

$= \pm 1, \Delta S_{jz} = 0$  occur for

$$\begin{aligned} |+\frac{1}{2}, +\frac{1}{2}\rangle \leftrightarrow |-\frac{1}{2}, +\frac{1}{2}\rangle & \text{ at } h\nu = g_{11}\beta H + Am + \frac{1}{2}a_{ij} \\ & + b_{ij}^2/4Am + \{I(I+1) - m^2\}B^2/2g_{11}\beta H, \\ |+\frac{1}{2}, -\frac{1}{2}\rangle \leftrightarrow |-\frac{1}{2}, -\frac{1}{2}\rangle & \text{ at } h\nu = g_{11}\beta H + Am - \frac{1}{2}a_{ij} \\ & + b_{ij}^2/4Am + \{I(I+1) - m^2\}B^2/2g_{11}\beta H. \end{aligned}$$

These occur as satellites on the hyperfine lines of isolated ions at

$$h\nu = g_{11}\beta H + Am + \{I(I+1) - m^2\}B^2/2g_{11}\beta H.$$

Transitions in which

$$\Delta S_{iz} = 0, \quad \Delta S_{jz} = \pm 1$$

occur at

$$h\nu = g_{11}\beta H \pm \frac{1}{2}a_{ij},$$

but these are not observed in our experiments as they are too weak.

The simplest way to derive the satellite line positions when  $H$  is perpendicular to the crystal axis is to interchange  $S_z$  and  $S_x$  in (A1). The terms in  $S_{i+}S_{j+}$  and  $S_{i-}S_{j-}$  may be neglected as they produce only very small energy shifts, so that one obtains a new spin Hamiltonian which is identical to (A1) with  $g_{11}$  replaced by  $g_{\perp}$ ,  $a_{ij}$  by  $b_{ij}$ ,  $b_{ij}$  by  $\frac{1}{2}(a_{ij} + b_{ij})$ , and when there is hyperfine structure  $A$  is replaced by  $B$ .

## Spin-Lattice Relaxation of $F$ Centers in KCl: Interacting $F$ Centers

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Spin relaxation of  $F$  centers in KCl has been observed by a field-sweep inversion recovery technique at liquid-helium temperatures. Intrinsic relaxation behavior was reported previously. Various kinds of extrinsic behavior are reported here. They include distorted resonance line shapes, unusually fast relaxation, and unusual field and temperature dependences of the relaxation. Such effects were always seen at low temperatures and low fields after the following treatments: high  $F$ -center concentrations, light exposure, the addition of certain impurities, plastic deformation, and low-temperature gamma irradiation. A model is presented which explains all of these effects and is consistent with the extensive lore involving the properties of  $F$  centers. This model identifies the extrinsic relaxation process as one compounded of spatial diffusion of Zeeman energy in the  $F$ -center system and cross relaxation from  $F$  centers to rapidly relaxing centers. These rapidly relaxing centers are composed of loosely bound clusters of  $F$  centers, which can be formed in a variety of ways.

### INTRODUCTION

IN an earlier paper (hereafter referred to as I) we presented measurements of the spin-lattice relaxation time of isolated  $F$  centers in KCl crystals as a function of temperature and magnetic field.<sup>1</sup> The measurements were interpreted in terms of relaxation by phonon modulation of the hyperfine coupling between the  $F$ -center electron and its surrounding nuclei. This interpretation is consistent with all the observed results except for what we term "extrinsic" behavior which varies from sample to sample, being most evident at low temperatures and low magnetic fields where the intrinsic relaxation times are very long.

The purposes of this paper are several: (1) to present our experimental data showing a wide variety of extrinsic behavior; (2) to show that the extrinsic behavior is in general due to interactions of the  $F$  centers with other paramagnetic centers; (3) to identify the paramagnetic centers which are involved; (4) to discuss the complex series of steps by which the  $F$  center relaxes

when its behavior is extrinsic; and (5) to identify those steps which must be dominant to explain the various kinds of extrinsic behavior which have been observed.

### THEORY

The intrinsic spin-lattice relaxation processes, which were considered in detail in Paper I, are either independent of magnetic field strength  $H$  or become more rapid as  $H$  is increased. A striking property of the extrinsic behavior, to be discussed below, is the reverse of this, the slowing of relaxation as  $H$  is increased. This behavior can be explained in two ways.

One possibility involves cross relaxation of  $F$  centers to a rapidly relaxing paramagnetic center whose  $g$  value differs from that of the  $F$  center. Under these conditions the two resonance lines overlap more and more as  $H$  is decreased, leading to a faster transfer of Zeeman energy from the  $F$  center to the other center which can then rapidly transfer it to the lattice. Processes of this kind have been discussed by Bloembergen *et al.*<sup>2</sup>

<sup>1</sup>D. W. Feldman, R. W. Warren, and J. G. Castle, Jr., *Phys. Rev.* **135**, A470 (1964).

<sup>2</sup>N. Bloembergen, S. Shapiro, P. S. Pershan, and J. O. Artman, *Phys. Rev.* **114**, 445 (1959).

Another possibility which can explain the field dependence involves spin lattice relaxation due to the modulation of the interactions among the  $F$  centers, a process which increases in importance as the Zeeman energy of the  $F$  center is reduced in comparison with the interaction energy. Calculations of the magnitude and of the  $H$  and temperature ( $T$ ) dependences of this process have been carried out by Kronig and Bouwkamp<sup>3</sup> and Caspers<sup>4</sup> who find an exponential dependence of the relaxation time on the ratio of the Zeeman energy of a center to its interaction energy with other centers. Temperley<sup>5</sup> and Orbach,<sup>6</sup> on the other hand, calculate a quadratic dependence. All of these calculations are in qualitative agreement with the observed  $H$  dependence. Broer<sup>7</sup> and Wright,<sup>8</sup> however, have also discussed this problem with quite different results.

Due to the disagreement among the various authors and due to the complexity of the calculations involved, no reliable estimate is available of the magnitude of such relaxation processes. Because of this, no estimate can be made of interesting physical parameters such as the separation between centers for which this relaxation process becomes significant. One conclusion that can be drawn from these references,<sup>3-8</sup> however, is that since the interaction energy under consideration is due to magnetic dipole-dipole forces or exchange interactions, it is very strongly dependent on the spacing between centers. The relaxation will therefore occur predominantly at sites of unusually close spacing of the dipoles. These considerations have led to proposals such as that of Van Vleck<sup>9</sup> in which spin-spin-induced relaxation occurs rapidly at a small number of clusters of centers while the other centers relax by transferring their Zeeman energy to the clustered centers.

### Steps Involved in Relaxation

Consider now what happens following a perturbation that heats up the spin system. Energy is transferred from the spin system to the lattice by relaxation processes. Relaxation by either of the field-dependent processes mentioned above involves the same complex series of primitive steps.<sup>10</sup> Each step will be characterized by a time identified as follows:

$\tau_d$ : the time taken for the spatial diffusion of the Zeeman energy of an  $F$  center up to the vicinity of a fast relaxing center, which will be called an  $X$  center for

convenience. The diffusion occurs by means of a series of simultaneous flips of two neighboring  $F$  centers. It conserves Zeeman energy, is independent of  $T$  and  $H$ , and is strongly concentration dependent.<sup>10</sup>

$\tau_t$ : the time taken for the direct energy transfer to an  $X$  center from a nearby  $F$  center. This process involves a simultaneous spin flip in which Zeeman energy is conserved.  $\tau_t$  is independent of temperature.<sup>2</sup>

$\tau_X$ : the time taken for the transfer of energy from an  $X$  center to the lattice. Depending upon the model assumed for the  $X$  center,  $\tau_X$  can depend in various ways on  $H$  ( $H^0, H^2, H^4$ , etc.). Its dependence on  $T$  will be at least  $T^{-1}$  and, at low  $H$ , is likely to be  $T^{-7}$ ,  $T^{-9}$ , or exponential.<sup>1</sup> If the  $X$  center is inhomogeneously broadened as the  $F$  center is, we must consider the possibility that each part of the  $X$  line relaxes with a different characteristic time.<sup>11</sup>

Each of the above steps must be taken *sequentially* during the extrinsic relaxation of the  $F$  center according to our model. Consequently the relaxation will occur in a time which is a suitable sum of  $\tau_d$ ,  $\tau_t$ , and  $\tau_X$  and which will, in general, be different in the various parts of the line. This will cause a distorted  $F$  line during relaxation. There are additional relaxation processes, characterized by a time  $\tau_s$ , which do not conserve Zeeman energy but lead to spectral diffusion within the  $F$  and  $X$  lines.<sup>12</sup> Such processes oppose any distortion and tend to restore the lines to their "normal" shape. The experimentally determined "hole healing time"  $\tau_{hh}$ , to be discussed below, is a measure of  $\tau_s$ .

