Magnetic Resonance and Rapid Passage in Irradiated LiF†

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(Received April 4, 1960)

The experimental result of Portis that at room temperature the paramagnetic dispersion signal ($d\chi_m'/dH$) of radiation-induced paramagnetic centers in LiF has the shape of an undifferentiated Gaussian curve and lags the modulation field by 90 degrees has been confirmed. His theory, explaining this result as a manifestation of rapid-passage behavior, has been tested over a range of experimental parameters and appears valid. In terms of this theory we found that the spin-lattice relaxation time $T_1=1.5\times10^{-4}$ sec at room temperature.

The prediction has been made by Portis that, if $\omega_m T_1\gg1$, where ω_m is the modulation frequency, the rapid-passage signal should lag the modulation field by 180 degrees. A lag of 130 degrees has been found at 4°K in LiF, using a modulation frequency of 23 cps, and the phase appears to approach a constant value. The same phase shift (130°) can be found at room temperature by using 400-cps modulation and can be interpreted as indicating that $T_1=2.6\times10^{-3}$ sec at 4°K. It seems more likely, however, that at 4°K the assumption made by Portis that $T_2\gg T_1$ fails, and that spin-spin effects make the situation more complex.

An argument is presented that the magnetic resonance arises from the F center. From its shape we have obtained a value for the hyperfine splitting: $h_\gamma=32\pm1$ gauss. This result is compared with those of other workers who have reported resolved structure in LiF, and the conclusion is reached that the resolved structure resonances probably do not arise from the F center.

PORTIS[1] found an unusual response when the magnetic resonance of irradiated LiF was investigated with a spectrometer tuned to detect the dispersion χ_m'. His spectrometer employed a small field modulation at 280 cps, superimposed on a slowly varying dc field. In this technique a signal, proportional to $d\chi_m'/dH$ and in phase with the modulation, is expected. Instead, he found a broad resonance at room temperature which was 90 degrees out of phase with respect to the modulation. Moreover, the line shape did not resemble the derivative of a dispersion, but rather an undifferentiated Gaussian curve.

Similar phenomena have been observed recently by Feher *et al.*,[2] by Ludwig *et al.*,[3] and by Feher[4] in semiconductors, and we have found that irradiated NaF responds in the same manner as LiF.

This unusual behavior was explained by Portis in terms of rapid passage; the analysis was amplified in a subsequent technical report.[5] Rapid passage was first discussed by Bloch,[6] who obtained an expression for the signal from a single homogeneously broadened line when the spectrometer was tuned to the dispersion, with the resonance saturated ($\gamma^2H_1^2T_1T_2\gg1$), and the dc magnetic field swept rapidly through the line, the spin system having been permitted first to come to equilibrium with the field set off resonance.

The F-center resonance in alkali halides can be thought of as arising from spins in a continuous distribution of local fields. The spins interact weakly, giving rise to the concept of spin packets of a width much smaller than the over-all distribution. Portis in his theoretical treatment visualizes the modulation field as sweeping back and forth through many of these narrow overlapping spin packets under rapid-passage conditions. In the following sections we review this theory and then describe our own experiments.

One of the serious problems in magnetic resonance in solids arises out of overlapping of lines. In particular, Kawamura and Ishiwatari[7] have shown in KCl that resonances from two centers, F and M, contribute to the observed line. Now the fact that rapid-passage signals are 90 degrees out of phase with respect to the modulation of the magnetic field while, in the usual case, signals are in phase, permits two overlapping resonances of different relaxation times to be disentangled. We have in fact found a resonance in irradiated LiF which is in phase with the modulation, resembles the usual dispersion derivative, and is of the order of ten percent of the amplitude of the rapid-passage resonance. An in-phase absorption curve $d\chi_m''/dH$ of roughly the same amplitude as the in-phase dispersion curve was also found. One conclusion of this work is that the rapid-passage resonance arises from the F center and that the more typical in-phase resonances arise from another center. The saturation condition must be satisfied for rapid passage to occur; this implies that under ordinary experimental conditions the F-center absorption χ_m'' is small (at saturation $\chi_m''\propto1/T_1$), and that the signal detected when the spectrometer is tuned to the absorption (the resonance which exhibits the resolved structure reported by Lord,[8]

† Sponsored by the Office of Naval Research, the Army Signal Corps, and the Air Force; it is based on a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics at the Massachusetts Institute of Technology.

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[1] A. M. Portis, Phys. Rev. **100**, 1219 (1955).

[2] G. Feher, R. C. Fletcher, and E. A. Gere, Phys. Rev. **101**, 1784 (1956).

[3] G. W. Ludwig, H. H. Woodbury, and R. O. Carlson, J. Phys. Chem. Solids **8**, 490 (1959).

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

[5] A. M. Portis, Technical Note No. 1, Sarah Mellon Scaife Radiation Laboratory, University of Pittsburgh, Pittsburgh, Pennsylvania (unpublished).

[6] F. Bloch, Phys. Rev. **70**, 460 (1946).

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

[8] N. W. Lord, Phys. Rev. **105**, 756 (1957).

Wolga,[9] and Kim *et al.*[10]) therefore comes from another, less numerous, center—possibly the M center. The study of rapid-passage behavior and identification of the observed resonances with the optical absorption bands and models are the parallel subjects of this paper.

THEORY OF RAPID PASSAGE IN INHOMOGENEOUSLY BROADENED LINES

Bloch[6] showed that under rapid-passage conditions the signal obtained from a homogeneous line is described by the following expressions for the magnetization:

$$M_x=\pm M\frac{\cos\omega t}{(1+\delta^2)^{\frac{1}{2}}},\quad M_y=\mp M\frac{\sin\omega t}{(1+\delta^2)^{\frac{1}{2}}},\quad M_z=\pm M\frac{\delta}{(1+\delta^2)^{\frac{1}{2}}},$$

where the rf field is given by $H_x=H_1\cos\omega t$, $H_y=-H_1\sin\omega t$, and $\delta=[H(t)-\omega/\gamma]/H_1$. The sign to be taken depends on whether at time $t=0$, δ is positive or negative (γ is assumed to be positive). The amplitude of the rotating component of magnetization is a maximum at the line center rather than the minimum expected from a dispersion signal; the breadth of the line is determined by the rf field strength H_1. The rapid-passage conditions are equivalent to the assumption that the amplitude of the magnetization vector **M** does not change during passage through the line but remains constant at a level determined by the field in which the spin system was permitted to come to equilibrium before the sweep was begun. The sign of the detected signal depends on whether this field is above or below resonance.

