additively colored sample containing 8×10^{16} F centers/cc.

X-irradiated crystals show the same behavior with respect to $W(t)$ as a function of concentration and temperature.

Figure 4 also shows that $W(t)$ is independent of the magnetic field in which the relaxation occurred. This field independence held for all crystals regardless of the method of coloring and regardless of whether the crystal was optically bleached.

It can be shown that the recovery rates of the crystals containing essentially only F centers are not appreciably affected by the residual M centers. The additively colored crystal and the x-irradiated crystal of Fig. 2 having about $10^{17}F$ centers/cc agree well in F-center concentration, recovery rate, and in the temperature dependence of the recovery rate although the ratios of the peak F-band optical density to peak M-band optical density are 100 and 35, respectively.

The temperature dependence exhibited by the dilute F-center system shows that the process which determines the recovery rate for this system involves the transfer of the F-center Zeeman energy to the crystal lattice rather than to some intermediary system which then transfers the energy to the lattice. Any transfer to an intermediary must be rapid compared to the final transfer to the lattice.

Without a specific model for the relaxation mechanism, it is impossible to determine the expected magnetic field dependence of T_1 for dilute F centers, even if we are given the fact that a one-phonon process is involved. If a Debye spectrum of lattice vibrations is assumed, $1/T_1$ should vary as $H_0{}^2$, provided that the coupling between the electron spin and the lattice modes is independent of H_0. The origin of $H_0{}^2$ dependence is clearly shown by Pake.[18]

Defects or impurities are apparently crucial in determining the T_1 of dilute F centers observed in this work. This fact is made apparent from the measurements of McAvoy et al.[19] In crystals of higher purity, they obtain a T_1 of 1350 sec at 2.1°K in crystals at an F-center density of 5×10^{16}/cc. Extrapolation of the data of Fig. 4 leads to a value of T_1 shorter than 1350 sec by a factor of 2 at this concentration.

Since the relaxation rate even in our most dilute crystals is apparently not that appropriate to the isolated F center, we will not consider in a detailed fashion possible relaxation mechanisms. One promising candidate for relaxation of the isolated F center is a mechanism employing phonon modulation of the hyperfine interaction. A calculation on such a basis has been made by Deigen and Zevin.[20]

One objection to the usual relaxation rate calculations, such as that of Deigen and Zevin, is that they neglect the effect of defects and impurities in the crystal on the lattice spectrum. Kochelaev,[21] using a theory of imperfect lattices due to Lifshits,[22] has found that such effects may be important. His T_1 for chrome alum, for example, is independent of the magnetic field, whereas Van Vleck's[23] calculation for chrome alum, using unperturbed lattice vibrations, yields a T_1 inversely proportional to $H_0{}^2$.

However, an attempt to use the theory of Kochelaev to explain the H_0 independence of the F-center results meets with difficulties. The relaxation rate calculated by this theory goes as the $\frac{4}{3}$ power of the concentration of the impurities which scatter phonons well. The experimental trend of T_1 for F centers is toward concentration independence at low concentrations. An explanation which postulates that the impurities characteristic of the starting material are responsible for the scattering, and that the F centers themselves are impotent as scatterers, is contradictory to the findings of Pohl.[24] From thermal conductivity experiments, Pohl finds that coloring a crystal causes a large increase in the scattering of long-wavelength phonons.

On the positive side, an attempt to explain the observed $T_1(t)$ for F centers is unencumbered by one difficulty which plagues the study of many other electron spin systems at low temperatures. This difficulty is the problem of the so-called "phonon bottleneck."[25,26] Van Vleck's calculation for chrome alum indicates that each mode of the lattice "on speaking terms" with the spin system is interrupted some 10^{10} times/sec by the spin system. Such a high interruption rate should result in these modes "on speaking terms" being heated to the spin-system temperature, rather than the spin system being cooled to the bath temperature. A calculation for the F-center system yields a value of 100 interruptions/sec for each of these modes whose frequency is equal to the Larmor frequency of the spins. For such a low interruption rate, the modes "on speaking terms" should not be heated above the bath temperature. The low interruption rate for the case of the F-center system is a result of the long relaxation time and high dilution of this system.

As the concentration of F centers is increased in these crystals, $W(t)$ increases with the concentration, and its temperature dependence weakens. This combination of effects indicates that the coupling which limits the relaxation rate is, in this case, between the F centers themselves, and not between the F center, or something tightly coupled to the F center, and the crystal lattice.