### Relaxation with Different Limiting Steps

In this section we discuss the implications of assuming that a suitable average of one of the times  $\tau_d$ ,  $\tau_t$ , or  $\tau_X$  is enough larger than the others so that it alone determines the relaxation. We will use the symbol  $\bar{\tau}$  to indicate this average. It is a spatial average for all of those  $F$  centers in the crystal with a given hyperfine environment.

#### *Diffusion Limited*

If  $\bar{\tau}_d > \bar{\tau}_t$  and  $\bar{\tau}_X$ , diffusion controls the relaxation. If  $\bar{\tau}_s$  is long, the Zeeman energy in each part of the  $F$ -center line diffuses to the  $X$  center independently of the other parts of the  $F$  line. Since the concentration of  $F$  centers corresponding to the center of the line is higher than elsewhere in the line, and since spatial diffusion is concentration dependent, the center of the  $F$  line will relax more rapidly than the wings. If, however,  $\bar{\tau}_s$  is short compared to  $\bar{\tau}_d$ , this line distortion effect will be washed out and an average  $\bar{\tau}$  will be measured for the whole line. Since  $\bar{\tau}_d$  does not differ widely over the line, the average  $\bar{\tau}$  will not be much different

<sup>3</sup> R. De L. Kronig and C. J. Bouwkamp, *Physica* **5**, 521 (1938).

<sup>4</sup> W. J. Caspers, *Physica* **26**, 778 (1960).

<sup>5</sup> H. N. V. Temperley, *Proc. Cambridge Phil. Soc.* **35**, 256 (1938).

<sup>6</sup> R. Orbach, *Proc. Roy. Soc. (London)* **A264**, 485 (1961).

<sup>7</sup> L. J. F. Broer, *Physica* **10**, 801 (1943).

<sup>8</sup> A. Wright, *Phys. Rev.* **76**, 1826 (1949).

<sup>9</sup> J. H. Van Vleck, in *Advances in Quantum Electronics*, edited by Jay R. Singer (Columbia University Press, New York, 1961).

<sup>10</sup> A similar sequence of steps has been discussed by Jeffries [C. D. Jeffries, *Dynamic Nuclear Orientation* (Interscience Publishers, Inc., New York, 1963), Chap. 4.] for the analogous problem in nuclear relaxation.

<sup>11</sup> M. F. Deigen and V. Ya. Zevin, *Zh. Eksperim. i Teor. Fiz.* **39**, 1126 (1960) [English transl.: *Soviet Phys.—JETP* **12**, 785 (1961)].

<sup>12</sup> A. M. Portis, *Phys. Rev.* **104**, 584 (1956).

from  $\bar{\tau}_d$  at the center of the line and will be independent of  $\bar{\tau}_s$  if  $\bar{\tau}_s$  is short enough. In any case, the relaxation time will be independent of  $T$  and  $H$  but strongly concentration dependent.

#### *X-Center Limited*

If  $\bar{\tau}_X > \bar{\tau}_d$  and  $\bar{\tau}_t$ , the relaxation of the  $X$  center controls the relaxation. If  $\bar{\tau}_s$  is long, each part of the  $F$  line will be in equilibrium with a corresponding part of the  $X$  line. The various parts of the  $X$  line must serve as channels, not only for their own relaxation, but also for that of the  $F$  centers in equilibrium with them. The relaxation time for each part of the  $F$  line will, therefore, be given by  $\bar{\tau} = \bar{\tau}_X(C_F + C_X)/C_X$ , where  $\bar{\tau}_X$  is the  $X$ -center relaxation time and  $C_F$  and  $C_X$  are the  $F$ - and  $X$ -center concentrations, all corresponding to a fixed position in the  $F$  line. If the  $F$  and  $X$  lines do not exactly overlap, so that  $C_F/C_X$  is not the same for the several hyperfine environments, it can be seen that there will be a resulting distortion of the  $F$ -line shape. Again, a short  $\bar{\tau}_s$  will obscure this effect and give an average  $\bar{\tau}$ . Since  $C_F/C_X$  may be field-dependent due, for instance, to differing  $g$  values, a field-dependent relaxation time may be expected. Strong temperature and  $F$ -center concentration dependences will occur, high concentrations leading to long relaxation times, the inverse of the more usual relationship.

#### *Cross Relaxation Limited*

If  $\bar{\tau}_t > \bar{\tau}_d$  and  $\bar{\tau}_X$ , energy transfer between the  $F$  and  $X$  centers controls the relaxation. The transfer time  $\bar{\tau}_t$ , can vary by many orders of magnitude over the  $F$  line, being determined by its overlap with the  $X$  line.<sup>2</sup> In an extreme case, when the  $X$  and  $F$  lines overlap only in their far wings,  $\bar{\tau}_t$  may be very large except at the edge of the  $F$  line nearest the  $X$  line. This will give a very distorted line shape during recovery if  $\bar{\tau}_s$  is long. If  $\bar{\tau}_s$  is short, spectral diffusion will play a crucial role in relaxing the rest of the line. Spectral diffusion should therefore be considered as an essential step in any relaxation process where  $\bar{\tau}_t$  is longer than  $\bar{\tau}_d$  or  $\bar{\tau}_X$  anywhere in the line.

### EXPERIMENTAL TECHNIQUES

The various measurements involved in this experiment, such as the determination of relaxation time and temperature, were performed exactly as in Paper I. In brief, for relaxation time, the net magnetization of the  $F$  centers was perturbed and its recovery to the thermal equilibrium value was monitored with a 9 Gc/sec EPR spectrometer; for temperature, the vapor pressure of liquid helium in contact with the sample was measured.

The techniques of crystal preparation and sample coloration were the same as in I except as noted below. Crystals referred to as "HR" were prepared in a horizontal zone refiner, and were identical to those used in I. Those referred to as "VG" were grown in a vertical

floating-zone apparatus<sup>13</sup> because of the convenience afforded by this technique for the addition of impurities. Those crystals referred to as "SP" were formed on a seed crystal as it was slowly withdrawn from a melt. Crystals were obtained from the Harshaw Chemical Company for comparison purposes. Samples were colored by additive coloring, electrolytic coloring, and gamma-irradiation techniques. The details of these procedures are identical to those given in I.

It was found desirable to measure the concentration of certain defect centers in addition to the  $F$  center. The measurement was performed optically with a Cary Model 14 spectrophotometer after the relaxation time determinations were completed. The limit of detectability for defect centers was about  $2 \times 10^{13}$  cm<sup>-3</sup>. If the presence of a center is not reported, its concentration was below this limit (except where noted). The Cary spectrophotometer was also used for the series of irradiations reported below.

Careful optical measurements of a survey nature were made on various samples at room temperature, both before and after coloring, for wavelengths longer than 200 m $\mu$ . This was done to search for the presence of unknown impurities or defects. The only absorption bands that were detected other than the  $F$  and the  $M$  bands were a very weak impurity band at 247 m $\mu$ , discussed in Paper I, and the "OH" and "O<sub>2</sub>" bands<sup>14,15</sup> found in Harshaw crystals and in some of our crystals which had been purposely doped. No absorption band corresponding to a trapped hole center was ever detected.

Careful microwave measurements of a survey nature were occasionally made at various temperatures both before and after coloring. The O<sub>2</sub> resonances<sup>15</sup> were observed when the corresponding optical band was present; the  $F$ -center relaxation time was observed to be very short in these samples. No other resonances were observed; in particular, the  $V_k$ - and  $H$ -center resonances<sup>16,17</sup> that were expected to show up in the gamma-irradiated crystals were not observed. The lack of these resonances is consistent with the observations that the production of  $V_k$  centers is very inefficient in crystals like ours having low concentrations of heavy metal impurities,<sup>16,18</sup> and that the production of  $H$  centers is inefficient at low irradiation levels.<sup>17</sup>

### RESULTS

The special sample treatments that were invariably found to give extrinsic relaxation times, i.e., ones

<sup>13</sup> R. W. Warren, Rev. Sci. Instr. **33**, 1378 (1962).

<sup>14</sup> H. W. Etzel and D. A. Patterson, Phys. Rev. **112**, 1112 (1958).

<sup>15</sup> W. Känzig and M. H. Cohen, Phys. Rev. Letters **3**, 509 (1959).

<sup>16</sup> T. G. Castner and W. Känzig, Phys. Chem. Solids **3**, 178 (1957).

<sup>17</sup> W. Känzig and T. O. Woodruff, Phys. Chem. Solids **9**, 70 (1958).

