

Electron Spin Resonance and Optical Absorption of Electron Excess Centers in KCl*

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(Received May 9, 1961)

The effect of various conditions of optical bleaching and thermal annealing on the electron spin resonance and optical absorption of additively colored KCl has been studied. With extended optical bleaching the resonance linewidth narrows and the resonance saturates less readily. The presence of R , M , N , or R' centers is unrelated to the dominant features of the changes in resonance behavior; the optical absorption associated with the magnetic centers appears to remain in the region of the F band.

INTRODUCTION

ALTHOUGH the electron spin resonance technique has provided a very detailed picture of the structure of the F center in KCl and other alkali halides,^{1,2} it has been strikingly unsuccessful in giving any information about other electron excess centers. In particular, there has been no conclusive verification of the Seitz models for the M and R_1 centers,³ both of which should be magnetic. Many groups have studied the magnetic properties of crystals containing electron excess centers, both by the resonance technique⁴⁻⁹ and by studies of the static magnetic susceptibility.^{10,11} It appears clear from this work that there are changes in the nature of the magnetic resonance in crystals containing bleaching products of the F band, but these changes have not been conclusively correlated with any optical band. Both resonance⁹ and static susceptibility¹⁰ measurements indicate that bleaching of the F band produces a more rapid decrease in the density of magnetic centers than of the centers giving optical absorption in the F band. This is contrary to expectation if one assumes that the sole result of the bleaching is to convert F centers into magnetic R , M , or N centers.

In a study, at this laboratory, of the temperature dependence of the relaxation time of F centers it was noted that the presence of R , M , and N centers seemed to produce marked variations, from sample to sample, of the saturation behavior of the F center resonance at room temperature. These changes in the saturation behavior appeared to be a more sensitive measure of the presence of other centers than did the changes in line-

width already noted,^{6,7} and a systematic study of these effects seemed an obvious way to attack the problem of the magnetic properties of the M , R , and N centers. The principal conclusion of the work is that the M , R , and N centers do not appear to be responsible for the behavior noted above, indirectly supporting the hypothesis of nonmagnetic R , M , and N centers.

The next section of the paper outlines the methods of crystal preparation and measurement. The results of the experiments as well as the discussion of these results are in the following section. Finally the principal conclusions are summarized.

EXPERIMENTAL METHODS

Crystal Preparation and Treatment

The bulk of the crystals used in this study were Harshaw crystals of KCl cleaved to roughly a centimeter square by a millimeter thick. They were additively colored by standard techniques³ to a variety of F center concentrations, the usual density being about 3×10^{17} centers per cc.

Two procedures were adopted to prepare crystals containing "pure" F centers¹² from these additively colored crystals. The usual method was to anneal the crystal at 580°C for 3 min and then to quench the crystal to room temperature on a copper block. An alternative procedure was to convert the F centers to U centers,¹³ H^- replacing Cl^- substitutionally, by heating the additively colored crystals to 580°C under 250 psi of hydrogen for 5 min. The U centers could then be converted back into F centers at room temperature, without appreciable coagulation, by x irradiation (5 cm from a tungsten target at 150 kvp and 12 ma with $\frac{1}{8}$ -in. aluminum filter for 10 min). Typical values for the ratio of peak F absorption to peak M absorption were 50 for the quenched crystals and 300 for the hydrogen-treated crystals, hereafter referred to as hydrided crystals.

After preparation, and during the quench for the quenched crystals, the crystals were handled in red light to prevent optical bleaching in the F band during handling. This does not, of course, prevent bleaching effects in the bands at longer wavelengths. Although

* Supported by the U. S. Atomic Energy Commission and the Alfred P. Sloan Foundation.

[†] National Science Foundation Predoctoral Fellow.

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⁶ H. Kawamura and K. Ishiwatari, J. Phys. Soc. Japan **13**, 33 (1958).

⁷ G. A. Noble and J. J. Markham, Bull. Am. Phys. Soc. **5**, 419 (1960).

⁸ W. E. Bron and R. S. Title, Bull. Am. Phys. Soc. **6**, 113 (1961).

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¹¹ R. T. Bate and C. V. Heer, J. Phys. Chem. Solids **7**, 14 (1958).

¹² J. D. Konitzer and J. J. Markham, J. Chem. Phys. **32**, 843 (1960).

¹³ H. Pick and W. Martienssen, Z. Physik **135**, 309 (1953).

the crystals were stored in the dark at room temperature, several weeks of storage produced marked changes in both the optical and resonance properties of these crystals. No investigation of these changes was made.