Portis carried out an integration over the contributions by the various spin packets of the inhomogeneous line in an interval H_m determined by the modulation field $H_m\cos\omega_m t$. We will not repeat the calculations but will attempt to make the results physically plausible. The assumption is made that T_2 can be replaced by T_1 in the Bloch equation, since direct spin-spin interaction should be negligible.

The integrations are carried out over the distribution of spin resonances $h(\omega-\omega_0)$ in much the same way as in the theory of saturation of inhomogeneously broadened lines. Here, however, the analysis is related only to the component of magnetization that is in phase with the rf field, i.e., the dispersion χ_m'.

Consider the case in which $H_1/H_m<\omega_m T_1<1$. Under these conditions a relatively long time is spent at the ends of the modulation cycle, and the magnetic vector **M** of each packet in the line is able to reach the thermal equilibrium level corresponding to one or the other of these fields. After equilibrium has been reached at one end, the intermediate region is swept; equilibrium is again reached at the other end and a return sweep through the spins is made. Since the sign of the instantaneous signal depends on whether the sweep has come from high or low field, the resonance signal is at the modulation frequency and not at the second harmonic. It lags the modulation field by 90 degrees and is proportional to the density of spins in the region of modulation H_m. If this density varies little over the width of the modulation, the resonance observed as the dc field is slowly swept will have the shape of $h(\omega-\omega_0)$.

Consider next the situation when $H_1/H_m<1<\omega_m T_1$. In this case a portion of the spectrum which has been pulsed by the sweep of the magnetic field will not have recovered when the magnetic field reappears. Imagine a packet near the high end of the modulation sweep; let the sweep be initially at the opposite end, and let the instantaneous magnetization of the spin packet under consideration correspond to this low field. Then during the time that the sweep approaches the packet, the magnetization increases slightly. At resonance this magnetization flips over and points in the opposite direction (see the expression for M_z above), although the amplitude does not change. During the relatively short portion of the cycle when the modulation field is greater than the resonance field of our spin packet, the amplitude of **M** decreases as the system attempts to restore the reversed vector to thermal equilibrium. Upon reappearance of the sweep, **M** again turns over and the amplitude approaches a value corresponding to some average of the low fields. After many cycles, $|M|$ will approach an equilibrium level determined by the length of time spent above and below the field of the spin packet. If these times are equal, i.e., if the packet is at the center of the modulation region, $|M|$ will be zero. The instantaneous signals arising from packets at the two extremes will have opposite senses and will here be of maximum amplitude; the sinusoidal resonance signal lags the modulation field by 180 degrees. Again the shape of the resonance, as the dc field is varied, will be $h(\omega-\omega_0)$.

TABLE I. Amplitude and shape of the magnetic dispersion (χ_m') signal to be expected under various field conditions.

General conditions	
$dH_0/dt<\omega_m\Delta H$	(Quasistatic variation of main field)
$H_1<\Delta H$, $H_m<\Delta H$	(No line distortion by modulation and rf fields)
$\omega_m H_m<\gamma H_1^2$, $dH_0/dt<\gamma H_1^2$	(Adiabatic rapid passage)
$\gamma H_1 T_1>1$	(Saturated resonance)

Condition	Amplitude	Shape of resonance
$\frac{H_1}{H_m}<\omega_m T_1<1$, $\frac{dH_0}{dt}<\omega_m H_m$	$\frac{M_z}{H_z}\frac{2H_m\omega_m T_1}{H_1}\sin\omega_m t$	$h(\omega-\omega_0)$
$\frac{H_1}{H_m}<1<\omega_m T_1$, $T_1\frac{dH_0}{dt}<H_m$	$-\frac{M_z}{H_z}\ln\frac{2H_m}{H_1}\cos\omega_m t$	$h(\omega-\omega_0)$

[9] G. J. Wolga, Ph.D. thesis, Physics Department, Massachusetts Institute of Technology, 1957 (unpublished); G. J. Wolga and M. W. P. Strandberg, J. Phys. Chem. Solids **9**, 309 (1959).

[10] Y. W. Kim, R. Kaplan, and P. J. Bray, Bull. Am. Phys. Soc. **3**, 178 (1958); **4**, 261 (1959).

It is apparent that these two examples are limiting cases. As $\omega_m T_1$ passes through 1, a continuous change of the signal phase is expected. The change in phase as the temperature is lowered and T_1 increases is one of the subjects that have been studied in this investigation.

Portis studied several other cases, the conditions for which have not been reached in the experiments described here. His results, relevant to this work, are summarized in Table I, which gives the resonance responses to be expected, provided the general conditions stated are satisfied.

These expressions suggest a number of experiments. From the change of signal level with respect to H_m and to H_1, values for T_1 can be obtained. If the temperature can be raised high enough, or H_1 made small enough, the saturation condition $\gamma H_1 T_1 > 1$ will no longer be satisfied and a resonance of the usual shape and phase should be found, again yielding a value for T_1. If the temperature is lowered, one expects a continuous shift of phase from 90 to 180 degrees. The change of modulation frequency which gives the same shift of phase will give information on the temperature dependence of T_1. Since the line shapes are directly $h(\omega-\omega_0)$, one can check for consistency with the shape expected from F-center electrons interacting with nearest-neighbor nuclei.[11] A value for the interaction constant of the electron with the nuclei of the first shell can be obtained.

EXPERIMENTAL PROCEDURES

The spectrometer used in this investigation will be described in detail elsewhere.[12] It operates at K band (1 cm) and employs superheterodyne detection. The local oscillator is locked 30 Mc/sec away from the signal-klystron frequency. The signal klystron in turn is locked to the resonant frequency of a reference cavity using an i.f. Pound frequency stabilizer. The sample is in a high-Q transmission cavity operating in the TE_{011} mode. A microwave bridge permits observation of either the dispersion (χ_m') or the absorption (χ_m''). A signal proportional to $\chi_m H_1$ is detected. Field modulation at 23 cps is used most often, although provision is made for modulation detection at 400 cps. Phase-sensitive detection of the resonance signal is employed and the resulting dc signal plotted on a recorder.