<sup>18</sup> C. J. Delbecq, B. Smaller, and P. H. Yuster, Phys. Rev. **111**, 1235 (1958).

shorter than the intrinsic time reported in I, are: (1) the introduction of a sufficiently high  $F$ -center concentration, (2) the exposure of colored crystals to light absorbed in the  $F$  band, (3) the addition to the crystal of OH impurities as it was grown or, apparently, as it was colored, and (4) the production of  $F$  centers by gamma irradiation at 77°K with no warming of the sample before measurement of its relaxation time. Observations involving the first two effects have been reported by Ohlsen and Holcomb<sup>19</sup> and by Holton and Blum.<sup>20</sup> The measurements illustrating these effects are presented below in Figs. 1-4 and in Table I.

Two additional important effects are discussed below: (5) the spontaneous distortion of the  $F$ -center resonance line sometimes observed during relaxation, and (6) the relaxation of distortions purposely introduced in the

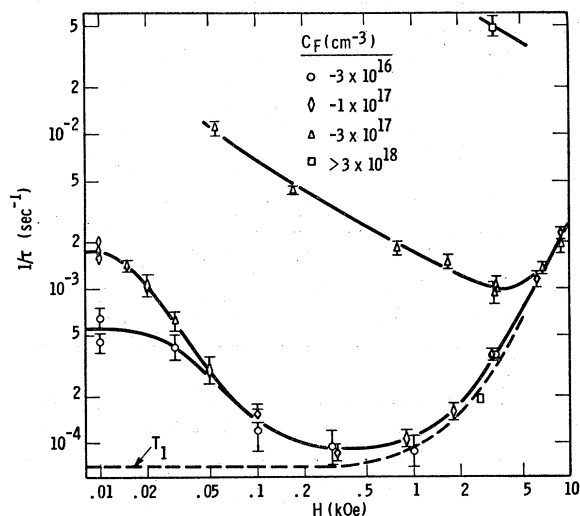


FIG. 1. Field dependence of  $1/\tau$  at 4.2°K for different  $F$  center concentrations. Measurements are shown for four samples, labeled A in Table I, prepared in the same way and differing only in their  $F$ -center concentrations. The dashed curve labeled  $T_1$  corresponds to the intrinsic relaxation time for isolated  $F$  centers discussed in Paper I.

line. Results are also presented of the effect on the extrinsic relaxation time of variations in temperature, crystal orientation, and stress.

### Concentration Effect

Measured values of  $\tau$ , the  $F$ -center relaxation time constant, versus  $H$ , the magnetic field strength, at 4.2°K are shown in Fig. 1 for four samples colored in the same way (electrolytically) from the same starting material (HR) but differing in their  $F$ -center concentration. Table I, Sec. A, includes information about the

<sup>19</sup> W. D. Ohlsen and D. F. Holcomb, Phys. Rev. **126**, 1953 (1962).

<sup>20</sup> W. C. Holton and H. Blum, Phys. Rev. **125**, 89 (1962).

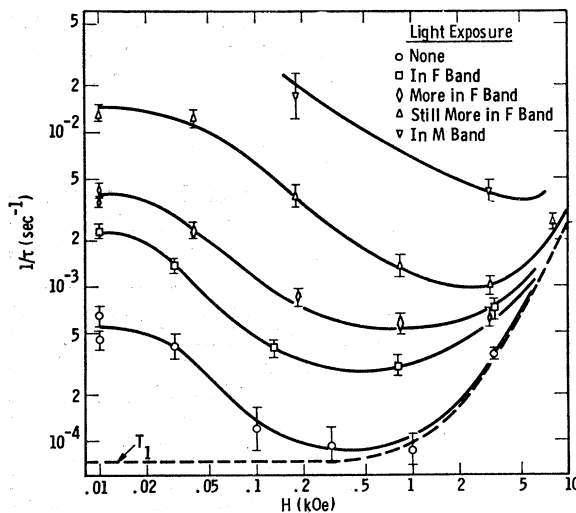


FIG. 2. Field dependence of  $1/\tau$  at 4.2°K for different light exposures. Measurements are shown for a single sample, labeled B in Table I, after four successive exposures to light. The dashed curve labeled  $T_1$  corresponds to the intrinsic relaxation time.

preparation and subsequent handling of these crystals as well as the optically determined concentrations of the major defect centers,  $F$ ,  $M$ , and  $OH$ . A high  $F$ -center concentration is seen to be correlated with both a high  $M$ -center concentration and a drastically shortened low field relaxation time. At sufficiently low  $F$  center concentrations, the relaxation time approaches the intrinsic value described in Paper I and shown in Fig. 1 by a dashed line labeled  $T_1$ .

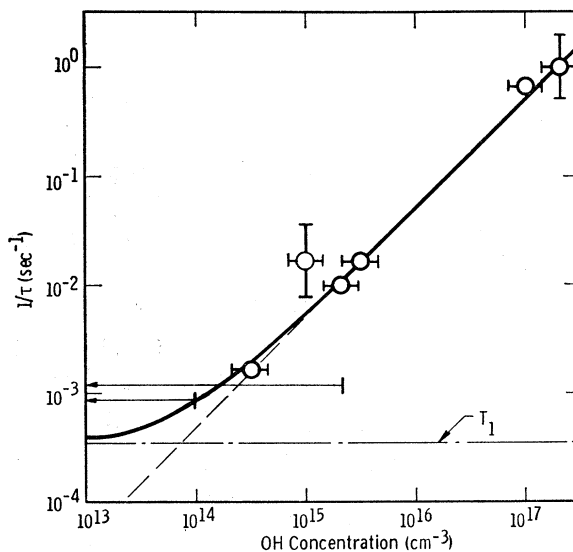


FIG. 3. Dependence of  $1/\tau$  on OH concentration. Measurements are shown for eight samples, labeled C and D in Table I, colored in the same way to the same  $F$ -center concentration from starting materials of differing OH content. The broken curve labeled  $T_1$  corresponds to the intrinsic relaxation time. The arrows leading to the left indicate that the OH content of these samples could not be measured but was less than the value indicated by the vertical bar.

TABLE I. Relevant properties and treatments of special KCl samples. The A crystals and the B crystal were electrolytically colored after being grown in a horizontal zone refiner (HR). The C and D crystals were additively colored. The C crystals were grown in a vertical floating zone grower (VG). Crystals D6, D7, and D8 were grown by seed pulling (SP).

Sample	Grower	Crystal preparation		Light exposure after quenching	$C_F^a$ (cm <sup>-3</sup> )	$C_M^{a,b}$ (cm <sup>-3</sup> )	$C_{OH}^{a,c}$ (cm <sup>-3</sup> )	$\tau^d$ (sec)
		Gas	Additive					
A medium pale	HR	HCl	None	None	$3 \times 10^{16}$	$3 \times 10^{13}$ (VD)	$\leq 1 \times 10^{14}$	2800 <sup>e</sup>
A medium	HR	HCl	None	None	$1 \times 10^{17}$	$3 \times 10^{14}$ (VD)	$\leq 1 \times 10^{14}$	2800 <sup>e</sup>
A medium dark	HR	HCl	None	None	$3 \times 10^{17}$	$3 \times 10^{15}$	$\leq 1 \times 10^{14}$	110
A dark	HR	HCl	None	None	$> 3 \times 10^{18}$	$3 \times 10^{17}$	$\leq 1 \times 10^{14}$	20
B medium pale	HR	HCl	None	None	$3 \times 10^{16}$	$3 \times 10^{13}$ (VD)	$\leq 1 \times 10^{14}$	2800 <sup>e</sup>
				In <i>F</i> band	$3 \times 10^{16}$	$\sim 3 \times 10^{14}$	$\leq 1 \times 10^{14}$	1500
				More in <i>F</i> band	$3 \times 10^{16}$	$1 \times 10^{15}$	$\leq 1 \times 10^{14}$	1600
				Still more in <i>F</i> band	$3 \times 10^{16}$	$3 \times 10^{15}$	$\leq 1 \times 10^{14}$	1000
				In <i>M</i> band	$3 \times 10^{16}$	$1 \times 10^{15}$	$\leq 1 \times 10^{14}$	240
C1	VG	N <sub>2</sub>	160 ppm KOH	None	$\sim 1 \times 10^{17}$	not measured	$2 \times 10^{17}$	$\sim 1$
C2	VG	wet N <sub>2</sub>	None	None	$\sim 1 \times 10^{17}$	not measured	$1 \times 10^{17}$	1.5
C3	VG	N <sub>2</sub>	100 ppm BaCl <sub>2</sub>	None	$\sim 1 \times 10^{17}$	not measured	$2 \times 10^{15}$	100
C4	VG	N <sub>2</sub>	1000 ppm SrCl <sub>2</sub>	None	$\sim 1 \times 10^{17}$	not measured	$\leq 2 \times 10^{15}$	800
D5		Harshaw		None	$\sim 1 \times 10^{17}$	not measured	$3 \times 10^{15}$	60
D6	SP	N <sub>2</sub>	None	None	$\sim 1 \times 10^{17}$	not measured	$1 \times 10^{15}$	$\sim 60$
D7	SP	N <sub>2</sub>	1% SrCl <sub>2</sub>	None	$\sim 1 \times 10^{17}$	not measured	$3 \times 10^{14}$	600
D8	SP	HCl	None	None	$\sim 1 \times 10^{17}$	not measured	$\leq 1 \times 10^{14}$	1200

<sup>a</sup> For simplicity the *F*, *M*, and OH concentrations were all calculated from the measured absorption coefficient at 300°K and an assumed cross section of  $3 \times 10^{-16}$  cm<sup>2</sup>; the absorption coefficients are accurate to 10%.