The relative concentrations of the different centers were changed both by optical bleaching in the F band and by thermal annealing. A 150-watt incandescent bulb, 15 cm from the sample, served as a source for the optical bleaching which was done at room temperature. The light was restricted to a bandwidth of 100 $m\mu$ centered on the F band by a filter with a maximum transmission of 70%. The high F center concentration required by the sensitivity limitations of the microwave spectrometer forced the use of crystals of very high optical density (the order of 4 at room temperature) at the peak of the F band. The optical bleaching, therefore, is *not* uniform despite the appreciable penetration of the bleaching light in the tail of the F band and the division of the total bleaching time into equal irradiation of both sides of the crystal. This nonuniformity does not alter the qualitative conclusions of this work.

Crystal Measurement

A Cary Model 14 spectrophotometer measured the optical density of the crystals in the range 200 $m\mu$ to 1100 $m\mu$, usually near liquid nitrogen temperature ($90 \pm 5^\circ K$) to obtain better resolution and to avoid bleaching during the measurement. Introduction of perforated metal screens as neutral filters into the reference beam reliably (to a density of ± 0.03) extended the range of the spectrophotometer to an optical density of four. Higher optical densities were estimated with less precision both by using additional screens and by extrapolating from data in the wings of the F band.

The magnetic resonance properties of the samples were measured with a conventional 3-cm microwave spectrometer using balanced bolometer detection.¹⁴ The Varian V-58 klystron, stabilized to a reference cavity, gave a maximum magnetic field amplitude ($2H_1$) of about one gauss at the sample. The lock-in detection system operated at 35 cps, usually with a peak-to-peak magnetic field modulation of 16 gauss.

The primary interest in this investigation was in the saturation behavior of the resonance (the dependence of the signal amplitude on the microwave power level). The procedure was to measure the peak-to-peak value of the signal (derivative of the absorption) at a series of power levels at intervals of 6 db as determined by a Hewlett-Packard calibrated attenuator. The theory of Portis¹⁵ predicts that a log-log plot of signal amplitude versus power will have the form indicated in Fig. 1 for a line which is inhomogeneously broadened. In the data presented here, the signal to noise was sufficient that for typical samples at intermediate power levels the signal amplitudes within a run reproduced within 5%.

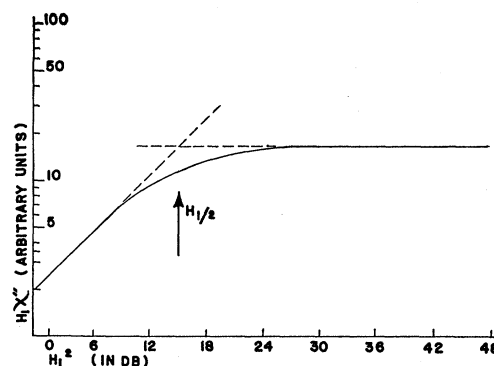


Fig. 1. Theoretical saturation plot for an inhomogeneously broadened spin resonance: $\gamma^2 H_1^2 = (T_1 T_2)^{-1}$.

The precision became worse at low powers because of the lower signal levels and at high powers because of background signals from "cavity resonances" and because of the problem of dispersion admixture.

There are a number of problems involved in the determination and interpretation of these saturation curves. For a finite size sample, the rf magnetic field is not uniform over the crystal and a saturation plot will show a more gradual break near $H_1/2$ than indicated in Fig. 1. This effect, noted by Castner,¹⁶ was not important in these experiments. Careful calibration procedures are required to determine H_1 quantitatively but in this investigation the primary concern was with the qualitative feature of the saturation plots. A serious problem in obtaining reliable saturation plots is the critical requirement that the microwave bridge be sensitive only to the absorption signal; a small admixture of dispersion signal, since it does not saturate, can dominate the signal at high power levels. During a run the bridge was balanced manually to be insensitive to dispersion by applying a shallow frequency modulation (~ 300 cps) to the klystron and adjusting the spectrometer to null the output signal at this frequency of modulation (a manual version of a standard AFC technique). This balance was maintained to better than a part in 300, and only occasionally did the asymmetry of the line indicate the presence of some dispersion signal.

The saturation plot is made assuming that the detector sensitivity is independent of the power incident upon the sample cavity. This constant sensitivity is one of the advantages of any spectrometer for which the detector bias is provided separately from the signal power. It was confirmed experimentally with a non-saturating sample and by a calibration procedure involving measurement of the dispersion sensitivity by frequency modulating the klystron.

In addition to the saturation plots, some measurements were made of the resonance linewidths and the g values. The quoted linewidths are the separations in

¹⁴ G. Feher, Bell System Tech. J. **36**, 449 (1957).

¹⁵ A. M. Portis, Phys. Rev. **91**, 1071 (1953).

¹⁶ T. G. Castner, Jr., Phys. Rev. **115**, 1506 (1959).

