Magnetic circular dichroic effects in the luminescence of F centers in KI, KBr, and KCl

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We have measured magnetic-field-induced circular polarization of the F-center emission in KI, KBr, and KCl at 1.9 K in fields up to 80 kG. Both diamagnetic (field-dependent) and paramagnetic (spin-dependent) effects have been observed. The latter requires a special technique in which the pump beam is modulated between right and left circular polarization. The expected behavior as a function of the frequency of the modulation has been observed. We have also measured the spin-lattice relaxation time in the relaxed excited state in KI and KBr for $B \geq 50$ kG. All the previous measurements indicate a value of the spin-orbit splitting, $|\lambda|$, of the order of 1 meV, which is considered a surprisingly small value from purely theoretical grounds.

I. INTRODUCTION

Until a few years ago little was known about the relaxed excited state (RES) of the F center. The principal experimental observation was that the radiative lifetime τ is quite long ($\tau \approx 1$ μsec). This fact led to various speculations about the nature of the RES.[1] In particular a $|2p\rangle$ diffuse wave function or a $|2s\rangle$, lower in energy than $|2p\rangle$, state was supposed to produce such a long radiative lifetime. These two ideas, which have been in contrast for a long time, are now assumed to be both partially correct. Indeed the diffuse nature of the wave function[2] and the $|2s\rangle$ character of the lowest level of the RES[3,4] have been confirmed by precise experimental results. However in spite of the previous significant achievements, the exact nature of the RES is still the subject of a lively debate.[5-7]

Several theoretical attempts[8-10] have been made in these last years to solve the problem posed by the phonon-electron interaction in the relaxed configuration. In one of the more complete vibronic models a proper dynamic Jahn-Teller theory has been developed in the strong-coupling limit[11] and in the weak-coupling limit.[12] In both cases analytical results have been derived for various quantities, such as the radiative lifetime and its change with an applied electric field, the polarization induced in the luminescence by electric fields, applied stress and magnetic fields and the isotropic g factors. Apart from the red shift induced in the emission energy by an applied electric field, the weak-coupling limit seems to account for most of the experimental data available, but a simultaneous fitting of all the data turns out to be impossible.

However, the previous analysis emphasizes the importance of the various magnetic effects exhibited by the RES.

The first measurements of the magnetic-circular-dichroic (MCD) effects in the luminescence of the F center were made by Fontana and Fitchen[13,14] in KF and KCl. Since the effect, which corresponds to a change in the zeroth-order moment of the luminescence band, is obtained for zero-spin polarization, it is known as "diamagnetic" effect. Subsequently Baldacchini and Mollenauer[15] extended the observation of the diamagnetic effect to KBr and KI and in addition made the first observation of dichroic effects which are associated with a nonzero electron spin polarization in the RES. These latter are known as "paramagnetic" effects. It has been deduced[16] from the rate equations of the optical pumping cycle of the F center that it is impossible to obtain at the same time a finite polarization, P_ρ, and a significant population in the RES with a pump beam of any kind of linear (π) or circular (right σ^+, left σ^-) polarization. However an oscillating polarization can be obtained if the beam is modulated between right and left circular polarization. The amplitude of P_ρ is strongly dependent on the frequency of modulation. We used this method to produce a nonzero value of P_ρ in order to observe the paramagnetic effect. We have recently confirmed in[17] KI and[18] KBr the results obtained previously[15] and in particular we have measured the paramagnetic effect as a function of the modulation frequency.

In this paper, we report the values of the diamagnetic effect and an accurate analysis of the paramagnetic effect at the temperature of 1.9 K and in magnetic fields up to 80 kG for F centers in KI, KBr, and KCl. In Sec. II, we will discuss in detail the solutions of the rate equations for the polarization of the RES and of the ground state. In Sec. III we will give precise definition of the dichroic signal to be measured. The experimental apparatus will be presented in Sec. IV and the main results plus some interpretations in Secs. V and

VI. A brief discussion will be given in Sec. VII about the spin-lattice relaxation time in the RES, and conclusions will be drawn in Sec. VIII.