<sup>b</sup> The  $C_M$  values labeled (VD) represent *M* center concentration too low to be measured; the values given were estimated from a relationship given by van Doorn (see Ref. 22).

<sup>c</sup> The OH absorption was measured before coloring.

<sup>d</sup>  $\tau$  was measured at 4.2°K and 3.5 kOe; the values are accurate to 20%.

<sup>e</sup> The value 2800 sec is the intrinsic time  $T_1$ .

### Light Effects

Measured values of  $\tau$ , the relaxation time constant, versus field at 4.2°K are shown in Fig. 2 for the sample of lowest *F*-center concentration discussed above. Table I, Sec. B, gives further details of this crystal and its treatment. The data show the influence of successive irradiations with light. The lowest curve of Fig. 2, corresponding to the longest relaxation time, was determined before any exposure of the crystal to light. The next three curves of progressively shorter relaxation times were measured after each of three successive room temperature irradiations by light absorbed in the *F* band. In addition to shortening the relaxation times, irradiation caused a steady increase in the *M*-center concentration of these crystals as is indicated in Table I. Other aggregate centers were presumably also formed, but at such low levels as to be undetectable.

The top curve of Fig. 2 resulted from an additional room temperature irradiation by light absorbed, in this case, in the *M* band. This exposure reduced the *M* band by a factor of 3, but shortened the relaxation time still further.

### Impurity Effect

The techniques of crystal preparation (reported in Paper I) that were found to be sufficient to achieve intrinsic relaxation times resulted in crystals with very low concentrations of both OH and divalent impurities. Conversely, impure crystals exhibiting short relaxation times usually contain relatively large amounts of both OH and divalent impurities. Special crystals were,

therefore, prepared in an attempt to study independently these two types of impurities. The observed

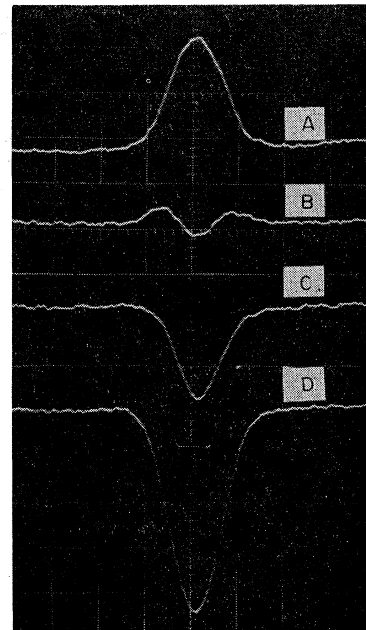


FIG. 4. Oscilloscope display of *F*-center absorption signal during recovery, showing a distorted line shape near saturation. *A* is the signal immediately after inversion; *B* is the signal near saturation showing the typical distortion; *C* occurs still later; and *D* is the signal when the spin system is in equilibrium with the lattice. The sample was prepared by gamma irradiation at low temperatures, and the measurements were taken at 1.2°K and 3.5 kOe. The *F*-center concentration was about  $2 \times 10^{17}$  cm<sup>-3</sup>.

relaxation times and other pertinent information for these crystals are given in Table I, Secs. C and D.

The C crystals were grown in a floating zone grower in a dry nitrogen atmosphere under identical conditions except that: C 1 had an addition of 160 ppm of KOH to its starting material; C 2 was grown in an atmosphere saturated with water; C 3 had an addition of 100 ppm of BaCl<sub>2</sub> to its starting material; and C 4 had an addition of 1000 ppm of SrCl<sub>2</sub> to its starting material. These four crystals were additively colored together to an *F*-center concentration of about  $1 \times 10^{17} \text{ cm}^{-3}$ .

The same coloring procedure was used for the group of D crystals. They differ from each other in the following respects: D 5 was a Harshaw crystal; D 6 was seed pulled in a dry nitrogen atmosphere; D 7 was seed pulled in dry nitrogen from a melt containing 1% SrCl<sub>2</sub>; and D 8 was seed pulled in an HCl atmosphere.

From Table I, Secs. C and D, it is apparent that there is a strong correlation between the relaxation times and the magnitudes of the OH band for both the C and D crystals. Figure 3 shows a plot of the reciprocal of the relaxation time constant  $\tau$  observed at 4.2°K and 3 kOe versus the OH concentration,  $C_{\text{OH}}$ , for the whole set of C and D crystals. The data are reasonably well described by the relationship  $1/\tau = 1/T_1 + \alpha C_{\text{OH}}$ , shown by the solid line in Fig. 3, where  $T_1$  is the intrinsic relaxation time and  $\alpha$  is a constant.

### Low-Temperature Gamma Irradiation

The limited number of samples colored by gamma irradiation at 300°K demonstrate a concentration effect consistent with that of the electrolytically colored crystals of Fig. 1.

The many samples irradiated at 77°K were purposely not warmed above that temperature until after the relaxation times had been measured at 4.2°K. Each of these showed the same anomalous behavior; even though their *F*-center concentrations were low (less than  $10^{17} \text{ cm}^{-3}$ ), their relaxation times were very short (less than 1 sec). Warming these samples to room temperature in the dark destroyed a large fraction of the *F* centers as determined both by optical absorption and microwave resonance measurements. The relaxation times when remeasured at 4.2°K were found to have increased drastically. Eventually, after being held at room temperature in the dark for many hours, the crystals gave relaxation times approximating the intrinsic value, and the *F*-center concentrations dropped further, to values about an order of magnitude below their initial values.

### Temperature Dependence

The extrinsic relaxation time was measured (as a function of magnetic field) at 2.1°K as well as 4.2°K for most of the samples discussed above. The precision of these measurements at fields other than 3 kOe was sufficiently poor ( $\pm 30\%$ ) so that only the following

weak statements can be made about the temperature dependence of the relaxation time: (1) As  $T$  increases, the relaxation time decreases; (2) the temperature dependence of  $1/\tau$  is less than proportional to  $T$ ; (3) this dependence appears to be somewhat different for different samples and magnetic field strengths.

### Orientation Dependence

The angle dependence of the relaxation time has been investigated in a number of crystals. No dependence of the relaxation time on crystal orientation has been observed.

### Elastic Deformation

Krupka and Silsbee<sup>21</sup> have shown that an *R* center is paramagnetic, has an anisotropic  $g$  value, and has a relaxation time which is very fast and is stress dependent. They found that a stress of about  $2 \text{ kg mm}^{-2}$  was sufficient to cause a large change in the relaxation time of the *R* center. Since an *R* center may be involved in the extrinsic *F*-center relaxation, it was suspected that the application of a stress might change the extrinsic relaxation time. Accordingly, stress experiments similar to those of Krupka and Silsbee were carried out.

A force was applied to selected crystals in the [110] direction and the extrinsic relaxation time was determined as a function of the stress. The maximum stress applied was about  $2.7 \text{ kg mm}^{-2}$ , approximately the yield strength of the crystal. The experiments were carried out at 3 kOe and for temperatures between 1.3 and 4.2°K. The crystals were oriented so that the magnetic field could be lined up in any direction in the (110) plane which was perpendicular to the applied stress. This was repeated for stress in the [100] direction. No changes in the relaxation times were observed within the experimental precision of  $\pm 20\%$ .