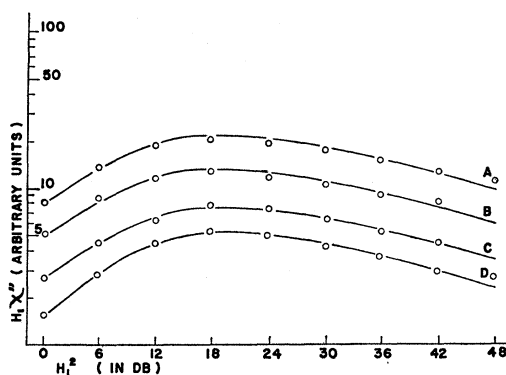


FIG. 2. Saturation plots for "pure" F centers in several crystals. A. Quenched crystal, XIV; $N_F \sim 3 \times 10^{17}$ per cc. B. Quenched crystal prepared by another group; concentration intermediate between A and D. C. Hydrided crystal, XIII; $N_F \sim 3 \times 10^{17}$ per cc. D. Quenched crystal; $N_F \sim 3 \times 10^{18}$ per cc.

magnetic field between the maxima in the derivative of the absorption signal.

EXPERIMENTAL RESULTS AND DISCUSSION

"Pure" F Centers

Results. Before investigating effects associated with complex centers it was imperative to establish the properties, in particular the saturation behavior, of the F center itself. Since there has been some question in the past whether F centers prepared by different techniques have identical properties,¹² two basic preparation techniques were used as described in the previous section. Figure 2 shows saturation plots for a few crystals, 3 prepared by us as outlined above and one prepared by another group in this laboratory. The points for crystals A, B, and C have been fitted by a single curve obtained by averaging data from runs on the order of 20 different crystals, all of which show a fit to this average curve comparable with those in the figure. Curve D, a sample with high F center concentration, is best fitted by displacing the horizontal scale by a factor of 1.25 in H_1 (to give a larger H_1). Except for this shift, the points lie on a single curve within the experimental precision.

The shape of the curve is unchanged if the magnetic field modulation amplitude is reduced by a factor of 10, indicating that the decrease in signal at high power is not a modulation effect. An admixture of dispersion signal would increase the signal at high power and likewise cannot be responsible for the observed decrease.

These samples, both hydrided and quenched, consistently gave linewidths of 45 ± 2 gauss (Kip *et al.*² reported 46 gauss) and, for those few samples where the g value was measured, a g of 1.996 ± 0.001 (Kip *et al.* obtained 1.995 ± 0.001). The resonance line shapes were Gaussian within the experimental precision. The ratios of the integrated optical absorption to the spin resonance intensity for a hydrided and a quenched sample were the same within an experimental uncertainty of

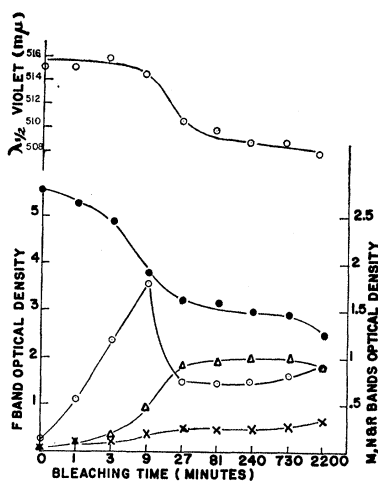


FIG. 3. Effect of optical bleaching on optical absorption of quenched crystal, XIV. Lower curves—peak absorption in various optical bands as a function of bleaching time. Upper curves—wavelength at violet half-height point of F band. \times , N Bands. \triangle , R Bands. \circ , M Bands. \bullet , F Bands.

20%. The optical absorption line shape measured at 90°K was the same for different samples and agreed with the results of Konitzer and Markham.¹²

These results indicate that the resonance properties in these samples are indeed characteristic of the F center itself, uninfluenced by effects of coagulation or interaction with other centers. The linewidth and g value are as given by Kip *et al.*² and the saturation behavior is that indicated in Fig. 2.

Discussion. The only disquieting feature of the results above is the departure of the saturation behavior (see Fig. 2) from that predicted by Portis¹⁵ (see Fig. 1). The experimental data reported are not in disagreement with Portis' experimental findings. Portis' highest power level corresponds to about 28 db on the plot of Fig. 2, where the fall-off from maximum is only about 10%, or the order of the accuracy of the measurements. The value of H_1 obtained from the present results, although estimated only roughly, agrees with that of Portis. Castner¹⁶ gives an extension of Portis' theory which will fit the curves of Fig. 2 if one assumes $T_1 \sim 10^{-4}$ sec and $T_2 \sim 10^{-6}$ sec. There are a number of problems with this interpretation, the most apparent being that one would expect a stronger dependence of T_2 on concentration. The whole question of the shape of the saturation plots is to be pursued in a separate investigation.

The purpose of this discussion was to establish the behavior of the F center resonance; having done this, the next step is to study the deviations from this behavior associated with the introduction of other color centers into the crystal.