The sensitivity of the spectrometer was determined by observing the resonance of lightly colored KBr and normalizing to 1 gauss. The g value (1.980) and line width (152 gauss) which were found for the F center in KBr agree well with the values quoted by Kip, Kittel, Levy, and Portis.[11] We found an extrapolated sensitivity of 5×10^{10} electron spins for a one-gauss line at room temperature. The rf field was of the order of 0.1 gauss at the sample and a 20-second time constant was used.

Phase measurements of the resonance signal with respect to the field modulation are a crucial part of the experiment. There is accurate phase control of the reference signal at the phase-sensitive detector. The angular variation of the phase is linear through a full 360 degrees, and the amplitude of the shifted signal does not vary significantly with phase.

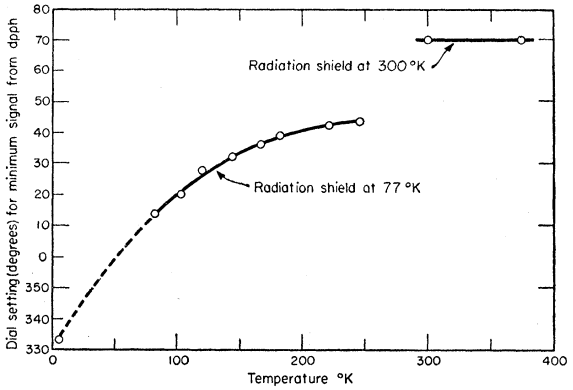

FIG. 1. Change of phase of the magnetic-field modulation which accompanies the decrease of skin depth with decreasing temperature.

The free radical, *dpph*, was used to determine that dial setting of the phase shifter which gives a maximum signal for a particular set of experimental conditions. Phase shifts of the rapid-passage resonance were measured with respect to this angle.

The phase of the signal from *dpph* can be determined to within a few degrees by setting the phase shifter so that a null response is plotted on the recorder as the dc magnetic field is swept through the resonance condition. The phase shifter was proven reliable. Maximum and minimum for a particular experiment were found consistently at the same dial setting.

Two instrumental phase shifts were found. The phase of the signal from the transformer driving the field-modulation coils was dependent on the power delivered to the modulating coils. A more important effect is that the attenuation of the modulation field, because of low skin depth in the cryostat and cavity walls, is accompanied by a phase shift. Thus the phase of the modulation field outside the cryostat is not the same as the phase at the sample. This can be a large effect. At 23 cps with about 6 mm of metal surrounding the sample, a shift of 100 degrees was found between room temperature and 4°K (Fig. 1). The effect will of course be greater at higher modulation frequencies.

We often ran successive curves at phase-angle intervals of 45 degrees. One would not expect a change in line shape with phase if the signal comes from a single paramagnetic center, but in many cases such a change has been found. The curves taken at 45-degree intervals permit mapping of this behavior. At other times the in-phase and in-quadrature angles were determined and curves run at each. Usually the spectrometer was tuned to detect the dispersion, but the absorption was also studied.

[11] A. F. Kip, C. Kittel, R. A. Levy, and A. M. Portis, Phys. Rev. 91, 1066 (1953).
[12] P. A. Miles and J. S. Hyde (to be published).

Absolute power measurements were made using a dc bridge and barretter. Measurements of the cavity parameters enabled us to arrive at the rf field at the sample. We estimate an internal consistency in these field values of 20% over the entire experiment and an absolute accuracy of 50%.

The crystals used in this work were for the most part produced by the Harshaw Chemical Company. They were purchased over a period of years and do not seem to be entirely uniform in colorability and impurity content. Most of the samples were cleaved from a new Harshaw crystal. In addition, resonance responses of LiF and NaF supplied by the Optovac Corporation were observed.

In general, the crystals were colored by γ irradiation from Co^{60}. The intensity of this source is of the order of 225 000 rep per hour. Periods of irradiation varying from 30 minutes to 180 hours were used, most measurements being made on samples irradiated 24 hours. These crystals are yellow. In addition, several measurements were made on a crystal lightly colored by x rays.

Optical absorption spectra were measured on a Cary Recording Spectrophotometer. We were able in all cases to reach the top of the F-center absorption band (except in the 180-hour irradiation, where a height corresponding to the known width at half height of the F-center band in LiF was reached, permitting calculation of the peak absorption). The number of F centers was determined from the optical absorption spectrum by using the Smakula formula,[13] assuming an oscillator strength of unity. Our experience in coloring the crystals is described in the appendix.

The samples were cleaved to approximately 2×2×6 mm and were located on the cavity axis. The rf field, H_1, varied by about 20% over a sample of this size.

EXPERIMENTS

Systematic Mapping under Variation of rf Field and Modulation Amplitudes

As has been indicated, we have found that under certain experimental conditions the phase of the dispersion signal from irradiated LiF is not the same in all portions of the resonance. Thus no angle of the phase shifter can be found where the signal is everywhere zero. At one setting of the phase shifter the signal will resemble a bell-shaped rapid-passage resonance, while 90 degrees away it is a typical derivative of a dispersion. The relative amplitudes depend on the experimental conditions.

An initial experiment was the mapping of this behavior. An arbitrary temperature choice of −178°C was made. Five curves were run at 45-degree phase angles for several rf fields between 0.2 and 0.003 gauss and modulation depths between 2 and 50 gauss. This particular crystal contained 9×10^{17} F centers per cm^3.

[13] A. Smakula, Z. Physik **59**, 603 (1930).

The following results were obtained:

1. With H_1 constant at 0.2 gauss, the in-phase signal increased relative to the in-quadrature signal as H_m increased. At 2-gauss modulation the ratio was 1:5; at 50, 1:2.
2. With H_m constant at 10 gauss, the in-phase signal increased relative to the in-quadrature signal as H_1 increased from 0.02 to 0.2 gauss.
3. At 10-gauss modulation and 0.02-gauss rf field, the in-phase signal was small: about $\frac{1}{10}$ of the rapid-passage signal; i.e., the line shape changed little with phase and an angle could be found where the signal was nearly zero throughout the line.
4. At $H_1=0.003$ and $H_m=30$ gauss the in-phase and in-quadrature signals were nearly equal whereas at $H_1=0.006$ and $H_m=50$ gauss the in-phase signal was about $\frac{1}{3}$ of the in-quadrature signal. This is a strong reversal of the trend established at higher H_1.
5. At $H_1=0.003$ gauss, the ratio of in-phase to in-quadrature signals did not change with H_m. Again, this differs from the result at higher rf fields.