### Line Shape Distortions

As noted in Paper I, special attention was paid to the *F*-center line shape during its recovery from inversion. Midway in the recovery the spin system becomes momentarily saturated with no microwave absorption occurring. A careful examination of the line at this time is a sensitive test for distortions of its shape. When relaxation occurred with the intrinsic time constant, the usual line shape was seen with nothing strange occurring at saturation. When the relaxation was extrinsic, however, the resonance had on certain occasions a characteristic distortion during recovery as illustrated in Fig. 4. In Fig. 4, A is the resonance signal immediately after inversion, B is the signal near saturation illustrating this characteristic distortion, C occurs still later

<sup>21</sup> D. C. Krupka and R. H. Silsbee, Phys. Rev. Letters 12, 193 (1964).

in the relaxation and apparently exhibits the same distortion, and  $D$  is the signal occurring when the spin system is in equilibrium with the lattice and the distortion has disappeared. The signals in Fig. 4 were taken at 1.2°K and 3 kOe on a sample which had been plastically deformed several percent by compression in the  $[100]$  direction before being colored by gamma irradiation at room temperature to an  $F$ -center concentration of  $2 \times 10^{17}$  cm $^{-3}$ . This characteristic distortion always took the symmetric form shown in Fig. 4. A similar form was reported by Holton and Blum.<sup>20</sup>

The distortion was especially evident in samples prepared in one of three ways: (1) squeezing a crystal before coloring it by gamma irradiation at 300°K, (2) coloring a normal crystal by gamma irradiation at 77°K with the measurement of its spin relaxation being completed without further warming, and (3) coloring a crystal having a relatively high OH content by additive or electrolytic techniques. In such samples, the distorted signal occurring at nominal saturation, as in Fig. 4B, was as much as 20% of the signal height before inversion. Nonexponential recoveries from inversion were usually seen when the distorted signals were evident. Because of this, such samples have poorly defined relaxation times.

### Hole Healing

By suitable techniques, discussed in Paper I, one can invert the spin populations corresponding to only a part of the  $F$ -center line. This distorted  $F$ -center line will return to its normal shape in two ways, by the usual spin-lattice relaxation or by "hole healing" processes. The latter processes are distinguishable from the former since they cause a "hole" inverted in the  $F$  line to disappear by spreading out into the rest of the line. Figure 5 illustrates this process. One could measure a diffusion coefficient  $D$  for this spreading process, but, for simplicity, we determine the time  $\tau_{hh}$  taken for a hole 10 Oe wide to decay by diffusion to  $\frac{1}{3}$  of its original size. It can be shown that under these conditions and at high fields,  $D$  and  $\tau_{hh}$  are related by  $D\tau_{hh} \cong 200$  Oe $^2$ . Shown in Fig. 6 are plots of  $1/\tau_{hh}$  versus  $H$  made at 4.2, 2.1, and 1.3°K for two crystals. The crystal giving the lower curve has an  $F$ -center concentration of  $1 \times 10^{17}$  cm $^{-3}$ . It is the same crystal as the one shown in Fig. 1 indexed with diamonds. The crystal giving the upper curve in Fig. 6 has a higher  $F$ -center concentration. Due to the experimental difficulties involved in measuring small values of  $\tau_{hh}$ , the points shown on the upper curve were determined in the following indirect manner: Holes twice the usual width were inverted in the  $F$ -center line. The hole healing time was measured and  $\frac{1}{4}$  of that value was plotted in Fig. 6. This scaling step, appropriate for diffusion processes, allows a comparison with values obtained in the other way.

It can be seen from Fig. 6 that  $1/\tau_{hh}$  has the appearance of a sum of two terms, one of which increases as the

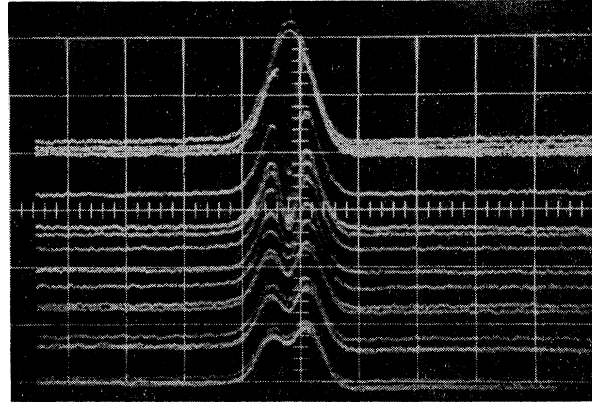


FIG. 5. Oscilloscope display of the recovery of a hole inverted in the  $F$ -center resonance line. Reading from the top of the picture to the bottom, two traces are shown of the normal line followed by a trace of the line immediately after its central portion was partially inverted. The remaining traces, taken at one-second intervals, show the recovery of the inverted hole. The sample was colored electrolytically to an  $F$ -center concentration of about  $3 \times 10^{17}$  cm $^{-3}$ . The measurements were made at 4.2°K and 3.5 kOe; the spin relaxation time was found to be several minutes.

field is increased and the other, as the field is decreased. Increasing the  $F$  center concentrations was always found to decrease  $\tau_{hh}$  without any alteration of its field dependence. Exposing a colored crystal to light caused a similar decrease in  $\tau_{hh}$  without any change in its field dependence. These observations for  $\tau_{hh}$  are clearly similar to the concentration and light effects on  $\tau$ , the spin-lattice relaxation time.

Figure 6 shows that  $1/\tau_{hh}$  is independent of temperature over the range investigated, 1.3–4.2°K. This is in contrast to the behavior found for  $\tau$ . Above about 10°K (depending upon crystal treatment)  $\tau$  is smaller than  $\tau_{hh}$  and relaxation occurs before hole healing can take place.

At 4.2°K and a field of 3 kOe,  $\tau/\tau_{hh} = 200 \pm 100$  for most of the crystals investigated. The rest of the crystals had a significantly smaller value of  $\tau/\tau_{hh}$  and included all of the crystals showing the characteristic distortion illustrated in Fig. 4.

### DISCUSSION OF RESULTS

A marked similarity is observed in the field dependence of the extrinsic relaxation times measured for crystals prepared with: (1) high  $F$ -center concentrations (shown in Fig. 1); (2) light exposure (shown in Fig. 2); and (3) high OH concentrations (measured but not shown). The temperature dependences are also similar for these treatments. In view of this, an attempt will be made to find one explanation for the extrinsic relaxation which is common to all of these as well as most of the other extrinsic effects.

### Identification of the $X$ Center

To affect the relaxation time constant  $\tau$ , the above crystal preparations must alter one or more of the

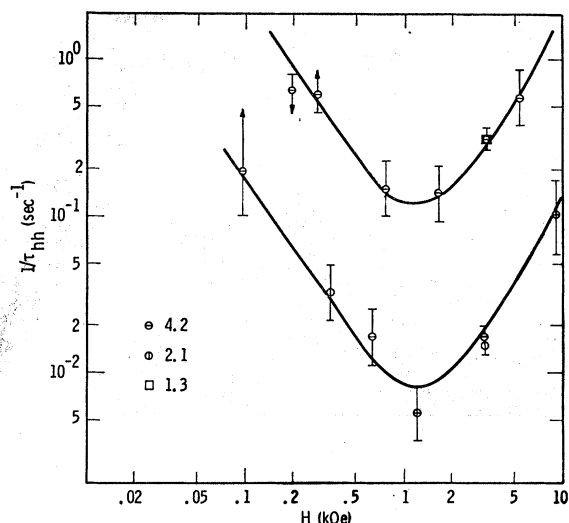


FIG. 6. Field dependence of  $1/\tau_{hh}$ . Measurements are shown for two samples at three temperatures. The lower curve corresponds to an electrolytically colored crystal, labeled A Medium in Table I, having an  $F$ -center concentration of  $10^{17} \text{ cm}^{-3}$ ; the upper curve, to another crystal with a higher  $F$ -center concentration. The arrows through some of the circled points indicate a large experimental uncertainty in the direction indicated.

quantities  $\bar{\tau}_d$ ,  $\bar{\tau}_X$ ,  $\bar{\tau}_i$ ,  $\bar{\tau}_s$ ,  $C_F$ , and  $C_X$ . The various  $\bar{\tau}$ 's are properties of the  $F$  center and the  $X$  center and depend, in some cases, upon their concentrations. Now, treatments like (2) and (3) above, which effect  $\tau$  without appreciably changing the  $F$ -center concentration or, presumably, the identity of the  $X$  center, can do so only because  $C_X$  changes. It follows, then, that one way to identify the  $X$  center is to attempt to correlate changes in  $\tau$  (which are considered to be due to changes in  $C_X$ ) with changes in the concentration of some known defect. If this correlation can be accomplished convincingly, the  $X$  center is identified as this defect.

To investigate possible correlations of this sort, we divide the defects that might be present into three groups: (1) aggregate centers, i.e.,  $M$ ,  $R$ ,  $N$ , etc., consisting of several  $F$  centers bound closely together by strong forces, (2) loosely bound clusters of  $F$  centers, which will always be found in a random distribution of  $F$  centers and which may be formed abundantly by special crystal treatments, and (3) impurity centers and other kinds of defect centers.