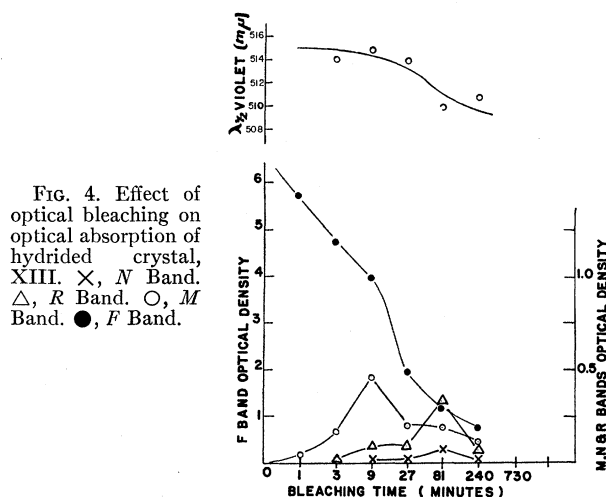
Optical Bleaching Experiment

Results. A quenched and a hydrided crystal were exposed to a series of optical bleaches by light in the F band at room temperature as described above. The total elapsed bleaching time increased by a factor of three in successive runs and optical and resonance measurements were made after each bleach.

Figures 3 and 4 summarize the optical results, showing the peak absorption for the various bands as the crystal is bleached. The qualitative behavior for both samples agrees with the results of Petroff.¹⁷ In both samples the *F* band drops rapidly as the *M* band grows; the *M* then goes through a maximum and the *R* and *N* bands develop at the expense of the *M*. At about the same time the *F* band broadens to the violet (Petroff's *B* band). The striking difference between the samples is the much greater stability of the coloration in the quenched crystal, the optical conversion of *F* back into *U* centers in the hydrided crystals giving extensive bleaching. An important feature of the bleaching of the quenched crystal is the stability of all the bands between 27 and 730 min.

Figures 5 and 6 show the magnetic resonance saturation behavior after the successive bleaches, with the curves normalized by shifting the vertical (but not horizontal) scale to give coincidence at low power levels. The deviation from the saturation plot of the pure *F* center is very marked, the relative signal at the highest power being increased by a factor of 30 by the bleaching. There is no change between 730 and 2800 min, suggesting that whatever conversion or coagulation was occurring is essentially complete. The saturation plot corresponding to these final stages has been observed in a number of heavily bleached crystals, suggesting that this plot is characteristic of a heavy bleach. Unfortunately, in a crystal with an order of magnitude higher *F* center concentration, the saturation plot after a heavy bleach roughly corresponded to that of the 81-min bleach, not to that of the most heavily bleached crystals of Fig. 5. Whether this was related to the extreme non-uniformity of the bleaching or whether the final state after bleaching depends on the mean *F* concentration remains an open question.

There are some additional features of the resonance measurements to be noted. The line narrows^{7,8} with



¹⁷ S. Petroff, Z. Physik 127, 443 (1950).

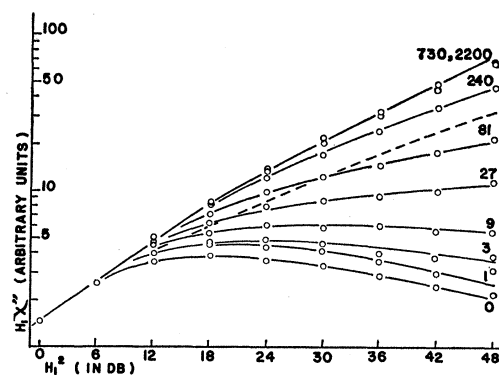


FIG. 5. Resonance saturation plots at various bleaching times for the quenched crystal, XIV. The dashed line is discussed in the text.

bleaching to a width of 35 ± 2 gauss in the final stages. The linewidth is independent of rf power in the early and late stages of bleaching but in the intermediate stages the line is broader at low power than at high. The *g* value after extended bleaching remained the same as that for the *F* center, 1.996 ± 0.001 . No evidence was seen of the change in *g* value reported by Kawamura and Ishiwatari.⁶ However, our *g* measurements were made only on crystals in the initial and final stages of bleaching. The line shape after an extended bleach, measured carefully only in the very densely colored crystal for which the heavily bleached saturation behavior is different from that for the lower concentrations, is not quite Gaussian. Compared with a Gaussian of the same peak-to-peak derivative width the resonance after bleaching shows somewhat more signal in the tails, though much less than a Lorentzian curve of the same width.

Finally, Figs. 7 and 8 show the variation with bleaching of the integrated areas of the optical absorption and of the spin resonance absorption at low rf powers, where the integrated magnetic absorption is proportional to the number of centers contributing to the resonance irrespective of their saturation behavior.