A relaxation process which is independent of magnetic field and crystal temperature has been discussed by Bloembergen and Wang.[27] In this process, Zeeman energy is transformed into exchange energy, which is then coupled to the lattice. The process requires that the exchange energy be large compared to the Zeeman energy and, therefore, this process cannot be used to explain the observations on F centers. If the exchange interaction were as strong as required for this process, the hyperfine line broadening of the F center would be averaged out and not observed.

A more reasonable explanation for the temperature and magnetic-field independence is provided by the process of spin diffusion to a rapidly relaxed impurity. This process has been discussed for the case of nuclear relaxation by Bloembergen,[28] Hatton and Rollin,[29] and, most recently, by Blumberg.[30] The case of nuclear relaxation by spin diffusion is complex enough so that only a somewhat rough theory has been given. For the case of F centers, the problem is even more complex due to the hyperfine broadening, which is large compared to the broadening that would result from the dipole-dipole interaction alone. This hyperfine broadening severely limits the rate of spin diffusion, because of the

[18] G. E. Pake, in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2.

[19] B. R. McAvoy, D. W. Feldman, J. G. Castle, Jr., and R. W. Warren, Phys. Rev. Letters 6, 618 (1961).

[20] M. F. Deigen and V. Y. Zevin, Soviet Phys.—JETP 12, 785 (1961).

[21] B. I. Kochelaev, Doklady Akad. Nauk S.S.S.R. 131, 1053 (1960).

[22] I. M. Lifshits, Zhur. Exptl. Teoret. Fiz. 18, 293 (1948).

[23] J. H. Van Vleck, Phys. Rev. 59, 724 (1941).

[24] R. O. Pohl, Phys. Rev. 118, 1509 (1960).

[25] J. H. Van Vleck, Quantum Electronics, edited by C. H. Townes (Columbia University Press, New York, 1960).

[26] P. W. Anderson, Phys. Rev. 114, 1002 (1959).

[27] N. Bloembergen and S. Wang, Phys. Rev. 93, 72 (1954).

[28] N. Bloembergen, Physica 15, 386 (1949).

[29] J. Hatton and B. V. Rollin, Proc. Roy. Soc. (London) A199, 222 (1949).

[30] W. E. Blumberg, Phys. Rev. 119, 79 (1960).

difficulty involved in making multiple-spin transitions which conserve energy.

The mechanism assumed for the spatial diffusion of magnetization involves mutual spin transitions via the dipole-dipole interaction between those spins whose spectral location permits such a process to conserve energy. The validity of this assumption will be considered in later paragraphs.

The rate at which spin diffusion can restore equilibrium depends on the mean-square step length divided by the average step time, that is, on the diffusion constant. The mean-square step length should be independent of concentration for steps between randomly occupied sites on a regular lattice. As the concentration is reduced, the probability of each length of step is reduced in proportion to the reduction in concentration so that the average step length is unchanged. The step time has been calculated by Portis[31] to be inversely proportional to the square of the concentration. Thus $W(t)$ should vary as the second power of the F-center concentration in the high-concentration range. The data of Fig. 2 for the x-irradiated crystals are simply not accurate enough or carried to high enough concentration to either confirm or rule out such a concentration squared behavior.

Some discussion must be made concerning the validity of the results of Portis. Anderson[32] has considered, in a general framework, diffusion problems of a nature similar to the problem which is of interest here. However, Anderson's conclusions, which are somewhat at variance with those of Portis, result from an assumption which is not appropriate for the case being considered here. This assumption is that the diffusion transitions themselves are the only factor limiting the state lifetime. A self-consistent calculation then leads to the conclusion that a $1/r^3$ interaction, as in spin diffusion, should result in slow diffusion, while interactions which fall off faster than $1/r^3$ should not result in diffusion at all. Actually, at least one concentration-independent mechanism exists which broadens the spin states more than do the mutual electron-spin transitions themselves. Given such a broadening, diffusion will occur, albeit slowly, for interactions which fall off as any power of r. This broadening, which is discussed in the following paragraphs, justifies Portis' use of perturbation theory.