#### Aggregate Centers

The various aggregate centers are considered to be prime suspects for the  $X$  center since their concentrations are affected by high  $F$ -center concentrations, light exposure, OH content, and thermal treatment in the same way as  $1/\tau$ . All of these treatments, that have been shown in the Results section (or Paper I) to reduce  $\tau$ , are known to increase the aggregate center concentrations. Evidence for the increased concentrations is as follows: (1) The aggregate center concentrations

depend upon the  $F$ -center concentration and increase with it at least linearly. This has been shown in detail for  $M$  centers by van Doorn.<sup>22</sup> It is presumably also true for other aggregate centers. (2) The aggregate center concentrations increase with light irradiation. This is true of all the aggregate centers, at least for low light exposure, as shown, for instance, by Petroff.<sup>23</sup> (3) The aggregate center concentrations are very sensitive to the presence of impurities, especially OH and the alkaline earths. This has been observed for  $M$  centers in detail by Sonder and Sibley using crystals colored both by electron bombardment<sup>24</sup> and by gamma irradiation.<sup>25</sup> Their conclusion is that the presence of OH or  $O_2$  causes an increase in the  $M$ -center concentration, while the addition of alkaline earths causes a reduction. Finally, (4) the aggregate center concentrations decrease with thermal annealing at only a few hundred degrees above room temperature. This has been shown for all of the aggregate centers by Tomiki.<sup>26</sup>

We have shown that the simplest aggregate center, the  $M$  center, cannot be directly involved in the  $F$ -center relaxation, since a reduction in the  $M$ -band concentration by optical bleaching leads to faster relaxation. This observation is consistent with the non-magnetic properties anticipated for the  $M$  center according to the model proposed by van Doorn and Haven<sup>27</sup> and measured for this center by Sonder<sup>28</sup> and by Gross.<sup>29</sup>

The  $R$  center, on the other hand, cannot be dismissed in this fashion even though it is much lower in concentration than the  $M$  center. The  $R$  center is usually the next most concentrated aggregate center and has the properties required of the  $X$  center, i.e., it is magnetic, has very fast spin-lattice relaxation, and has little  $g$  shift.<sup>21</sup> Unfortunately the  $R$ -center optical absorption is, under most conditions, so weak as to be unobservable. The  $R$  center has optical bleaching properties which are quite different from those of the  $M$  center. Because of these factors, it is not possible to bleach the  $R$  center selectively, as was done for the  $M$  center, and correlate changes in  $\tau$  with changes in the  $R$ -center concentration. Indirect arguments bearing on this correlation are presented below.

#### Cluster Centers

Clusters of loosely bound  $F$  centers are expected to have many of the characteristics of the tightly bound aggregate centers. Because of this, the properties of the  $X$  center which appear to be related to aggregate centers

<sup>22</sup> C. Z. van Doorn, Phys. Rev. Letters 4, 236 (1960).

<sup>23</sup> St. Petroff, Z. Physik 127, 443 (1950).

<sup>24</sup> E. Sonder and W. A. Sibley, Phys. Rev. 129, 1578 (1963).

<sup>25</sup> W. A. Sibley and E. Sonder, Phys. Rev. 128, 540 (1962).

<sup>26</sup> T. Tomiki, J. Phys. Soc. Japan 15, 488 (1960).

<sup>27</sup> C. Z. van Doorn and Y. Haven, Philips Res. Rept. 11, 479 (1956).

<sup>28</sup> E. Sonder, Phys. Rev. 125, 1203 (1962).

<sup>29</sup> H. Gross, Z. Physik 164, 341 (1961).



probably fit clusters just as well. On the other hand, some of the observations reported in the Results section are consistent with the model for the  $X$  center based on loose clusters, but not the model based on aggregates. These observations and the pertinent arguments are:

(1) Crystals gamma-irradiated at low temperatures have very short relaxation times but, as shown by Faraday, Rabin, and Compton,<sup>30</sup> exhibit unusually low aggregate center concentrations. This behavior can be explained by clusters. The explanation is based on the observation that irradiation creates high concentrations of defects, like  $F$  centers, in spatially confined regions. Experimental evidence of spatial confinement is found by Gilman and Johnson,<sup>31</sup> Lambert and Guinier,<sup>32</sup> and Smallman and Willis.<sup>33</sup> They conclude that irradiation of LiF at room temperature generates clusters of defects in regions of about 50 Å diameter. Warming the crystals above room temperature was found to cause a monotonic increase in the size of the cluster. Most of their investigations involve neutron irradiation, but Gilman and Johnson mention that irradiation with 1.5 MeV electrons gives effects much like those observed after neutron bombardment. Our irradiation with 0.5 MeV gamma rays creates large numbers of 0.5 MeV electrons. We, therefore, expect the effects observed by the above investigators who use neutrons or 1.5 MeV electrons in LiF to be qualitatively similar to the effects that we observe using 0.5-MeV gamma rays in KCl. In addition, using an extrapolation of the results of Gilman and Johnson to lower temperature, we anticipate that irradiation at 77°K will form clusters smaller than 50 Å in diameter. The  $F$  centers formed in these regions cannot move appreciably at low temperatures either to be destroyed at other defects, to form the more tightly bound aggregate centers, or to diffuse away from each other, destroying the clusters. Upon warming the crystal, diffusion occurs rapidly, and all of these things can happen. Now, if aggregate centers were  $X$  centers, one would expect to observe a reduction in the relaxation time upon heating since more aggregates are formed. If clusters were the  $X$  centers, one would expect to observe an increase, since clusters are destroyed. A drastic increase in relaxation time is observed. This is inconsistent with the aggregate model but quite consistent with the cluster model for the  $X$  center.

(2) Crystals that were plastically deformed and then gamma irradiated at room temperature have unusually fast relaxation. There is, however, evidence that no unusually high concentration of aggregate centers exists after such treatments.<sup>34</sup> Now, it is known that an unusually large number of  $F$  centers are produced as a

result of this deformation.<sup>35</sup> It is speculated that extra  $F$ -centers are formed in high concentrations in the highly localized slipped regions of the crystal.<sup>35</sup> The enhanced relaxation is probably due to clusters in the regions of unusually high  $F$ -center concentration.

(3) The work of Krupka and Silsbee<sup>21</sup> shows that strain fields strongly affect the relaxation time of  $R$  centers. If  $R$  centers were responsible for the extrinsic relaxation, one might under some circumstances, expect to observe an effect of the strain on the  $F$ -center relaxation. Such an effect was looked for but not observed.

(4) In the work of Ohlsen and Holcomb<sup>19</sup> an attempt was made to correlate the observed extrinsic relaxation time with aggregate center ( $M$ ,  $R$ , and  $N$ ) concentrations. No simple correspondence could be found.

(5) One further point of discrimination against aggregate centers involves their concentration relative to that of cluster centers. The light exposures discussed in the Results section cause aggregate centers to grow fairly slowly. We have measured the efficiency of their creation and find it to be very low.<sup>36</sup> Delbecq<sup>37</sup> has found similar results. His interpretation of the aggregate center growth may be stated as follows: During short irradiations (such as ours) most of the photons absorbed do not create aggregate centers, but instead form clusters. Appreciable concentrations of  $M$  centers are formed only after an initial "delay" period;  $R$  centers, which are apparently formed from  $M$  centers, grow at an even slower rate.

Thus it appears that for our irradiations, clusters are much more common than aggregates. If each is a fast relaxer, the cluster will dominate as the  $X$  center.

#### *Impurities and Other Defects*

It is unlikely that an impurity or defect other than aggregate or cluster centers can have the same properties discussed in the last two paragraphs which the  $X$  center has displayed. The impurities which have been considered, such as  $O_2$ ,  $OH$ ,  $NO_2$ ,  $NO_3$ ,  $U$ , and  $U'$  centers are all known to have very low concentrations, and fail to have at least some of the properties of the  $X$  center. Defects which have been considered, such as holes, vacancies, and interstitial atoms and molecules, are those involved when  $F$  centers are produced by irradiation. Of necessity these defects are produced in concentrations of the same order of magnitude as the  $F$  centers themselves. Of them the  $V_k$ ,  $H$ , and vacancy are considered to be the most likely suspects for the  $X$  center since they have strong magnetic moments or effective electric charges. Our reason for eliminating these as the  $X$  center is threefold: (1) We have evidence from the absence of detectable microwave and optical absorption, that the concentrations of  $V_k$  and  $H$  centers

<sup>30</sup> B. J. Faraday, H. Rabin, and W. D. Compton, Phys. Rev. Letters **7**, 57 (1961).