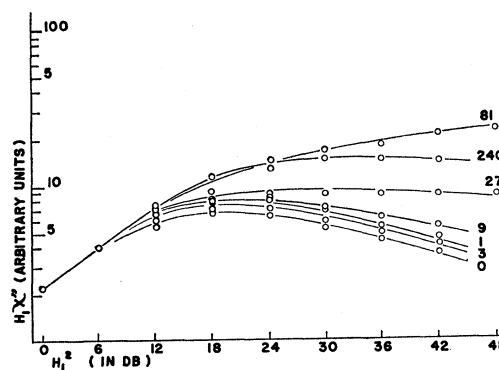


FIG. 6. Resonance saturation plots at various bleaching times for the hydrided crystal, XIII.

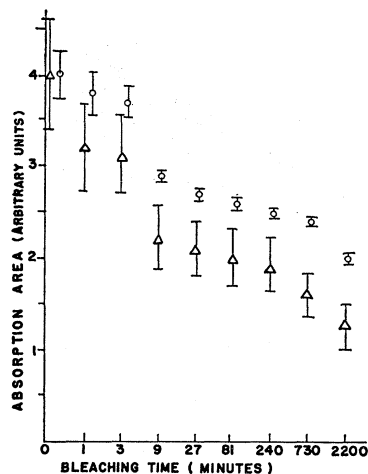


FIG. 7. Relative intensity of the optical absorption and of the resonance absorption as a function of bleaching time for the quenched crystal, XIV. O, optical F Band. Δ , ESR Absorption.

Discussion. A number of qualitative features of the resonance data suggest that the effect of the bleaching is to convert F centers (linewidth of 45 gauss and saturation behavior of Fig. 2) to another center (linewidth of 35 gauss and saturation behavior of the heavily bleached sample in Fig. 5). There are two reasons for doubting that the picture is this simple. First, with this model, it should be possible to express any saturation plot as a linear combination of any other two (a correction resulting from the difference in linewidths amounts to only a few percent). The dashed line in Fig. 5 is one-half the sum of the 2200-min plot and a plot for "pure" F centers. It clearly does not fall into the sequence of plots. Similarly, a number of plots obtained after thermal anneals (Curve III of Fig. 9 for instance) do not fall into the sequence of Fig. 5, nor does the 240-min bleach of the hydrided crystals. The second difficulty with this picture is the problem of reconciling the stability of the optical absorption after 27 min of bleaching with the continued growth, until 730 min, of the resonance at high power levels. One would expect to see a continued change in some feature of the optical absorption if a conversion of F to some other center continued into this range of bleaching.

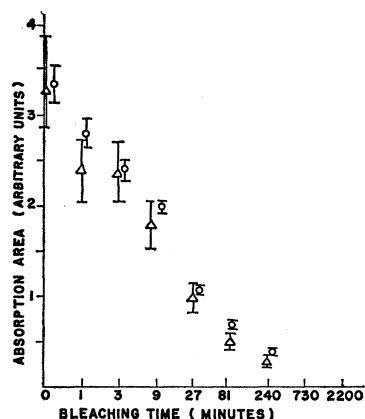


FIG. 8. Relative intensity of the optical absorption and of the resonance absorption as a function of bleaching time for the hydrided crystal, XIII. O, Optical F Band. Δ , ESR Absorption.

Although it might be possible to explain these results in terms of three magnetic centers, we prefer an interpretation involving either the formation of some complex of F centers or the conversion of the F center to another center, during the first 27 min of bleaching, resulting in a narrower resonance line. The subsequent changes in the saturation behavior are believed to result from a redistribution of these centers within the crystal which influence the relaxation behavior of the resonance, perhaps giving a distribution of values of the product T_1T_2 , the mean of which is shorter than the value of T_1T_2 for the "pure" F center.

Correlation of Resonance and Optical Results

Whatever model is used to describe the changes in the resonance properties, one can attempt to establish whether there exists an important influence of the usual electron excess centers, R , M , N , and R' , on the magnetic behavior. After considerable effort had been devoted to trying to find such a correlation it gradually became clear that the gross effects observed in the resonance experiments were unrelated to the presence of these bands.

The main purpose of this section is to discuss a few specific results, primarily from experiments on crystal XIV, which establish the *absence* of a correlation between the presence of the various centers and the changes in magnetic behavior. Despite the ambiguities introduced by the possibility of a changing distribution of relaxation times, it seems possible to show this lack of correlation.

The arguments as formulated below show that the magnetic changes do not result from an appreciable contribution to the resonance by the various centers. Similar arguments may, of course, be applied to the same experimental results to show that, in addition, the changes do not result from the interaction of non-magnetic R , M , N , or R' centers with the F centers.