The energy level of an electron spin state is shifted by the dipole-dipole interaction of the electron spin with distant nuclear spins. Nuclear-nuclear spin rearrangements result in variations of the resultant magnetic field at the electron, and, thus, in a broadening of the level. (For nearby nuclei, the large hyperfine fields suppress spin rearrangements.) This variation will be found to have a magnitude which corresponds to a frequency spread $\Delta\omega$ which is much larger than $1/T_2$ (nuclear). A self-consistent lifetime of a given state must then be somewhere between T_2 (nuclear) and $1/\Delta\omega$. The mechanism is very similar to the nuclear-nuclear interaction studied by Herzog and Hahn.[33]

Using the T_2 measurements of Clark[34] on other alkali halides, one can estimate a nuclear resonance linewidth in KCl of about 2 gauss. A somewhat conservative calculation of the effect of nuclear rearrangement includes nuclei further than 16 Å from the F center. At 16 Å the dipole field of the electron spin is down to 2 gauss. The mean-squared field at the F center from such distant nuclei is 10^{-3} gauss^2. The nuclear-rearrangement width is then about 3×10^{-2} gauss, or $\Delta\omega = 6 \times 10^5$ sec^{-1}. The self-consistent lifetime of the state, as far as an energy determination is concerned, is then between 1×10^{-3} sec and 2×10^{-6} sec. A value for the lifetime of 5×10^{-5} sec, or a linewidth of 10^{-3} gauss, should be reasonable. It should be noted that the full nuclear rearrangement width, $\Delta\omega$, rather than the self-consistent lifetime estimated here, would be the important quantity to consider in the *spectral* spin diffusion problem.

One further point needs discussion, and that is the assumption of a 2-spin first-order process. Bloembergen et al.,[35] have pointed out the importance in spectral spin diffusion of some of the higher-order multi-spin processes. In spectral diffusion such multiple-spin processes are of importance, because they can cover big steps in the spectral domain. In the spatial domain such processes have no special advantage, but must still be considered since, their rates are functions of higher powers of the concentration of F centers than is the case for the process we have considered already.

The step times for the higher order processes differ from that of the assumed process by multiples of the factor $(\sum_j H_{ij}^2)_{av}/\Delta H^2$. $\sum_j$ represents a summation over intermediate states. H_{ij}^2 represents the interaction between the state i and an intermediate state j. ΔH^2 is the mean-square amount by which the intermediate states do not conserve energy. In units of magnetic field, ΔH^2 is about $(45)^2$ gauss^2, while at a concentration of 10^{18} F centers/cc, $(\sum_j H_{ij}^2)_{av}$ is about 10^{-2} gauss^2 according to Kip, Kittel, Levy, and Portis.[2] Therefore, it is concluded that the assumption of a two-spin first-order process is reasonable.

If the concentration dependence of $W(t)$ in Fig. 2 represents a spin diffusion process, with an impurity system being the ultimate thermal contact with the lattice, one further implication comes from the data. The fact that 3×10^{18} F centers/cc are relaxed at the rate of 3×10^{-2}/sec or faster imposes a condition on the permissible concentration and T_1 of the impurity system, which must fit into any future identification of the important impurity paramagnetic species in such samples. The condition can be stated roughly as

$$C_{imp}/(T_1)_{imp} > 10^{17} \text{ sec}^{-1} \text{ cm}^{-3}.$$

[31] A. M. Portis, Phys. Rev. **104**, 584 (1956).
[32] P. W. Anderson, Phys. Rev. **109**, 1492 (1958).
[33] B. Herzog and E. L. Hahn, Phys. Rev. **103**, 148 (1953).
[34] W. G. Clark, thesis, Cornell University, 1961 (unpublished).
[35] N. Bloembergen, S. Shapiro, P. S. Pershan, and J. O. Artman, Phys. Rev. **114**, 445 (1959).

Although there is no obvious connection between the two experiments, the observed concentration dependence of the relaxation time of the F center may be related to the finding of Lüty[36] that there is a concentration dependence of the F-center luminencence. Lüty finds that at a concentration of 10^{18}/cc the radiationless transitions are five times as probable as the radiative, while at low concentration the radiative transition predominates.

B. Crystals Containing Derived Centers

Figures 5–7 show plots of the initial recovery rates as a function of the concentrations of M, N, and R centers. It is assumed that the initial rate most sensitively reflects the effects of any process which increases the recovery rate. Plots of the rate associated with the point at which the recovery curve has fallen to $1/e$ of its initial value are consistent with the plots of the initial rate.

Each of these three figures shows qualitatively the same result. The variations of the recovery rate do not vary monotonically with the M-center concentration. The possibility of either N centers or R centers affecting the recovery rate is more likely. The recovery rate varies roughly as the second power of the R- or N-center concentration in Figs. 5 and 6. In Fig. 7 the recovery rate is not so sensitive to the R- or N-center concentration.

As mentioned previously, a thermal bleach of 15 min at 150°C was always found to restore the unbleached recovery rate to crystals which had been bleached.