<sup>31</sup> J. J. Gilman and W. G. Johnson, J. Appl. Phys. **29**, 877 (1958).

<sup>32</sup> M. Lambert and A. Guinier, Compt. Rend. **244**, 2791 (1957).

<sup>33</sup> R. E. Smallman and B. T. M. Willis, Phil. Mag. **2**, 1018 (1957).

<sup>34</sup> A. S. Nowick, Phys. Rev. **111**, 16 (1958).

<sup>35</sup> P. V. Mitchell, D. A. Wiegand and R. Smoluchowski, Phys. Rev. **121**, 484 (1961).

<sup>36</sup> R. W. Warren, Bull. Am. Phys. Soc. **9**, 543 (1964).

<sup>37</sup> C. J. Delbecq, Z. Physik **171**, 560 (1963).

are low; (2) the observed thermal stability of the  $V_k$ ,  $H$ , and vacancy defects<sup>18,17,38</sup> are not consistent with our annealing results; and (3) various evidence<sup>39</sup> indicates that if the defect made simultaneously with the  $F$  center is located too close to it, the stability of the  $F$  center is decreased so that it either recombines with the other defect or loses its electron to it.

#### Summary of Identification

Our conclusion from the above discussions is that an acceptable model for the  $X$  center is a group of loosely clustered  $F$  centers. Clusters can explain all of our observations discussed above, while the models involving aggregate centers, impurities, or other defects are each inconsistent with some of the observations. It is of course possible that each of these other centers can contribute significant relaxation under special circumstances.

#### Consequences of the Identification of the $X$ Center

The  $X$  center has been tentatively identified as a cluster. Some of the properties of the  $X$  center will be deduced from simple arguments about the expected properties of clusters. With these properties we will indicate the relative importance of the different steps involved in the relaxation process for several experimental conditions.

#### $g$ Value of Clusters

Since the  $F$  centers in a cluster are loosely coupled, the  $g$  value of a cluster is close to that of an isolated  $F$  center, probably much closer to the  $F$ -center value than to that of the  $R$  center (which itself is quite close to the  $F$ -center value<sup>21</sup>). Following the arguments of the theory section, cross relaxation from the  $F$  center to a cluster should be fast, taking a time approximately equal to that needed for a single mutual spin flip in the spatial diffusion process. It follows that cross relaxation should not limit the relaxation.

#### Linewidth of Clusters

Since the  $F$  centers in a cluster are coupled, the wave function describing any one electron must be a linear combination of  $F$  center wave functions centered on the two or more vacancies involved. The hyperfine coupling of this electron to any one of the nearby nuclei will then be reduced. For the case of equal spacing between the  $F$  centers in a cluster it will be reduced by a factor equal to the number of coupled  $F$  centers, while the number of nuclei contributing to the hyperfine broadening will

be increased by the same factor. This kind of situation leads to effects classified as exchange narrowing.

If the hyperfine splitting could be resolved, for the simplest case of two coupled centers, one would observe twice as many hyperfine lines with half the usual separation.<sup>40</sup> Such a resonance spectrum has been observed for donor atoms in silicon,<sup>41</sup> and has been interpreted in terms of exchange narrowing by Slichter.<sup>42</sup> Similar but weaker spectra due to coupled groups of three and four donor atoms in silicon have subsequently been reported.<sup>43</sup> The donor concentration in this case was  $4 \times 10^{17} \text{ cm}^{-3}$ .

Since the hyperfine structure of the  $F$  resonance in KCl is unresolved, the only effect of exchange between  $F$  centers that could be observed is a change in the line shape. We have calculated the linewidth expected for the case of equal spacing by counting the number of ways in which a given hyperfine splitting can be brought about by all of the different possible arrangements of the nuclei involved. The calculation indicates that the line is narrowed by exchange by a factor of about  $(nm)^{1/2}$ , where  $n$  is the number of  $F$  centers clustered together and  $m$  is the number of equivalent nuclei per  $F$  center. This calculation is patterned after the one of Kip *et al.*<sup>44</sup> devised to determine the linewidth of isolated  $F$  center, where  $n=1$ . The narrowing for the case of unequal spacing within a cluster is expected to be less extreme than for equal spacing.

Exchange narrowing of  $F$ -center clusters in KCl has not been reported in the literature, but there are several arguments that suggest that these effects should be and, perhaps, have been observed. These are

(1) In most experiments the  $F$ -center concentration is of the same order of magnitude ( $10^{17} \text{ cm}^{-3}$ ) as that for which exchange effects are observed in silicon.

(2) Kawamura and Ishiwatari<sup>45</sup> and others<sup>46</sup> have observed a narrowing of the  $F$ -center resonance in KCl after prolonged light irradiation. They assumed this was caused by the conversion of  $F$  centers to another kind of paramagnetic center. Kawamura and Ishiwatari identified this as the  $M$  center. Since the  $M$  center is now believed to be nonparamagnetic,<sup>28,29</sup> some other defect should be used to explain their observations. We believe that the cluster center is this defect. We support this proposal by noting that the light treatment which produced the line narrowing observed by Kawamura and Ishiwatari is just the treatment which, as we have

<sup>40</sup> William Low, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Suppl. 2, p. 157.

<sup>41</sup> R. C. Fletcher, W. A. Yager, G. L. Pearson, A. N. Holden, W. T. Read, and F. R. Merritt, *Phys. Rev.* **94**, 1392 (1954).

<sup>42</sup> C. P. Slichter, *Phys. Rev.* **99**, 479 (1955).

<sup>43</sup> G. Feher, R. C. Fletcher, and E. A. Gere, *Phys. Rev.* **100**, 1784 (1955).

<sup>44</sup> A. F. Kip, C. Kittel, R. A. Levy, and A. M. Portis, *Phys. Rev.* **91**, 1066 (1953).

<sup>45</sup> H. Kawamura and K. Ishiwatari, *J. Phys. Soc. Japan* **13**, 33 (1958).

<sup>46</sup> P. R. Moran, S. H. Christensen, and R. H. Silsbee, *Phys. Rev.* **124**, 442 (1961).

<sup>38</sup> R. Onaka and I. Fujita, *Phys. Rev.* **119**, 1597 (1960).

<sup>39</sup> F. Lüty, in *Halbleiterprobleme*, edited by F. Sauter (F. Vieweg and Sohn, Braunschweig, 1961), Vol. VI, p. 238; H. Bauser and F. Lüty, *Phys. Stat. Solidi* **1**, 608 (1961).

postulated, produces cluster centers. The line narrowing observed by them, a factor of 1.23, is in fair agreement with  $2^{1/2}=1.41$ , which is the value expected of the simplest cluster composed of two  $F$  centers.

(3) Holton and Blum<sup>20</sup> have observed a resonance line shape for  $F$  centers in KCl which they decompose into two components, one with the properties of the  $F$  center, and the other, narrower by a factor of 1.42, which shows up only when aggregate centers are also present. No correlation could be found between this second component and the concentration of  $M$  centers or of any other known defect. It is probably also due to clusters.

(4) Resonance measurements of  $F$  centers in LiF have been made by various investigators with conflicting results. Holton and Blum,<sup>20</sup> for instance, find the resolved hyperfine spectra in good agreement with calculations based on ENDOR measurements. Other investigators such as Kaplan and Bray<sup>47</sup> find evidence for the existence of two resonance lines due to two different centers. They identify one center as the  $F$  center and the other as a cluster of interacting  $F$  centers whose resonance line has been narrowed by exchange. The relaxation time of the cluster was found to be much less than that of the isolated  $F$  center. Our assumptions about the relaxation time of clusters in KCl are consistent with this.

#### *Field and Temperature Dependence*

Cluster centers are groups of loosely coupled  $F$  centers distributed throughout the crystal. Their effectiveness in relaxing  $F$  centers will vary. It increases as the number of included  $F$  centers and the strength of coupling between them increase. Within a volume containing a random distribution of  $F$  centers, the density of tight clusters will be less than that of looser clusters. Now, we have assumed that a cluster center is a rapidly relaxing  $X$  center only when the ratio of its coupling energy to the Zeeman energy exceeds a critical value. For a reasonably large magnetic field, only a few cluster centers will have sufficiently strong coupling to serve as  $X$  centers. As the field is lowered, more clusters can contribute to the relaxation, and the  $\tau_X$  for each cluster will decrease. In this way, one can qualitatively understand how a field-dependent relaxation time like that observed is a natural property of the cluster model. No attempt will be made to derive an analytic expression for this field dependence because we do not know the precise form of the field dependence of  $\tau_X$  for one cluster or the distribution of clusters expected for different crystal treatments.