II. POLARIZATION IN THE GROUND STATE AND IN THE RES

As stated above, when an intense pumping beam of appropriate wavelength is modulated between σ^+ and σ^-, then it is possible to obtain an oscillating polarization and a significant population in the RES. A large value of P_ρ is essential to probe spin-dependent dichroic effects in the luminescence of F centers.

We assume that the pumping beam has constant intensity and that its polarization is sinusoidally modulated. Therefore, indicating with u_+ (u_-) the pump rate out of the $M_s=+\frac{1}{2}$ ($M_s=-\frac{1}{2}$) ground-magnetic substate,[16] we have

$$u_+ + u_- = U \quad \text{and} \quad u_- - u_+ = UP_s \sin\omega t .$$

P_s is the dichroic differential absorption, which is maximum for pumping at a dichroic peak, and whose value coincides with the polarization of the ground state P for a steady saturating pumping. The polarization is defined as, $P=(n_+ - n_-)/(n_+ + n_-)$, where n_+ (n_-) is the population of the $M_s=+\frac{1}{2}$ ($M_s=-\frac{1}{2}$) magnetic sublevel.

By using the rate equations[16] that govern the dynamics of optical pumping, after tedious but straightforward calculations, the following expression for P is obtained:

$$P=\overline{P}+(A^2+B^2)^{1/2}\sin(\omega t+\varphi), \quad \varphi=\tan^{-1}(B/A). \tag{1}$$

P_ρ is given by the same expression where $\overline{P}$, A, and B are replaced by $\overline{P}_\rho$, A_ρ, and B_ρ. These coefficients are given by the following relations:

$$\overline{P}=\frac{P_0}{1+\epsilon U T_1}, \tag{2a}$$

$$A=(1-2\epsilon)P_s\left\{\frac{U}{2}\left[\frac{2\epsilon}{1-2\epsilon}\,\frac{1}{T_r}+\omega^2\tau\right]\times\left[\omega^4\tau^2+\omega^2+\left(\frac{1}{T_r}\right)^2\right]^{-1}\right\}, \tag{2b}$$

$$B=-P_s\left\{\omega\,\frac{U}{2}[2\epsilon+(\omega\tau)^2]\left[\omega^4\tau^2+\omega^2+\left(\frac{1}{T_r}\right)^2\right]^{-1}\right\}, \tag{2c}$$

and

$$\overline{P}_\rho=(1-2\epsilon)\,\frac{P_0}{1+\epsilon U T_1}, \tag{3a}$$

$$A_\rho=-(1-2\epsilon)P_s\,\frac{(1/T_r T_1)+\omega^2}{\omega^4\tau^2+\omega^2+(1/T_r)^2}, \tag{3b}$$

$$B_\rho=-(1-2\epsilon)P_s\,\frac{\omega[(1/T_p)-\omega^2\tau]}{\omega^4\tau^2+\omega^2+(1/T_r)^2}. \tag{3c}$$

Here, ϵ, called the spin-mixing parameter, represents the probability for one spin to be reversed in one optical cycle, T_1 is the spin-lattice relaxation time in the ground state, $1/T_p=\epsilon U$, $T_r^{-1}=T_1^{-1}+T_p^{-1}$, τ is the radiative life-time of the RES, and P_0 the thermal equilibrium value of the ground-state polarization, P. The solutions given above are obtained by making the following approximations: $\tau[\frac{1}{2}U+(1/T_1)]\ll 1$ and $\tau/T_{1\rho}\ll 1$. The first one is well satisfied at the pumping levels used in our experiment: $U_{\max}\leq 10^5\ \text{sec}^{-1}$, since $\tau\simeq 10^{-6}$ sec and $T_1^{-1}\leq 10^2$ for the highest fields used.[19] The second approximation, where $T_{1\rho}$ is the spin-lattice relaxation time in the RES, is satisfied at least at low magnetic fields, $B\leq 30$ kG.[16]

The amplitudes of the time-dependent optically induced polarizations can be expressed in a simpler analytical form in particular interesting ranges of frequency as follows:

(i) $\omega\approx\tau^{-1}$,

$$|P|\cong P_s\,\frac{U}{2}\tau\,\frac{[(1-2\epsilon)^2+(\omega\tau)^2]^{1/2}}{1+(\omega\tau)^2}, \tag{4a}$$

$$|P_\rho|\cong(1-2\epsilon)P_s\,\frac{1}{[1+(\omega\tau)^2]^{1/2}}.$$

(ii) $1/T_r\ll\omega\ll 1/\tau$

$$|P|\cong P_s\,\frac{U}{2}\tau\left[(1-2\epsilon)^2+\left(\frac{2\epsilon+(\omega\tau)^2}{\omega\tau}\right)^2\right]^{1/2}, \tag{4b}$$

$$|P_\rho|\cong(1-2\epsilon)P_s.$$

(iii) $\omega\approx 1/T_r$, $T_r\cong T_p$,

$$|P|\cong\frac{1}{[1+(\omega T_p)^2]^{1/2}}, \tag{4c}$$

$$|P_\rho|\cong(1-2\epsilon)P_s\,\frac{\omega T_p}{[(1+\omega T_p)^2]^{1/2}}.$$

(iv) $\omega\simeq 0$,

$$|P|\sim P_s\,\frac{\epsilon U T_1}{1+\epsilon U T_1}, \tag{4d}$$

$$|P_\rho|\sim(1-2\epsilon)P_s\,\frac{1}{1+\epsilon U T_1}.$$

Hence, the polarizations P_ρ are independent of the pumping power, proportional to U, in ranges (i) and (ii) and strongly dependent on U in ranges (iii) and (iv). In any case there is a wide region, of frequencies $1/T_r\cong 1/T_p\ll\omega\ll 1/\tau$, in which a large value of polarization is created in the RES by this kind of optical pumping. Usually $1/\tau\approx 10^6$ and $1/T_p\approx 10^4$ at its maximum, hence a large plateau exists where $|P_\rho|=(1-2\epsilon)P_s$. Taking for P_s the values 0.4, 0.15, and 0.05, and for ϵ the values 0.24, 0.04, and 0.01, as given in Ref. 16, the amplitude of P_ρ is approximately 0.21, 0.14, and 0.05 for KI, KBr, and KCl, respectively. These numbers have to be taken cautiously because the values of P_s and ϵ are known only roughly. It is interesting to note that in range (ii), while P_ρ assumes a well-defined value, P has a practically negligible value. In addition, P decreases when ω increases, while P_ρ goes to zero both at high frequencies and at low frequencies for $\epsilon U T_1 \gg 1$, which is generally the case in this work.

III. DEFINITION OF THE QUANTITIES TO BE MEASURED

The luminescence experiments are concerned with the amount of σ^+, σ^- light emitted in response to pumping into the absorption band of the F center with σ^+, σ^-, or π polarized light. Thus it will be convenient to adopt the notation $I^{\pm}_{\pm,0}$ to describe the luminescence intensities where the superscript + or − refers to the σ^+ or σ^- polarization, respectively, of the emitted light, and where the subscript refers to the polarization (σ^+, σ^-, or π) of the pump light.

In the measurement of the diamagnetic effect, the pump beam has a steady polarization, and hence the luminescence intensities I^+ and I^- are each time independent. But it can be shown[20] that if the luminescence is analyzed by the combination of modulating $\frac{1}{4}\lambda$ plate and linear polarizer, its intensity will be given by

$$I_\alpha(t) = \tfrac{1}{2}(I^+_\alpha + I^-_\alpha) + \tfrac{1}{2}(I^+_\alpha - I^-_\alpha) a_1 \sin(\omega_0 t) . \quad (5)$$

The subscript α can be +, −, or 0; the coefficient a_1 is determined by the amplitude of the modulation drive; ω_0 is the fundamental frequency of the modulator and higher odd harmonics have been dropped. As a measure of the diamagnetic effect we define the quantity

$$S_{d,\alpha} = \frac{I^+_\alpha - I^-_\alpha}{I^+_\alpha + I^-_\alpha} . \quad (6)$$

In Sec. IV it will be shown how the diamagnetic effect (6) can be measured in practice.