The interpretation of these results, supported by a number of other experiments, is as follows: At the highest rf fields, resonances from two or more centers are detected. One of these is an out-of-phase rapid-passage response and the other a normal inhomogeneously broadened line of about the same width as the rapid-passage line. This latter center is radiation-induced and has a shorter relaxation time T_1. The expressions for the rapid-passage signal level derived by Portis show that it does not increase proportionately to H_m and H_1. Thus, as H_1 and H_m increase, the signal level does not increase as rapidly as it does for an ordinary inhomogeneously broadened resonance. Hence the in-phase signal level shows a relative increase.

At lowest powers we have concluded that the in-phase and in-quadrature signals arise from a single center, the saturation condition $\gamma H_1 T_1 > 1$ is failing, and conversion from rapid passage to normal resonance behavior occurs. The Portis equations indicate that the phase of the rapid-passage signal and the degree of saturation are

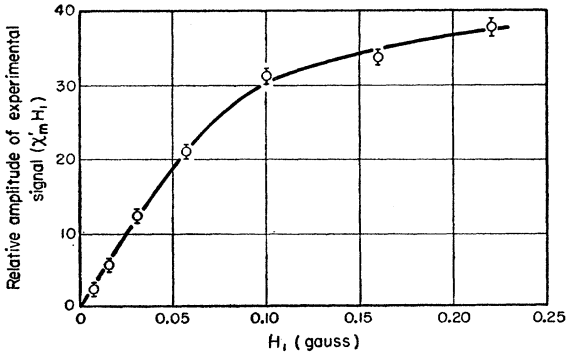

FIG. 2. Saturation of the rapid-passage resonance with increasing rf field (room temperature, 10-gauss field modulation).

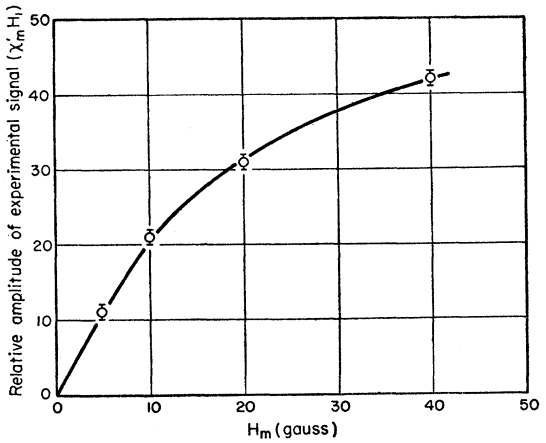

FIG. 3. Saturation of the rapid-passage resonance with increasing magnetic-field modulation (room temperature; $H_1=0.2$ gauss).

independent of H_m; the fifth result above is in agreement with this.

When we studied only the rapid-passage response, the experimental parameters of 10-gauss modulation and 0.02-gauss rf field intensity were selected. (At 4°K we found that further reductions to 2-gauss modulation and 0.006-gauss rf field intensity were needed if complications by signals other than the rapid-passage signal were to be avoided.)

Change of Signal Level with rf Field Strength

The observed change of signal level with H_1 is shown in Fig. 2. These data were taken at 10-gauss field modulation, room temperature, and on a heavily irradiated crystal ($N_F=3.4\times10^{18}/\text{cm}^3$). The phase shifter was carefully adjusted so that the signals came entirely from the rapid-passage resonance. At high powers the curve fits the Portis equation. We can make an evaluation of T_1 using any two points on this curve. All combinations of the four high-field points yield fairly consistent values with an average of $T_1=1.4\times10^{-4}$ second. A markedly different value is found from the low field points however; T_1 is three to four orders of magnitude shorter with these values. We suggest that this departure is because the adiabatic condition, $\omega_m H_m<\gamma H_1^2$, is failing; this occurs at $H_1=10^{-2}$ for $H_m=10$ gauss, $\omega_m=2\pi\cdot23$.

Change of Signal Level with Modulation Field Strength

Figure 3 shows a plot of the amplitude of the rapid-passage curve as the sweep is increased. For this experiment a crystal was selected which originally contained 10^{18} F centers per cm^3. It had been used extensively for resonance experiments at +150°C and at this temperature some thermal bleaching occurred. Nevertheless this particular crystal had been used in many different experiments, and the results obtained were consistent with those from crystals which had not been exposed to high temperatures. The largest modulation was of the order of 10% of the over-all line width, while $H_1=0.2$ gauss, for this experiment.

As expected, we find a saturation type of behavior. Again one can calculate a value for T_1 using any pair of points. We find $T_1=2\times10^{-4}$ sec at highest modulation and 10^{-3} sec at lowest modulation. This is in fair agreement with the T_1 calculated in the preceding section.

Thus it is shown that the Portis equations are essentially correct in predicting the amplitude dependence and that the proposed explanation of the observed increase of in-phase with respect to quadrature signals at high H_m and H_1 is therefore reasonable.

Resonance Behavior at Low Power Level

The in-phase and in-quadrature curves obtained at low power levels and at +150°C are shown in Fig. 4. They illustrate the increase of the in-phase curve with decreasing H_1. At lowest fields, rapid-passage response has nearly disappeared. Similar results were obtained with the same experiment at room temperature, although the transfer to ordinary resonance behavior was somewhat less complete.

Assuming $\gamma H_1 T_1=1$, for $H_1=0.012$, we find $T_1=4.7\times10^{-5}$ sec at +150°C. The consistency with our other determinations of T_1 (the value is about 3 times shorter than at room temperature) is evidence that at low fields the resonances arise essentially from a single source.

Response of Various Crystals

It appears from the foregoing that a second broad inhomogeneous resonance, which has a significantly shorter spin-lattice relaxation time, is present. The experimental effects arise both from it and from the F center. The obvious suggestion is that the other resonance arises from the M center. Optical absorption spectra are shown in Fig. 11, where the M center is associated with the band at 4400 A. This center is thought to be composed of two missing halogen ions and one missing alkali ion with a single trapped electron. The electron would very likely interact with surrounding nuclei much as the F-center electron. The lower symmetry of the center probably would serve to decrease the spin-lattice relaxation time.