R bands. The ratio of R_1 to R_2 was constant in these experiments and they will be considered together. Figure 9 and Table I summarize the magnetic and optical results of one of two similar experiments involving a thermal annealing of a heavily bleached crystal. (The difference between Curves I and II represents the effect of storing the sample in the dark at room temperature for 3 weeks, showing the presence of some defect mobility at room temperature). A thermal anneal at 115°C for 10 min, taking the crystal from Curve II to III, reduced the R bands by a factor of 5 to about their value after only 1 min of bleaching, while the resonance intensity at low power actually increased by 20%, and at high power decreased by only 40%. The line remained narrow. If the R centers were contributing significantly to the total resonance intensity, the same increase in low-power signal, despite the factor of 5 loss in R concentration, would require a large conversion of R back into F . However, in that case there should be a

TABLE I. Summary of properties of crystal XIV during thermal annealing experiment. Large uncertainties both in the optical density and in λ_4 (violet) result from a high background level. The uncertainty in the optical density is roughly 0.1, but the relative uncertainty in comparing different runs is less.

Run	Treatment	Peak optical densities					λ_4 (violet)	Relative magnetic intensity	ΔH (gauss) (at medium power)
		F	R	M	N_1	N_2			
I	2200-min bleach	2.2	0.63	0.71	0.43	0.20	509 \pm 2		35 \pm 3
II	+3 weeks in dark	2.2	0.31	0.81	0.45	0.25	511 \pm 2	0.8	35 \pm 3
III	+10 min at 115°C	2.5	0.06	0.93	0.45	0.09	512 \pm 2	1.0	35 \pm 3
IV	+15 min at 155°C	3.3	0.03	1.35	0.12	0.02	516 \pm 2		42 \pm 3

pronounced reduction of the climb in the saturation plot and the low-power linewidth should increase. Neither is observed and we conclude that the R center is not responsible for the gross change of the magnetic behavior with bleaching.

Curve IV illustrates the danger of trying to establish correlations on the basis of parallel behavior of two properties of a crystal in just a few experiments. An anneal at 155°C (Curve IV), without the previous anneal at 115°C, would have strongly suggested the R band as the source of the climb in the saturation plots.

M band. The optical density at the peak of the M band and the ratio of the M peak to the F peak both fall by more than a factor of two between 9 and 27 min of bleaching. Choosing any reasonable measure of the change in resonance behavior, for example the ratio of the high-power signal to the low-power signal, the magnitude of the high-power signal, or the ratio of the concentration of the "new center" relative to the F center assuming the simplest two-center models, a plot of this measure as a function of time gives a smooth monotonic function with no indication of a kink or a break in the 9- to 27-min region. If the M center is contributing to the changes in the resonance it is difficult to see how the T_1T_2 distribution could be altered in just the manner needed to conceal all evidence of the factor of two decrease in M center density. An additional piece of evidence against the M band is that an anneal at 155°C (run IV of Fig. 9 and Table I) gives a substantial recovery toward the "pure" F center resonance behavior despite an appreciable increase in the concentration of M centers.

N bands. There are at least three bands apparent in the region of 1000 m μ . The two most prominent, at 970 m μ and 1025 m μ , will be denoted as the N_1 and N_2 bands for this discussion. The relative intensity of these two bands does not remain constant during bleaching or annealing as it does for the R bands and they must be considered individually. (The average of the two is given in Figs. 3 and 4—the ratio remained between 1:1 and 2:1 during the bleaching).

In crystal XIV the N_1 band increased by a factor of 1.7 between 730 and 2200 min after remaining constant from 27 to 240 min. The saturation plots, on the other hand, did not change in the final bleach but showed a marked increase in climb in the range 27 to 240 min.

To give the observed 15% decrease in low-power signal intensity between 730 and 2200 min (Fig. 7), assuming a magnetic N_1 , requires that the increase in N_1 concentration be compensated by a loss of F contribution to the resonance. With this picture one would again need a very special change in the T_1T_2 distribution for the centers to give identical saturation plots before and after this final bleach.

The argument against the N_2 is essentially the same as that against the R . In the 115°C anneal the N_2 is reduced by a factor of 3 (as opposed to 5 for the R 's) to a value corresponding to 9 min of bleaching. The changes in resonance behavior are too small to be interpreted as related to the change in N_2 density in any reasonable way, for the same reasons that were mentioned in discussing the R bands.

R' band. Scott¹⁸ describes an R' band which develops with extensive bleaching at temperatures above room temperature. A similar broad band appears under the resolved bands in the late stages of bleaching in this work. It has not been studied in detail, but the fact that it shows a marked growth in the final bleach where the resonance behavior has stabilized indicates that it is not responsible for the changes in the saturation properties of the resonance.