For measurement of the paramagnetic signal the incident intensity, modulated sinusoidally, may be written

$$i_\pm(t) = \tfrac{1}{2}(i_0)[1 \pm a_1 \sin(\omega t)] , \quad (7)$$

where with the modulator adjusted for optimum effect, $a_1 = 1.16$, and where once again, we have dropped higher odd harmonics. The luminescence response to the pump will then also be time dependent as follows:

$$I^\beta(t) = \tfrac{1}{2}(I^\beta_+ + I^\beta_-) + \tfrac{1}{2}(I^\beta_+ - I^\beta_-) a_1 \sin(\omega t + \varphi) , \quad (8)$$

where the superscript β will be (+) or (−), depending on whether σ^+ or σ^- light is detected. As a measure of the paramagnetic effect, it is convenient to define a quantity analogous to Eq. (6):

$$S^\beta_p = \frac{I^\beta_+ - I^\beta_-}{I^\beta_+ + I^\beta_-} . \quad (9)$$

We should emphasize that the quantity S^β_p contains all the properties of the polarization of the RES as outlined in Sec. II.

At this point it is convenient to recall that because of the factor a_1 in the modulated intensity (7), the same factor will appear in all the expressions calculated in Sec. II. Hence the values of P and P_ρ must be multiplied by the factor a_1.

IV. APPARATUS AND PROCEDURES

Although the theory may be rather difficult, the fundamental scheme of the luminescence experiments, shown in Fig. 1, is quite simple. The sample is optically pumped by a laser beam that propagates parallel to the direction of a magnetic field B. Luminescence emitted into a small solid angle centered about the B direction is then focused by a lens on the detector. The dc output from the detector is directly recorded, while the ac component is fed into a lock-in amplifier whose reference frequency is given by the oscillator which drives the $\pm\frac{1}{4}\lambda$ modulator. The lock-in output is then recorded.

For measuring the diamagnetic effect, the pump light has a fixed polarization, either π, or σ^+ or σ^- (produced by a linear polarizer plus a fixed $\frac{1}{4}\lambda$ plate), and the induced circular polarization in the luminescence is detected by using a $\pm\frac{1}{4}\lambda$ stress-plate[20] modulator oscillating at $\omega_0 = 20$ kHz, in conjunction with a linear polarizer (polaroid) as analyzer. The combination of these two elements gives a time-dependent intensity as in Eq. (5). Then if V_{ac} is the peak detector voltage and V_{dc} its dc level, it can be easily shown[20] that the diamagnetic signal S_d is given by:

$$S_d = \frac{1}{a_1}\left(\frac{V_{ac}}{V_{dc}}\right)_{dia} . \quad (10)$$

Hence, S_d can be easily deduced by the ratio of the two recorded signals if the lock-in gain is known.

For measuring the paramagnetic effect, the pump beam is modulated as in Eq. (7) by the combination of linear polarizer and modulating $\pm\frac{1}{4}\lambda$ plate (an electro-optic device), and the dichroism in the luminescence is detected by using a fixed $\frac{1}{4}\lambda$ plate, in conjunction with a linear polarizer. The analyzer can be set to transmit σ^+ or σ^- light. Once again, under the same conditions as given for Eq. (10) one has:

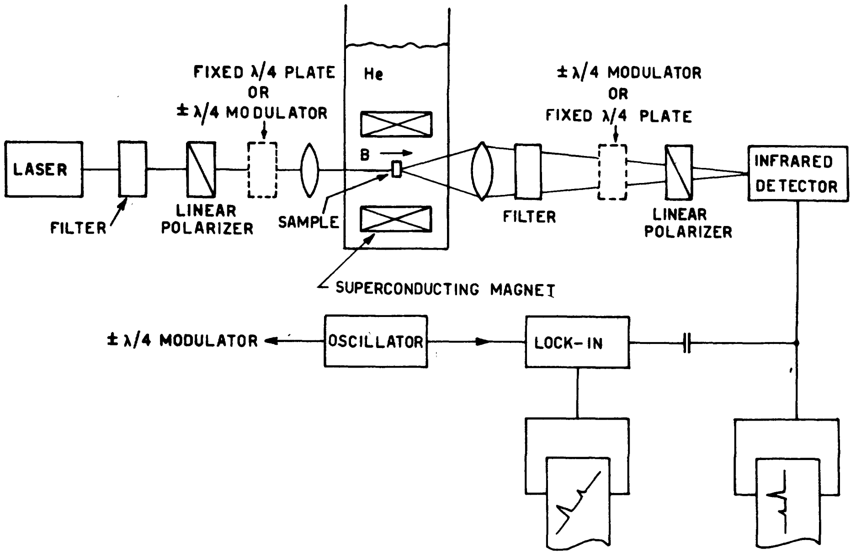

FIG. 1. Block diagram of the experimental apparatus. The $\pm\frac{1}{4}\lambda$ plate modulator is inserted in the luminescence beam and the fixed $\frac{1}{4}\lambda$ plate in the pumping beam for measuring the diamagnetic effect. By simple exchange of these two elements the paramagnetic effect can be measured.

$$S_p = \frac{1}{a_1}\left(\frac{V_{ac}}{V_{dc}}\right)_{para}, \tag{11}$$

where V_{ac} and V_{dc} refers to the detector output, and where $a_1 = 1.16$.

The absorption and emission bands of the F center in KI, KBr, and KCl are sketched in Fig. 2, along with the magnetic circular dichroism signals of the absorption bands. As can be seen from the figure, a He-Ne laser at 6328 Å for KI and KBr, and a Ar^+ ion laser at 5145 Å for KCl make very good pump sources, since the two wavelengths correspond closely to one of the peaks of the dichroic signal in the absorption bands. We would like to stress that the pumping on one of the dichroic peaks is essential in order to have the maximum differential absorption, and hence, the maximum value of P_s. The emission of the F center is at a photon energy too low to allow use of a photomultiplier as detector, except for KCl where an S-1 type photocathode can still be used. In any case a germanium-diode detector cooled to 0 °C, and having a noise equivalent power of $\simeq 10^{-11}$ W, has been used for the bulk of the measurements. Finally since the absorption and emission bands are widely separated, a colored glass filter (RG-1000 Schott), when placed in the luminescence beam, removes all trace of the 6328 or 5145 Å light. An ir color filter (KG-3 Schott) was used to block ir emission from the laser.

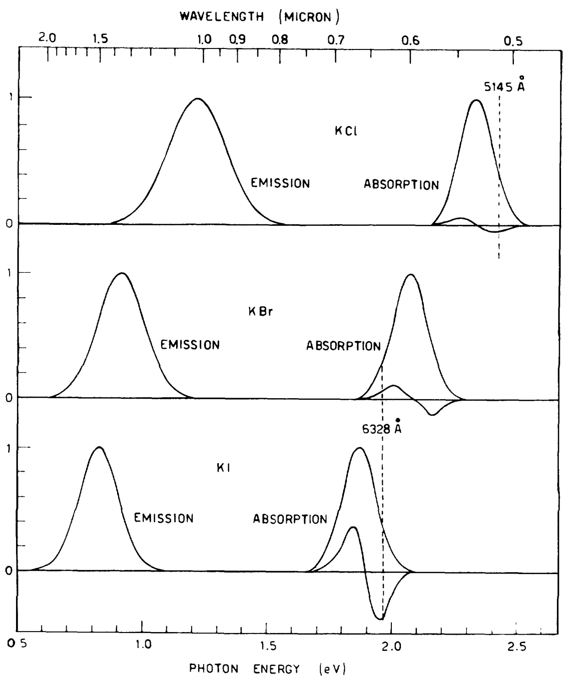

FIG. 2. Calculated Gaussian curves of absorption and emission at low temperature for F centers in KI, KBr, and KCl. Magnetic circular dichroism in absorption (derivative signals) and pumping light wavelength (vertical dotted lines) are also shown.