It should also be pointed out that as the recovery rate was increased by optical bleaching its temperature dependence weakened and vanished.
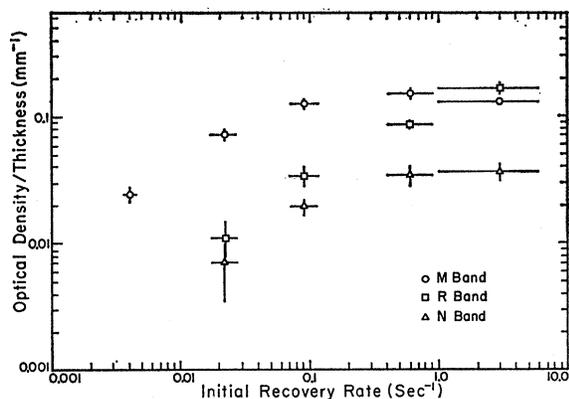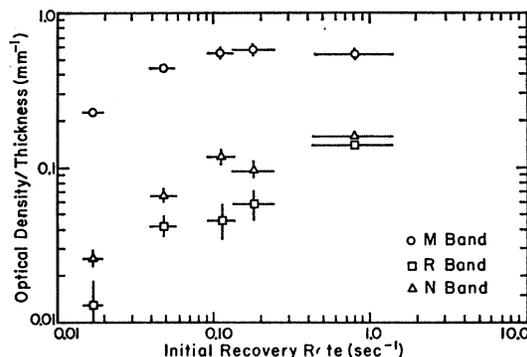

FIG. 6. Derived center concentrations, as measured by the ratios of optical densities to sample thickness, versus initial recovery rates. The recovery rates were measured at 2.0°K in a field of 3500 gauss. The derived center concentrations were varied by varying the temperature of a 15-min thermal bleach. Starting with the lowest recovery rate, the thermal bleaching temperatures were: 133, 118, 104, 94, and 79°C. The optical measurements were performed at the reduced temperature. Before bleaching, the additively colored crystals used had an F-center density of 2×10^{17}/cc.

Either the derived centers cause the increase in $W(t)$, or they merely accompany the increase. The experimental information is insufficient to decide between these two alternatives. The work of Moran, Christensen, and Silsbee[37] provides a warning as to the caution required in assigning a cause-and-effect relationship. In that work, deviations from the Portis[11] theory of the
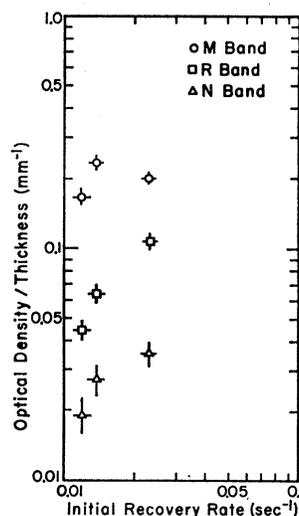

FIG. 7. Derived center concentrations, as measured by the ratios of optical densities to sample thickness, verus initial recovery rates. The recovery rates were measured at 2.0°K in a field of 3500 gauss. The derived center concentrations were varied by varying the length of an optical bleach during which the crystal was maintained at 0°C. Starting with the lowest recovery rate, the optical bleaching times in hours were: 0.5, 1, and 2. The optical measurements were performed at the reduced temperature. Before bleaching, the x-irradiated crystals used had an F-center density of 8×10^{16}/cc.

FIG. 5. Derived center concentrations as measured by the ratios of optical densities to sample thickness verus initial recovery rates The recovery rates were measured at 2.0°K in a field of 3500 gauss. The derived center concentrations were varied by varying the length of an optical bleach during which the crystal was maintained at 0°C. Starting with the lowest recovery rate, the optical bleaching times in hours were: 0, 1.5, 3, 6, and 11. The optical measurements were performed at room temperature. Before bleaching, the additively colored crystals used had an F-center density of 2×10^{17}/cc.

[36] F. Lüty (private communication).

[37] P. R. Moran, S. H. Christensen, and R. H. Silsbee, Phys. Rev. 124, 442 (1961).

saturation of inhomogeneously broadened lines were correlated with the optical absorption of the various derived centers. The correlation of effect with center would have been similar to that of the work presented here, if the optical bleaching had been carried only as far as it has been in this work. For longer bleaching times, they find that the optical absorption reaches saturation values, but the deviations from the Portis theory continue to increase with further bleaching.