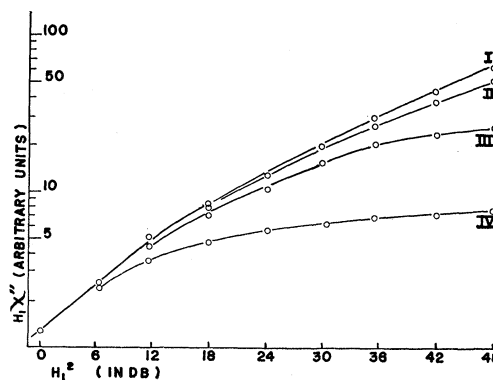


FIG. 9. Saturation plots for crystal XIV after various treatments. I. After 2200 min of bleaching. II. Same, but after 3 weeks storage in the dark. III. Same as II after 115° anneal for 10 min. IV. Same as III after 155° anneal for 15 min. See Table I for summary of other properties of this crystal.

¹⁸ A. B. Scott and L. P. Bupp, Phys. Rev. **79**, 341 (1950).

Other weak bands. One cannot rule out the possibility that any optical absorption band associated with the changes in magnetic behavior has so low an oscillator strength that it cannot be readily studied or that it lies outside of the region (230–1100 $m\mu$) studied in these experiments. The observation by Doyle¹⁹ that the total area under the various bands is constant with bleaching suggests that all of the excess electrons contribute to the optical absorption in the standard electron excess bands with an oscillator strength comparable to that of the *F* band. There seems little basis, then, to assume that one does not see the optical absorption from the “new” type of magnetic center.

F band. The negative correlations discussed above are the most compelling reasons for believing that the magnetic resonance centers in all stages of bleaching are, in large part at least, to be associated with the optical absorption in the region of the *F* band.

There is, in addition, some positive evidence in support of, or at least consistent with, this hypothesis. First, as Bron⁸ has noted, the narrowing of the spin resonance appears to be associated with the broadening to the violet of the *F* band, presumably corresponding to the development of the *B* band described by Petroff.¹⁷ During the bleaching the biggest changes both in optical and resonance linewidths occur in the bleach to 27 min. Also, after the thermal anneal at 155°C which reduces the climb of the saturation plot (run IV of Fig. 9 and Table I) the resonance linewidth has increased from 35 to 42 gauss (at intermediate power levels) and the width of the optical *F* band is reduced to nearly its original value (the presence of an *R'* band background reduces the accuracy to about $\pm 2 m\mu$). Second, despite a variation by a factor of 1.5 in the ratio of the resonance intensity at low power to the optical *F* band area, the roughly parallel behavior of these two intensities, plotted in Figs. 7 and 8, seems significant. The decrease in spin density relative to the optical density agrees qualitatively with the results of Lambe⁹ and of Sonder,¹⁰ indicating that some of the absorption in the region of the *F* band is associated with nonmagnetic centers if one supposes that the appropriate oscillator strengths are not much in excess of the “pure” *F* band strength. Most of the relative decrease appears to come in the early bleaching stages where the broadening of the optical line and the narrowing of the resonance line occur.

Note added in proof. The *F* band optical absorption areas plotted in Fig. 7 may be corrected for the presence of *M* and *R* absorption under the *F* band on the basis of the results of F. Okamoto [Phys. Rev. (to be published)]. As a result of this correction the optical *F* center absorption decreases more rapidly than the magnetic absorption rather than less rapidly. This result does not alter the conclusions of this paper.

We picture the bleaching as divided into three stages, or three different time scales, with the following rough

picture of each stage. In the first stage, up to 27 min, the prominent changes in the intensities of the *R*, *M*, and *N* bands occur and the *F* band broadens (Petroff's *B* band¹⁷). The *F* centers are either converted to a new center with a narrower resonance but optical absorption similar to the *F* absorption, or else they form simple complexes that result in a narrowing of the resonance but little change in optical absorption. In the second stage, 27 to 730 min, there is little change in optical behavior but the resonance becomes harder to saturate as the crystal is bleached. We suggest that there is a physical redistribution of centers within the crystal that results in a distribution of T_1T_2 values for the centers and that extended bleaching tends to reduce the mean value of this product. A possible mechanism is the formation of clusters of defects of sufficiently high density for dipolar interaction between spins to increase the packet width, $(1/T_2)$. Any nonuniformity among the clusters, as well as the locations of some centers within a cluster and some on the surface, will assure that any given sample will be characterized by a distribution of T_2 values, not by a unique value. This gives at least a possible explanation for the gradual climb in the saturation plot and for the observation that a single family of curves, such as those of Fig. 5, cannot fit every saturation plot for a given crystal. In the third stage, after 730 min, or more precisely, on a third time scale, one sees the beginning of the formation of further complexes (*R'* band) and perhaps colloidal potassium.