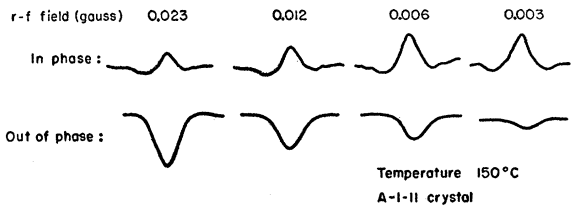

FIG. 4. The high-temperature, low-power dispersive response of LiF.

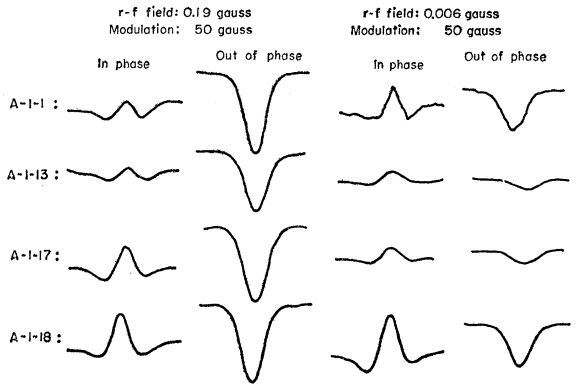

FIG. 5. High- and low-power in- and out-of-phase dispersive response of 4 different LiF crystals.

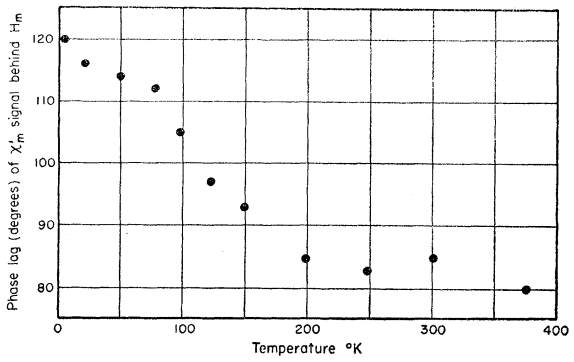

FIG. 6. Lag of rapid-passage signal χ_m' behind modulation field as function of temperature.

The optical absorption spectra show that the F center does not increase as rapidly as the M center under prolonged irradiation. Thus it is possible to change the ratio of F to M centers. Following this suggestion, we have run curves at high H_1 and low H_1, both in phase and quadrature, on four different crystals: A-1-1 ($N_F=1.3\times10^{17}$) colored by x rays; A-1-13 ($N_F=2\times10^{17}$) colored for two hours by Co^{60}; A-1-17 ($N_F=3.4\times10^{18}$) colored for 180 hours by Co^{60}; and A-1-18 ($N_F=10^{18}$) an Optovac crystal colored for 24 hours by Co^{60}. The curves are shown in Fig. 5.

The low-power curves show that the ratio of in-phase to quadrature amplitudes is nearly the same for each crystal; this confirms that at lowest powers the signals arise essentially from a single source.

At high powers the ratios of in-phase to quadrature signals differ among the crystals by more than a factor of two. Thus, two or more centers of different relative concentrations presumably contribute to the absorption. This is a crucial experiment which led directly to the interpretation advanced in this paper.

The identification with the M center is not conclusive, however. The crystal A-1-17 has the highest M/F ratio of any crystal used, yet the ratio of in-phase to quadrature signals for A-1-18 is at least as great.

A number of experiments along this line were carried out but the reproducibility leaves something to be desired. Each time a new crystal is put into the spectrometer, or a crystal is rotated, the coupling of the microwave cavity to the input and output guides changes, Q_L changes, and H_1 at the sample changes. The general trend is, however, well established. It may very well be that the M center is the only significant contributor to the in-phase high H_1 resonance, but we could not make positive identification.

Change of Phase of the Resonance with Respect to Variation of Experimental Parameters

No change in phase of the rapid-passage signal with respect to variation of H_1 over 20 db or with respect to variation of H_m over 10 db was noted. Within experimental error no variation in shift was found among the various crystals used in this investigation.

A phase shift of the resonance did occur when the temperature and the modulation frequency were changed. Figure 6 shows a plot of the change of phase with respect to temperature at 23-cps modulation. In these data the change of phase, which is related to the skin depth of the magnetic-field modulation and which increases markedly as the temperature is lowered, has been subtracted (see Fig. 1).

The result showed that a shift of only 40 degrees occurred between room temperature and 4°K. We did not reach the case predicted by Portis, where the reso-

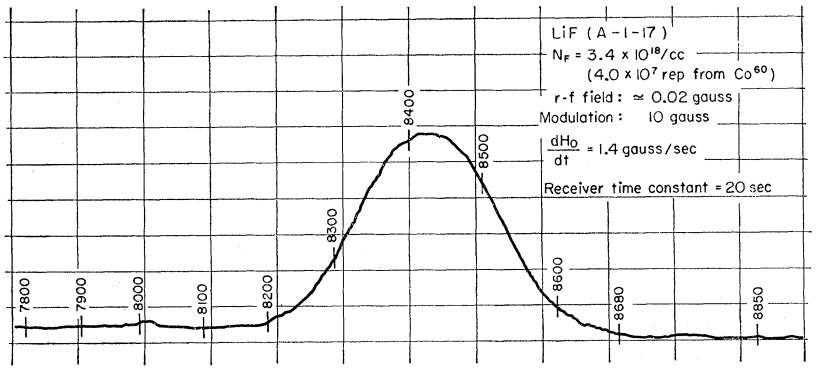

FIG. 7. The rapid-passage resonance at room temperature.

nance is 180 degrees out of phase with respect to the modulation. Extensive measurements at 4°K were not made, but the experiment was performed twice with consistent results. The phase of the signal does not change rapidly near liquid-helium temperature and may well approach a constant value.