Since the increased $W(t)$ in the optically bleached crystals is temperature independent, the limiting coupling must be to an intermediary between the F center and the lattice. Since the entire, not just initial recovery of the spin system is accelerated by a short optical bleach, all spins must in some way be affected by such a bleach. In the framework of spin diffusion as proposed in the previous discussion, such a temperature-independent universal increase of $W(t)$ could be accounted for in two ways. The optical bleaching may produce a general agglomeration of the color centers, a possibility which the appearance of the derived centers favors. With such an agglomeration, the spin-diffusion process would be greatly enhanced by the increase in the F center to F center dipole-dipole coupling which would accompany the reduction in spacing. (It is also possible that the spin diffusion is enhanced by a reduction of T_2 arising from *electronic* interaction of the F centers, in addition to the enhanced magnetic coupling.) Alternatively, one of the derived centers might be paramagnetic and have a short relaxation time. In this latter case, the increase of $W(t)$ would be a result of the reduced distance a spin would need to diffuse before being relaxed.

One can present a reasonably good case that the second alternative, namely, one or more derived paramagnetic species having a very short T_1, is not operative. The data of Fig. 5 show that the relaxation rate is increased by at least a factor of 10^3 from the rate of the pure F centers at the same concentration. With longer bleaching, this factor will apparently be even larger. Since the concentration of a paramagnetic derived center is certainly smaller than the F-center concentration at this stage of the optical bleaching, a T_1 for the derived center at least 10^4 shorter than for the F center is implied. It seems unlikely that a relaxation mechanism would be available which would simultaneously provide such an effective relaxation at 2°K for the derived center and such a weak relaxation for the F center, since most of their direct interactions with the lattice are probably similar.

The argument in the preceding paragraph does not apply to one possible class of "derived centers," namely, impurity paramagnetic ions whose valence has been changed by trapping electrons freed in the optical bleach. We have other grounds for believing that such defects were not affecting the relaxation. The thermal bleaching experiments summarized in Fig. 6 would require such a paramagnetic center to have thermal

bleaching properties essentially identical to those of the F coagulate centers. Such a state of affairs is unlikely.

Since the reasoning in the previous two paragraphs is by no means unopen to argument, we investigate how we would expect $W(t)$ to depend on concentration of a rapidly relaxed impurity, if the diffusion to a rapidly relaxing derived center were operative. This dependence can be easily obtained with a simple model of Bloembergen[28] for spin diffusion. In this model each rapidly relaxed impurity is assumed to bring about the relaxation of these spins within a radial distance R of itself, where R is roughly $\frac{1}{2}$ the average impurity spacing. $1/R$ then varies as the $\frac{1}{3}$ power of the concentration and the relaxation rate varies as the $\frac{2}{3}$ power of the concentration.

Such a concentration dependence is not consistent with either the N- or M-center concentration dependences of Figs. 5 and 6. The limited data of Fig. 7 for dilute x-irradiated crystals are closer to agreement with this $\frac{2}{3}$ power dependence. But, as in the work of Moran *et al.*, there is no clear correlation between the relaxation enhancement and the concentration of any single center.

CONCLUSIONS

We can sum up, fairly concisely, our experimental results for the low-temperature relaxation behavior of the pure F-center system in the Harshaw crystals used.

(1) For the dilute system $(C_F \approx 8 \times 10^{16}/\text{cc})$, T_1 is independent of external field H_0 from 1750 to 3500 gauss. The relaxation time appears to be inversely proportional to the temperature T, governed by the relation $T_1T = 1.0 \times 10^3$ sec-K°. The work of McAvoy *et al.*, with a product $T_1T = 2.7 \times 10^3$ sec-K°, demonstrates that the relaxation rate in our dilute crystals is governed by an impurity system.

(2) At F-center concentrations above 8×10^{16}, the T_1 becomes strongly concentration dependent, and a spin-diffusion mechanism is consistent with the temperature-independent and concentration-dependent T_1. In more pure crystals, with such a mechanism operative, the concentration dependence would only appear at higher F concentrations. The breakover point will give a measure of paramagnetic impurity concentration in the crystal.

For the derived centers, the T_1 measurements reported here yield several qualitative bits of information.

(1) The relaxation of the whole F-center system, in both x-rayed and additively colored crystals at concentrations of about 10^{17}–10^{18} F centers/cc is accelerated by a short optical bleach of the F band. Arguments have been presented to show that this shortening probably arises from a general coagulation of F centers, with a concomitant enhancement of the spin diffusion process. (Work on effects of bleaching in more pure crystals would help clarify this situation.) The alternative explanation for the bleaching enhancement involving production of derived paramagnetic centers with short T_1

is argued to be probably not correct. The relaxation rate continues to increase with optical bleaching over the full range of our experiments. Since the M-center concentration goes through a maximum within this range, we conclude that the M center plays no direct role in the relaxation enhancement.