Samples of KI, KBr, and KCl used in these experiments, were home grown by the Kyropulos method, additively colored, quenched in liquid nitrogen, cleaved to $\simeq 1$ mm thickness and mounted in the bore of a superconducting magnet in an optical dewar.[21] The samples were immersed in liquid helium, and all the experiments were performed at 1.9 K. The concentration of F centers was calculated by using the Smakula formula, where the oscillator strengths for KI, KBr, and KCl were taken as 0.83, 0.80, and 0.90, respectively. The values are $(4-7)\times 10^{16}$, $5\times 10^{16}/\text{cm}^3$, and $2\times 10^{16}/\text{cm}^3$ for F centers in KI, KBr, and KCl, respectively.

V. RESULTS AND INTERPRETATION

A. Diamagnetic effect

Figures 3 and 4 show the signals V_{ac} and V_{dc} as recorded with the experimental apparatus set to reveal the diamagnetic effect in KI and KBr, respectively. The labels $S_{d,\pm}$ and $S_{d,0}$ of the various ac signals are somewhat incorrect because a proportionality constant exists between V_{ac} and S_d, [see Eq. (10)]. The $S_{d,0}$ curves show a linear dependence on the field up to 50 kG for KI and up to 60 kG for KBr. These results are analogous to those obtained by Fontana and Fitchen in KF and KCl, except for the fact that the slopes of the curves are larger for KI and KBr. Because of the large spectral band of our detecting system, we have measured essentially a change of the zeroth moment of the band, just as was found for KF,[13] and KCl.[14] We did not try to make precise moments measurements by narrowing the spectral band because of problems posed by the signal-to-noise ratio. The nonlinear behavior at high fields represents instead a new unexpected result, which cannot be attributed to a change of the pumping intensity. Indeed the luminescence,

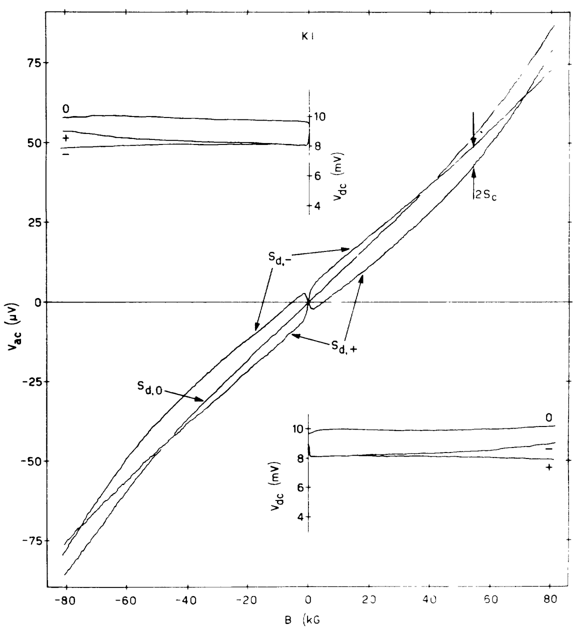

FIG. 3. Recorded diamagnetic signals and luminescence intensities for KI. The three curves refer to σ^+, π, and σ^- pumping light, and are obtained with $a_1 = 0.47$.