We measured the phase of the signal at a modulation frequency of 400 cps and room temperature. It was found that the signal lagged the modulation field by 130 degrees.[14]

If the Portis theory is correct, we conclude that a change of frequency from 23 to 400 cps is equivalent to a change of temperature from 300° to 4°K and that the dependence of T_1 on temperature is very weak. If we take a value of $T_1=1.5\times10^{-4}$ sec at room temperature, as indicated by the experiments discussed previously, $T_1=2.6\times10^{-3}$ sec at 4°K. It seems likely, however, that at this temperature complications arise because the assumption made by Portis that $T_2>T_1$ fails. In another paper[15] Portis calculated T_2 for a dilute inhomogeneous line; an evaluation of the expression derived there for our particular system yields a value of 2.7×10^{-3} sec. In the same paper it is pointed out that if $T_1>T_2$, spin-diffusion effects should be observable under saturation conditions. It is possible that it is this phenomenon which limits the phase shift to 130 degrees.

Line Shapes and g Values

We have made measurements of the shape of the rapid-passage line at room temperature, selecting experimental parameters such that the in-phase signal is nearly zero, thus lessening the possibility of line distortion. A reproduction of one of the experimental curves is shown in Fig. 7.

The physical basis by which one can calculate the envelope of the distribution of local fields has been discussed by Kip, Kittel, Levy, and Portis.[11] For six nearest neighbors, there are $(2I+1)^6$ possible combinations of the spins of the nuclei and these states divide into $2(6I)+1$ different local magnetic fields or hyperfine lines. For $I=\frac{3}{2}$, the populations are:

0	1	2	3	4	5	6	7	8	9
580	546	456	336	216	120	56	21	6	1,

where 0 corresponds to the center line and 9 to the two outermost lines.

Figure 8 is a plot of the experimental data from Fig. 7. The circles are theoretical points using the calculated distribution of states and assuming a hyperfine splitting which gives the best agreement with the experimental curve. The result is a separation between hyperfine lines of 32 ± 1 gauss. This exceeds the splitting reported by Lord[8] and Wolga[9] by a factor of two. This discrepancy will be discussed in the next section.

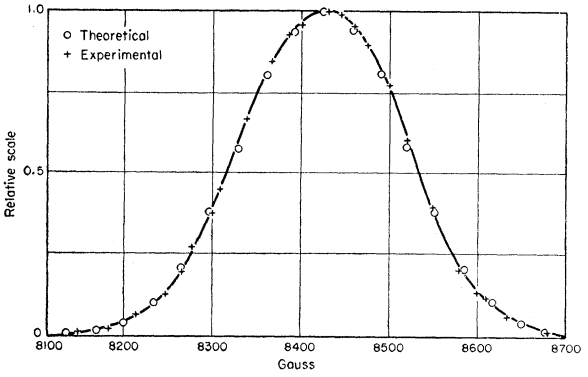

FIG. 8. Comparison of experimental line shape of magnetic resonance (Fig. 7) with theoretical line shape based on 32-gauss splitting of the hyperfine lines.

In this fit of the experimental curve we have assumed that interaction with second-nearest neighbors is negligible. Kip, Kittel, Levy, and Portis[11] showed in KCl that this interaction increases the half-width of the observed resonance by about 15%. We have, however, no information on interaction with second-nearest neighbors in LiF and have not introduced a correction.

We tried to get a good curve of the normal in-phase resonance which we find in irradiated LiF, so that the line shape could be studied (Fig. 9). The line shape is not uniquely determined since a slight change of the receiver phase shifter will add a large contribution to the signal from a rapid-passage resonance. It is our opinion that lack of symmetry of the curve is an instrumental effect that arises from mixing of χ_m' and χ_m'' or from too fast a passage through the over-all line, although it may be real since every attempt was made to eliminate these difficulties.

We have made measurements of the g value of the rapid-passage line and also of the in-phase resonance by comparison with the known g value of *dpph* (2.0036). The accuracy is not high but the g values of both resonances are certainly greater than those of the free electrons. We found $g_{\text{rapid passage}}=2.007\pm0.002$ and can only say that the g value of the in-phase resonance is greater than that of *dpph*.

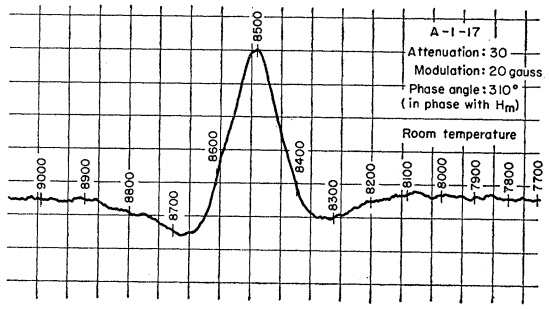

FIG. 9. The in-phase dispersion resonance in LiF.

[14] Subsequent experiments performed at Varian Associates by the author show that at 100-kc field modulation and room temperature the phase of the rapid-passage resonance in LiF lags by a full 180 degrees.

[15] A. M. Portis, Phys. Rev. **104**, 584 (1956).

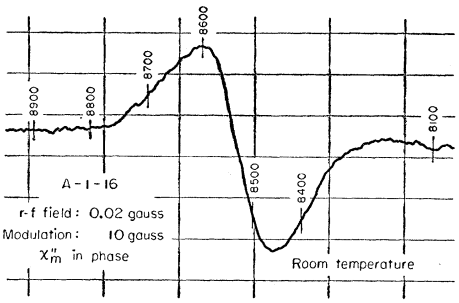

FIG. 10. Magnetic loss (χ_m'') in LiF.

Magnetic Loss χ_m''

Thus far in our discussion of the nature of the resonance behavior of LiF color centers no mention has been made of the magnetic-loss factor χ_m''. In fact, signals are obtained when the microwave bridge of the spectrometer is tuned to detect the absorption. We have found that at low powers ($H_1 \leqslant 0.02$ gauss) a typical derivative of an absorption curve is obtained. One such curve is shown in Fig. 10. At these power levels, the amplitude of the absorption curve is about the same as that of the in-phase dispersion curve. At highest powers, the amplitude of the absorption curve is much less than that of the in-phase dispersion curve and inhomogeneous saturation apparently occurs. It was difficult to carry out measurements of the absorption curve at high power levels, since in this case there are very large in-phase and quadrature dispersion signals. Very slight drifts of the microwave bridge give dispersive contributions to the resonance and distort the shape of the absorption curve.