(2) A thermal bleach at 150°C, which removes the optical absorption bands of M, R, and N, also restores the resonance relaxation rate to its value prior to optical bleaching. Hence, we conclude that the optical bleaching produces no significant *irreversible* changes in the spatial distribution of F centers.

Although they give no detailed information about the nature of the derived centers, our results are consistent with a picture of F-center coagulation along the lines suggested by Pick. That is, the various optical absorption bands result mainly from larger and larger agglomerates of F centers formed as a result of optically excited migration of F centers. As in the experiments of Moran *et al.*, we find little evidence for existence of one or more paramagnetic centers with resonance properties significantly different from those of the F center. Some of the derived centers are undoubtedly paramagnetic. It seems likely to us that these will be more fruitfully described as perturbed F centers (perturbed because of close association with other F centers) rather than as different entities.

Cooperative Optical Absorption in Solids

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A discussion is given of a mechanism for resonance energy transfer in the absorption of light by a pair of neighboring ions in a crystal, as recently demonstrated by Varsanyi and Dieke. An estimate of the probability for this process is given.

IN a beautiful experiment recently published Varsanyi and Dieke[1] have conclusively demonstrated the optical absorption of a photon by a pair of atoms in cooperation. The experiment consisted of detecting resonance fluorescence from a given state of a Pr^{3+} ion in a crystal irradiated in several photon wavelengths which a single Pr^{3+} ion does not absorb, but which correspond to the sum of the excitation energy of the emitting state and that of discrete lower excited states. It is clear that a "very tight binding" description is applicable, since the pertinent transitions occur in well shielded inner shells, and since, experimentally, the transition energies remain accurately unchanged from the sum of the individual excitation energies. The implications of this process on optical pumping were noted by the authors.

Some indication of a similar process may also have been observed by Milgram and Givens.[2]

The purpose of this note is to discuss the probable mechanism responsible for this effect, and to estimate its probability.

First, let us comment on why this process is an unusual one. It is clear that, to an excellent approximation, the initial electronic state of the crystal can be written as an antisymmetrized product of Heitler-London wave functions, with each ion in its ground state, and that after absorption of the photon two ions, A and B, are excited. That is, the final state is . . . $\psi_a \varphi_b$ . . ., differing from the initial state only in changes from . . . $\psi_o \varphi_o$ . . . The perturbing Hamiltonian associated with the incident radiation is of the form $\sum_l A(r_l) \cdot \nabla_l$, or $\sum_l e(r_l) \cdot r_l$, where r_l is the positions of the lth electron, A is the vector potential, and e is the electric field multiplied by the electronic charge. The atomic wave functions ψ_o and ψ_a for atom A (also φ_o and φ_b for B)) are orthogonal, so it is clear that one-electron operators cannot directly induce transitions involving more than one atom. Let us simplify the problem for clarification. Suppose each

[1] F. Varsanyi and G. H. Dieke, Phys. Rev. Letters **7**, 442 (1961).
[2] A. Milgram and M. P. Givens, Phys. Rev. **125**, 1506 (1962).
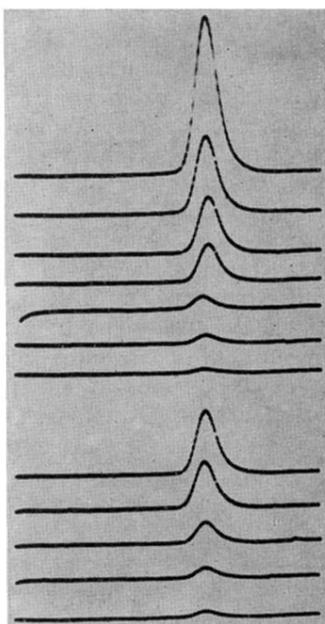
FIG. 1. Electron spin resonance signals obtained for various lengths of the recovery period following the saturation of the resonance. From top to bottom the lengths of the recovery periods in seconds were: 2600, 350, 200, 110, 25, 15, 5, 150, 50, 20, and 10. These data were obtained using an x-irradiated crystal containing 8×10^{16} F centers/cc. The relaxation took place in a field of 3500 gauss at a temperature of 1.4°K.