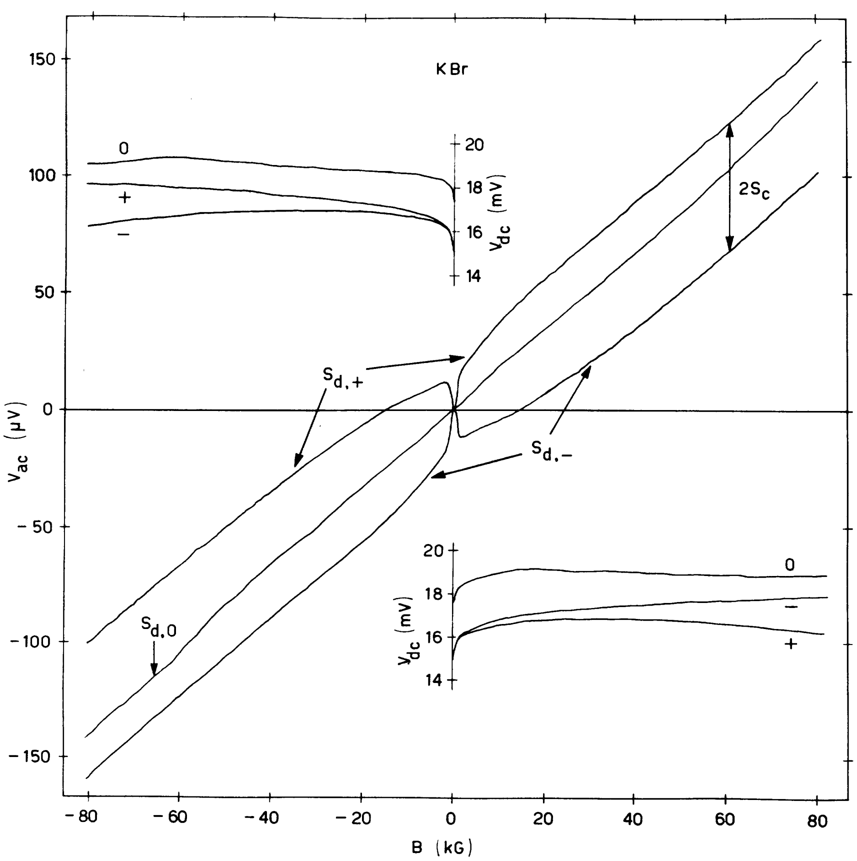

FIG. 4. The same as Fig. 3 for KBr with $a_1 = 0.52$.

TABLE I. Summary of the diamagnetic effect data.

Crystal	$\|C_d\|$ (10^{-8}G^{-1}) Fontana and Fitchen References 18, 19	Baldacchini and Mollenauer Reference 15	This work
KF	6 ± 1	⋯	⋯
KCl	9 ± 1	⋯	11 ± 1
KBr	⋯	16.3 ± 1.7	17 ± 2
KI	⋯	18.5 ± 1.2	19 ± 2

$V_{dc}(0)$ recorded at the same time does not show any sensible variation; the decrease at $B=0$, bigger in KBr than in KI, is probably due to the Porret-Lüty[22] effect. Another surprising fact was the net off-set of $S_{d,+}$ and $S_{d,-}$ from $S_{d,0}$. These signals have a marked dependence on the magnetic field near zero field, but, when properly corrected for the variation of $V_{dc}(+)$ and $V_{dc}(-)$ at $B\neq 0$, S_{d+} and S_{d-} show the same behaviors of $S_{d,0}$ and also the nonlinearity of high fields. The difference in the emission, $V_{dc}(+)\neq V_{dc}(-)$, is a consequence of a differential absorption of σ^+ and σ^- pump light of the F center in a magnetic field. This effect, which has some consequences for the paramagnetic signals, will be explained in more detail in Sec. V B. We will show also the reasons for the remarkable increase of $V_{dc}(0)$ near zero field for KI.

Except for very high fields the diamagnetic properties can be well described by:

$$S_{d,\alpha}=C_dB+\alpha S_c\,, \qquad (12)$$

where α has the values ± 1 or 0, and S_c (see Figs. 3 and 4) is a field-dependent quantity. Measurements analogous to those shown in Figs. 3 and 4 have been made for F centers in KCl. The main differences are: the slope of $S_{d,0}$ is smaller than in KI and KBr, the quantities $S_{d,+}$ and $S_{d,-}$ are almost indistinguishable from $S_{d,0}$ (S_c is about ten times smaller), and the "diamagnetic" effect is linear up to the maximum obtainable field ($\simeq$83 kG). We wish to make clear here that no attempt was made to identify the circular pump polarization absolutely with σ^+ and σ^-; hence the labels $S_{d,+}$ and $S_{d,-}$ might just as well be reversed in Figs. 3 and 4. Similarly, only the absolute value of C_d was actually found in these experiments. Values of $|C_d|$ were determined in two crystals of KI, one each for KBr and KCl, in various experimental runs and various pumping intensities. Table I shows the average of those values for KI, KBr, and KCl compared with the values for KI and KBr, given by Baldacchini and Mollenauer,[15] and for KCl and KF, given by Fontana and Fitchen.[13,14] Values of S_c will be given later in Sec. V.