The variability expected in the coupling strength of cluster centers in a given crystal can furnish an explanation of the temperature dependence of the relaxation time. According to our model, when  $X$  centers are cluster centers the  $F$ -center relaxation involves only

two important sequential steps, diffusion to a cluster center and the relaxation of that center. Many parallel paths of this sort should be considered, each involving cluster centers of a different strength of internal coupling and, therefore, of a different concentration and relaxation time. Those paths involving strongly coupled cluster centers are unimportant since there are so few of them that the diffusion step takes too long. Those paths involving very weakly coupled cluster centers are also unimportant, not due to diffusion limitations, but to the excessively long spin-lattice relaxation time of the cluster. The most effective paths therefore are those for which the diffusion time and the relaxation time are of the same order of magnitude, the optimum relationship depending upon the details of the clustering. Since the diffusion time is temperature independent, the total relaxation time would be expected to have a temperature dependence which is weaker than for the spin relaxation time alone, and which is somewhat sensitive to the manner in which the cluster centers are distributed through the lattice. The measurements reported above are consistent with these predictions.

#### **Distorted Line Shapes**

Whenever relaxation is extrinsic, the  $F$ -center line should be distorted to some extent during recovery. In the discussion above, we have included three different processes which cause the line to be distorted as shown in Fig. 4. In the diffusion step, the distortion is due to the strong dependence of diffusion on the  $F$ -center concentration corresponding to each part of the line. In the cross relaxation step (if the cluster center line has been narrowed) the distortion is due to the difference in the cross relaxation time for various parts of the  $F$ -center line. In the spin-lattice relaxation step, the distortion is due to the different relaxation rates and different line shapes of the  $F$  and  $X$  centers. The last process will yield an obvious distortion only if concentrations of  $F$  and cluster centers are approximately equal.

Reverse tendencies exist. The "hole healing" effect is a measure of these tendencies. Although little is known about the mechanisms of hole healing, it probably involves interactions among neighboring centers. It should, therefore, be effective in reducing distortions only if the different centers giving the distortion are intimately mixed with each other. This mixing always obtains for the first two processes discussed above where the centers giving the distortion are  $F$  centers with different hyperfine environments. The measured hole healing time is, then, an important parameter which allows us to predict the amount of distortion. In special cases where the  $F$  and  $X$  centers are not intimately mixed, the third process produces a distortion which will not be reduced by hole healing.

Crude estimates have been made which show that if the various defects are well mixed, hole healing should wash out the distortion when  $\tau/\bar{\tau}_{hh} > 100$ . In agreement

<sup>47</sup> R. Kaplan and P. J. Bray, Phys. Rev. **129**, 1919 (1963).

with this prediction, distortion are seen only when  $\tau/\bar{\tau}_{hh} < 100$ .

On the other hand, there is evidence that the crystals showing the characteristic distortion during recovery do not have well-mixed  $F$  and  $X$  centers. For example, distortions are most evident when samples are irradiated at 77°K or when deformed crystals are irradiated. These are both conditions for which clusters are expected to be numerous, probably comparable in number with isolated  $F$  centers, and located in regions separate from most of the  $F$  center. No identification can be made of the process responsible for the characteristic distortion.

### Hole Healing

The same mutual spin flip process which leads to spatial diffusion of Zeeman energy can also lead to spectral diffusion,<sup>12</sup> and therefore, to hole healing. The marked parallelism between the effect of various crystal treatments on both the extrinsic relaxation time and the hole healing time suggests some connection between them and emphasizes the extrinsic nature of hole healing. We have no explanation for the observed dependence on field and temperature.

### Size of the $X$ Center

Although the calculations referred to above<sup>3-8</sup> give little assistance in calculating the size of an  $X$  center, we can make estimates by referring to experiments. It should be recalled that a cluster is an  $X$  center only when the ratio of the coupling energy between its  $F$  centers to their Zeeman energy is large enough. As the field is decreased, more and more clusters satisfy this condition. The size of the average  $X$  center, therefore, will change as the field is changed; at low fields the average  $X$  center will contain more widely spaced  $F$  centers than at higher fields.

The maximum size of an  $X$  center at 3 kOe can be estimated from the following observations: As the  $F$ -center concentration is increased, the first evidence for extrinsic effects at this field is found when the concentration is about  $3 \times 10^{17} \text{ cm}^{-3}$ . This concentration cor-

responds to an average spacing between  $F$  centers of about thirty lattice sites; many  $F$  centers will be closer than this. The closer ones constitute the  $X$  centers.

Gilman and Johnson, Lambert and Guinier, and Smallman and Willis conclude, in experiments mentioned above,<sup>31-33</sup> that the defects formed in LiF by room-temperature irradiation are present in clusters whose diameters are about twenty lattice sites. Kaplan and Bray,<sup>47</sup> as mentioned above, have shown that many fast-relaxing centers are present in similar samples. These fast-relaxing centers are probably identical with or contained within the clusters and are therefore less than 20 lattice sites in diameter in LiF.

Estimates have been made<sup>30</sup> of the separation of  $F$  centers at which  $M$  centers form spontaneously. This distance is a lower limit to the size of a cluster. Due to some of the assumptions made, this estimate seems inappropriate, and no lower limit to the size will be estimated.

### CONCLUSIONS

There is extrinsic behavior of  $F$  centers in KCl which cannot be attributed to isolated  $F$  centers. This includes distorted resonance line shapes, unusually rapid spin lattice relaxation times, and unusual dependences of the relaxation time on magnetic field and on temperature. Such behavior is found only in crystals which have received special treatments such as high  $F$ -center concentrations, light exposure, the presence of impurities, plastic deformation, and low temperature gamma irradiation.

A model is proposed which explains this evidence within the constraints imposed by the considerable lore involving the properties of  $F$  centers. This model identifies the extrinsic relaxation process as one compounded of spatial diffusion of Zeeman energy in the  $F$ -center system and cross relaxation from  $F$  centers to rapidly relaxing centers which are composed of loosely bound clusters of  $F$  centers.

The field and temperature dependence of hole healing has been determined for samples which exhibit extrinsic relaxation. No explanation is presented.

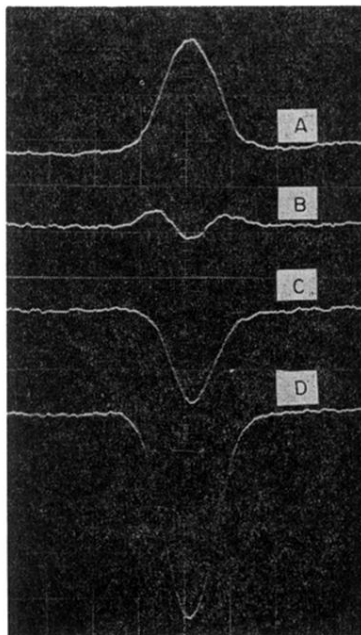


FIG. 4. Oscilloscope display of *F*-center absorption signal during recovery, showing a distorted line shape near saturation. *A* is the signal immediately after inversion; *B* is the signal near saturation showing the typical distortion; *C* occurs still later; and *D* is the signal when the spin system is in equilibrium with the lattice. The sample was prepared by gamma irradiation at low temperatures, and the measurements were taken at 1.2°K and 3.5 kOe. The *F*-center concentration was about  $2 \times 10^{17} \text{ cm}^{-3}$ .

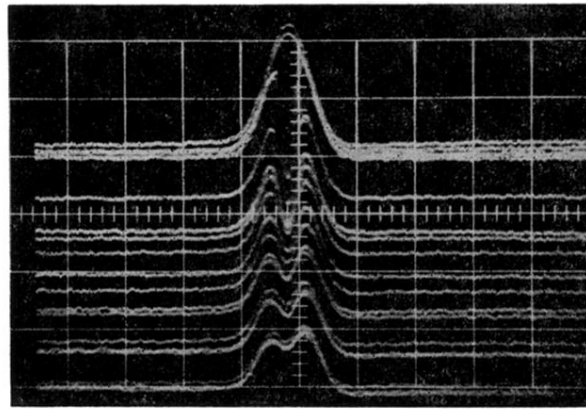


FIG. 5. Oscilloscope display of the recovery of a hole inverted in the *F*-center resonance line. Reading from the top of the picture to the bottom, two traces are shown of the normal line followed by a trace of the line immediately after its central portion was partially inverted. The remaining traces, taken at one-second intervals, show the recovery of the inverted hole. The sample was colored electrolytically to an *F*-center concentration of about  $3 \times 10^{17} \text{ cm}^{-3}$ . The measurements were made at 4.2°K and 3.5 kOe; the spin relaxation time was found to be several minutes.