Despite the high sensitivity of the spectrometer, it was not possible to detect the resolved structure in the LiF resonance found when the spectrometer is tuned to the absorption, probably because at K band a much smaller sample must be used than at X band, where the previous experiments were performed.

We comment parenthetically that we have found no indication that the absorption curve is ever out of phase with the magnetic-field modulation.

At lowest powers ($H_1=0.003$ gauss) in-phase χ_m' and χ_m'' and the quadrature rapid-passage signal χ_m' are of about the same amplitude, whereas at $H_1=0.02$ the rapid-passage resonance is ten times greater than either of the in-phase curves. As has been indicated, this behavior is interpreted in terms of interplay of the inhomogeneous resonances from two centers of different concentrations and relaxation times. At lowest powers the in-phase resonances are a mixture from the two centers, with the source that exhibits rapid-passage response being the dominating contributor. At higher powers the in-phase resonances come substantially from a single center while the rapid-passage resonance comes from the other center.

Miscellaneous Experimental Points

Impurity resonances. A number of indications of the presence of other very dilute paramagnetic centers have been found. As the rf field is increased or the temperature is lowered, these become more noticeable, in line with the interpretation that under these conditions the rapid-passage resonance is suppressed relative to resonances from centers with shorter T_1.

We observed the resonances of lightly colored crystals ($N_F=6.7\times10^{16}/\text{cm}^3$) and found a very complicated structure with marked anisotropy. Apparently these resonances are increasingly masked as the number of F centers grows. We speculate that they arise from impurity traps and are associated with the broad optical absorption band on the long-wavelength side of the F band (Fig. 11). The optical absorption spectra show that this band increases rapidly at low levels of irradiation but saturates quickly, while the F and M bands continue to grow.

NaF experiment. Rapid-passage response has been found in irradiated NaF. The relaxation time seems to be somewhat shorter than in LiF. The width at half height is of the order of 400 gauss. This material was chosen because NaF and LiF are the only alkali halides for which resolved structure studies have been successful. The fact that they each exhibit rapid-passage behavior supports the interpretation of this paper: T_1 is very long, χ_m'' of the F center is strongly suppressed, and the resonance of another less populous center, the hyperfine structure of which can be resolved, becomes dominant.

DISCUSSION AND COMPARISON WITH THE RESULTS OF OTHER WORKERS

Resolved Structure Studies

Resolved structure experiments have been reported by Lord,[8] Wolga,[9] and Kim *et al.*[10] Wolga examined lightly colored LiF (the samples were light yellow). He does not report a concentration of centers, but we have carried out optical absorption measurements on crystals colored exactly as his, and find $N_F=2\times10^{17}/\text{cm}^3$. He does report the number of centers in the crystal as determined by magnetic-resonance methods assuming no saturation: $N_F=2\times10^{14}/\text{cm}^3$. Wolga reports that under the conditions of his experiment the resonance is well within the region of inhomogeneous saturation. The preceding paper shows that the ratio of susceptibilities of unsaturated to saturated inhomogeneously broadened lines, everything else assumed to be constant, is $1/T_1\gamma H_1$. Wolga does not determine absolute values of H_1, but if T_1 is in the range from 10^{-4} to 10^{-5} sec, H_1 must be in the range from 0.6 to 6 gauss if the above discrepancy in values of N_F is to be explained. These rf field intensities seem high by one order of magnitude. In any event, satisfactory identification of the resonance with the F center has not been made.

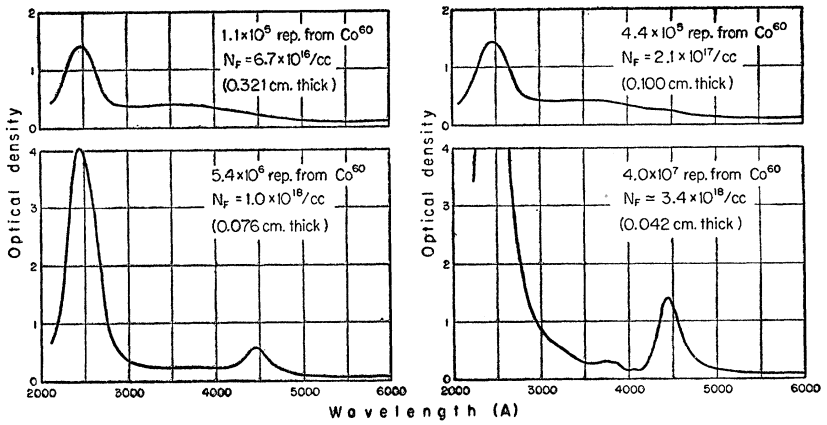

FIG. 11. LiF (Harshaw) optical absorption ($\log_{10}I_0/I$ vs λ) for various Co^{60} doses.

The curves obtained by Wolga show about nine resolved lines and the signal-to-noise ratio is not high enough to give any information about the over-all line shape. He reports a splitting of 17 ± 0.5 gauss and a g value of 1.996 ± 0.0004. The curve published by Lord, obtained on heavily irradiated crystals (the samples were dark brown), has a well-defined over-all line shape and eleven hyperfine lines. Lord reports $g=2.0029\pm0.0001$ and a splitting of 14 ± 0.1 gauss. It is therefore possible that Lord and Wolga have investigated the resonances from different centers.

In addition, Wolga determined analytically the breadth of individual hyperfine lines (assuming a Lorentzian line shape) if hyperfine structure is to be partially resolvable, as observed experimentally, and showed that this width is of the order of the hyperfine splitting. The over-all line obtained by Lord extends well over 400 gauss, with a signal-to-noise ratio such that one would expect to see the effect of only the central 15 of the 19 lines. Bringing these factors together, we see that a hyperfine splitting of 14 gauss can give rise to a resonance which extends only over about 200 gauss if the F-center model is correct.

Kim has studied samples which have been heavily irradiated with neutrons (the samples were black). It might be argued that the nature of the damage is essentially different, since the nuclear reaction $Li^6+n^1\rightarrow H^3(2.7\text{ Mev})+He^4$ (2.1 Mev) occurs. One might expect anisotropic damage because of thermal or displacement spikes. However, Gilman and Johnston[16] have argued effectively that for every fission 1500 defect pairs are produced by ionization. Thus, the damage essentially arises from this ionization and this method of coloring is basically no different from any other. These workers found no evidence of anisotropic damage.