Magnetic R, M, or N? The original aim of this project was to learn about the magnetic nature of the *R*, *M*, and *N* bands. Although it is clear that the gross effects measured here—the changes in linewidth and in relaxation behavior—are not related to the presence of these centers, the original question remains unanswered. If the oscillator strengths of the other bands are near unity, as suggested by Doyle,¹⁹ then one can estimate the possible relative contribution of each of these centers to the spin resonance signal. In the bleaching of the quenched crystal, the maximum contribution of each of the bands relative to the *F*-band optical absorption was: either *R* band, 11% at 730 min; *M* band, 17% after 9 min; total area in *N* band, 9% after 2200 min. If these values are taken as the relative contributions to the resonance signal, it is clear that it would be very easy to overlook the presence of a contribution to the resonance signal from these other centers. For these reasons and because of the variations, produced by bleaching, of the resonance behavior of the centers associated with the region of the *F* optical absorption, it will be very difficult to identify the presence of a resonance from these other centers by any simple subtraction process.

CONCLUSIONS

(1) The saturation behavior of the *F* center resonance is not that predicted by Portis but agrees with Castner's generalization of that theory. There is some question

¹⁹ W. T. Doyle, Phys. Rev. **111**, 1072 (1958).

about the validity of this interpretation, however, and the problem is to be pursued further.

(2) Bleaching an additively colored crystal narrows the resonance width from 45 gauss to 35 gauss peak-to-peak in the derivative and gives a center whose resonance saturates less readily than the "pure" F center resonance. The variation in saturation behavior cannot be interpreted in terms of a simple two-center model.

(3) The changes in the resonance behavior discussed here are not correlated with the presence of R , R' , M , or N bands in the crystal. However, because of the small relative optical density of these bands, one cannot conclude from these results that the corresponding centers are nonmagnetic.

(4) The optical absorption associated with most of the resonance intensity is associated with the region near the F band throughout the changes induced by bleaching (or possibly with other bands of very low oscillator strength). This optical and magnetic absorption may be due either to F centers in altered surroundings or to a different defect produced by bleaching of the F center.

(5) It is suggested that the change in saturation behavior after long bleaching time is evidence of the clustering of the magnetic centers.

Note added in proof. Very similar results have been obtained independently by H. Gross and H. C. Wolf [Naturwissenschaften 8, 299 (1961)].

PHYSICAL REVIEW

VOLUME 124, NUMBER 2

OCTOBER 15, 1961

Susceptibility of Gadolinium Iron Garnet below the Néel Point*

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(Received June 7, 1961)

Measurements of the spontaneous magnetization and the superposed paramagnetic susceptibility of gadolinium iron garnet have been repeated with a specimen of good stoichiometry, in the range of 2 to 300°K. It is concluded that the effective field which the Fe sublattices exert on the Gd ions causes paramagnetic saturation and consequently a reduction in susceptibility of the Gd sublattice. Good quantitative agreement is obtained by using molecular field theory without any adjustable constants, and in contrast to earlier interpretations, it is not found necessary to postulate appreciable antiferromagnetic interactions between the Gd ions.

INTRODUCTION

AMONG many other unusual properties, several of the rare-earth iron garnets are distinguished by relatively large variations of magnetic moment with applied field, at temperatures well below their Néel points. This effect was already observed in the early measurements of Pauthenet,¹ and ascribed by him as due to the weak nature of the exchange forces acting on the rare-earth ions, leaving them virtually free to orient in an applied magnetic field. This is consistent with the fact that the observed susceptibilities were all close to the free-ion values, varying with temperature approximately as $1/T$. In all cases small deviations from Curie's law were observed and these were interpreted by Pauthenet in terms of a weak antiferromagnetic interaction between the rare-earth ions themselves.

In this note we wish to draw attention to the fact that there is another, more important effect which will give rise to deviations from a simple Curie law, arising from ordinary paramagnetic saturation of the rare-earth moments in the exchange field produced by the iron sublattices.² The magnitude of this effect may be estimated from the observed value of the spontaneous magnetic moment, without the need of introducing any adjustable constants, and we have found that good agreement with experiment is obtained if it is assumed that the rare earth-rare earth interaction postulated by Pauthenet is in fact negligibly small. This conclusion is also in agreement with various susceptibility measurements in paramagnetic rare-earth gallium and rare-earth aluminum garnets.³⁻⁶

* Supported in part by the U. S. Air Force Cambridge Research Research Center, through European Office of the Research and Development Command.

¹ R. Pauthenet, *Ann. phys.* 3, 424 (1958).

² A brief discussion of this effect has previously been given by W. P. Wolf and J. H. Van Vleck, *Phys. Rev.* 118, 1490 (1960), and W. P. Wolf, *Reports on Progress in Physics* [The Physical Society, London (to be published)].

³ J. Cohen and J. Ducloz, *J. phys. radium* 20, 402 (1959).

⁴ R. Pauthenet, *J. phys. radium* 20, 388 (1959).

⁵ M. Ball, G. Garton, M. J. M. Leask, and W. P. Wolf, *Pro-*