The line shape and g values obtained by Kim are apparently the same as those found by Lord and presumably both resonances arise from the same center. But Kim has a very good signal-to-noise ratio and can resolve 29 or more lines. This is consistent with the argument above that the line found by Lord is too broad and cannot arise from the F center, assuming the usual model. Moreover, Kim found marked anisotropy. This suggests that an M center or similar aggregation of several vacancies is involved.

It is interesting to note that the splitting which we have found from the rapid-passage resonance is in fair agreement with the initial theoretical calculation of Gourary and Adrian.[17] The most recent calculation by these workers,[18] however, shows less splitting, The figures are:

Gourary and Adrian[17]	$h_\gamma=40.0$ gauss
Lord	$h_\gamma=14\pm0.1$ gauss
Wolga	$h_\gamma=17\pm0.5$ gauss
Hyde	$h_\gamma=32\pm1$ gauss
Gourary and Adrian[18]	$h_\gamma=19.0$ gauss

Identification of the Rapid-Passage Resonance

We have criticized other workers for concluding without sufficient evidence that they are observing the F-center magnetic resonance; in the present work, also, some doubt must remain as to whether the center which exhibits rapid-passage response is in fact the F center. The argument advanced by both ourselves and the other workers is that the F band is by far the strongest optical absorption band and should give rise to the strongest magnetic resonance. However, in previous work it was the absorption χ_m'' which was observed, and it has been shown that this quantity saturates with increasing H_1 at a level proportional to $1/T_1$. A center arising from fewer spins can easily give a stronger resonance if the relaxation time is shorter. On the other hand, it was found that the dispersion of an inhomogeneous line does not saturate. Thus the strongest magnetic resonance when the spectrometer is tuned to the dispersion very

[16] J. J. Gilman and W. G. Johnston, J. Appl. Phys. **29**, 877 (1958).

[17] B. S. Gourary and F. J. Adrian, Phys. Rev. **105**, 1180 (1957).

[18] B. S. Gourary and F. J. Adrian, "Wave Functions for Electron-Excess Color Centers in Alkali Halide Crystals," in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York and London, 1960), Vol. 10, p. 127.

likely comes from the center with the largest magnetic concentration.

Our experience indicates that the rapid-passage signal level is proportional to F-center concentration. No anisotropy has been found. The shape of the resonance is as expected when the principal broadening arises from interactions of an F-center electron with six nearest-neighbor nuclei. It seems likely that only a center with the symmetry of the F center could have a spin-lattice relaxation time long enough at room temperature to put it into the rapid-passage region. We concluded that the F center gives rise to the rapid-passage response.

ACKNOWLEDGMENT

The author is very greatly indebted to Professor P. A. Miles, with whom all phases of this work have been discussed in detail.

APPENDIX. OPTICAL ABSORPTION OF IRRADIATED LiF

It seems desirable to summarize our experience in coloring of LiF crystals with Co^{60}. The number of F centers was determined using the Smakula[13] formula as quoted in Landolt-Börnstein[19] and assuming an oscillator strength of unity. The numbers of F centers we have found produced in Harshaw LiF for various irradiation doses are:

dose (rep)	N_F/cm^3
1.1×10^5	6.7×10^{16}
1.6×10^5	1.5×10^{17}
4.4×10^5	2.1×10^{17}
9.6×10^5	5.2×10^{17}
5.3×10^6	1.0×10^{18}
4.0×10^7	3.4×10^{18}

The data show that coloration is more efficiently accomplished at low levels than at high levels, as is well known.

Typical absorption spectra for four levels of coloration, obtained using a Cary Recording Spectrophotometer, are shown in Fig. 11. Several interesting observations can be made. The broad band on the long-wavelength side is very pronounced relative to the F band at low coloration; at intermediate levels this band can barely be detected; at highest levels other bands begin to appear in this region.

The absorption curve for heaviest irradiation is of interest. To our knowledge, absorption peaks have not previously been reported at 4050 and at 3700 A. Delbecq and Pringsheim[20] do list bands at 3400 and 3800 A, which can be seen in the figure (Fig. 11).

[19] Landolt-Börnstein, *Zahlenwerte und Funktionen* (Springer-Verlag, Berlin, 1955), Vol. 1, Part 4, p. 981.

[20] C. J. Delbecq and P. Pringsheim, J. Chem. Phys. **21**, 794 (1953).

PHYSICAL REVIEW VOLUME 119, NUMBER 5 SEPTEMBER 1, 1960

Saturation of the Magnetic Resonance Absorption in Dilute Inhomogeneously Broadened Systems*

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(Received April 4, 1960)

The existing theory due to Portis for the saturation of inhomogeneously broadened resonances is discussed and a new theoretical formulation of the problem is developed using an expression for the transition probability first given by Rabi. For γH_1 greater than both T_1^{-1} and T_2^{-1}, the rf field interacts with spins precessing in the frequency interval γH_1; this expression permits explicit calculation of the resulting magnetic loss. No assumption is made of the shape of the individual (homogeneously broadened) spin packets in weak exciting fields. For F centers in alkali halides, the results are identical with those of Portis, but the underlying physical reasons differ.

SPIN systems that give rise to magnetic resonance absorption may be classified as homogeneous or inhomogeneous. A homogeneous resonance arises from unpaired spins placed in identical local magnetic fields and precessing at the same characteristic frequency except for a bandwidth due to mutual coupling. An inhomogeneous resonance is caused by spins spread over a continuous distribution of local fields and precessing at a variety of Larmor frequencies. The responses of these two types of systems to a large rf field (H_1) are quite different. The loss part of the rf susceptibility, χ'', for a homogeneous line saturates as $1/H_1^2$ with an accompanying change of line shape, but for a dilute, inhomogeneous line, as $1/H_1$ with no change in line shape.[1]

Bloch[2] and Bloembergen, Purcell, and Pound[3] have

* Sponsored by the Office of Naval Research, the Army Signal Corps, and the Air Force; based on a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics at the Massachusetts Institute of Technology.

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[1] A. M. Portis, Phys. Rev. **91**, 1071 (1953).

[2] F. Bloch, Phys. Rev. **70**, 460 (1946).

[3] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).