B. Paramagnetic effect

Figure 5 shows the signals S_p^+ and S_p^- along with the luminescence intensities V_{dc} for KI at two frequencies of modulation; Fig. 6 shows the same quantities for KBr. The signals are shown as a function of positive magnetic field, and the two frequencies have been chosen in the frequency range (ii) (see Sec. II) for the left-hand side (a) of the figures and in range (iv) ($\omega \ll 1/T_p$) for the right-hand side (b). Figure 7 shows the same signal for KCl as a function of positive and negative field and for a single frequency of modulation in range (ii). In each case, the data were taken by switching the fixed $\frac{1}{4}\lambda$ plate of the analyzer back and forth between (+) and (−) position every few seconds while the magnetic field is slowly varying. The figures show the actual plot of data as recorded. Once again, no attempt was made to identify the (+) and (−) positions of the analyzer absolutely with σ^+ and σ^-. The luminescence intensities are reported in Figs. 5–7 because of their step structure, which represents a difference between the σ^+ and σ^- emission. The difference is clearly increasing with the magnetic field. At first sight this behavior would seem strange, but it is easily explained if one looks carefully at the symmetry of the two experiments, diamagnetic and paramagnetic. Indeed the pumping beam modulated between σ^+ and σ^- is equivalent for the dc luminescence to a stationary π incident light. Hence the luminescence variation measured in the paramagnetic experiments is exactly the difference, $(I_0^+ - I_0^-)$, of the diamagnetic signal $S_{d,0}$ as defined in (6). The values of $|C_d|$ obtained from measurements as in Figs. 5–7 agree, within the experimental errors, with those obtained previously from the diamagnetic experiments (Sec. V A). The small decrease of the luminescence at zero field is probably due to the Porret-Lüty[22] effect, as in the diamagnetic effect. The only exception [Fig. 5(a)] where an increase is observable, will be explained in the next section. Except near zero field, the mean value of luminescence is constant and it has been used in (11) to obtain the paramagnetic signal S_p reported

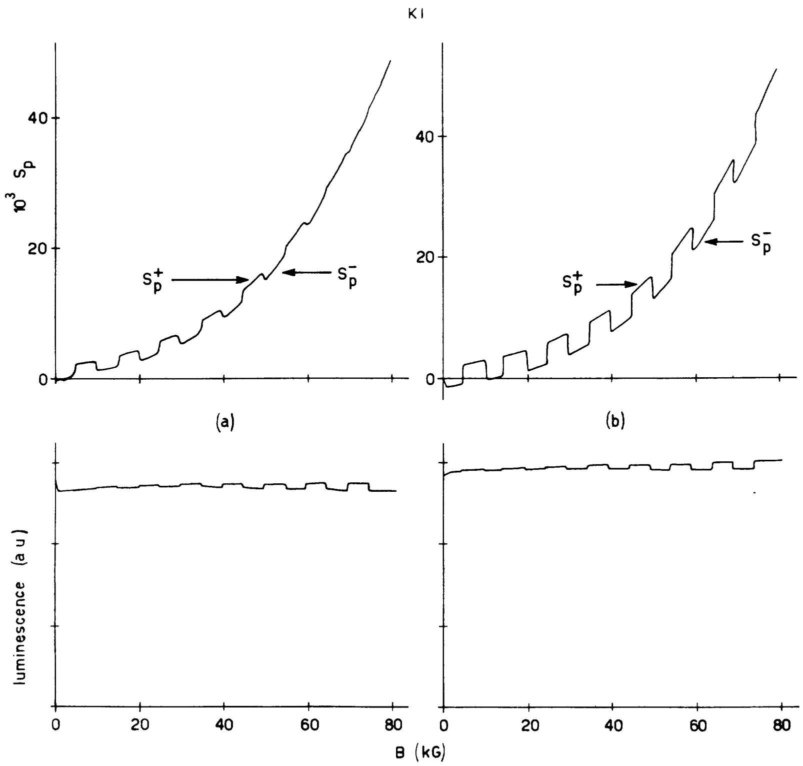

FIG. 5. Recorded paramagnetic signals and luminescence intensities for KI as a function of magnetic field, for two values of the frequency of modulation; (a) $\nu = 20$kHz; (b) $\nu = 70$Hz. For detail see text.

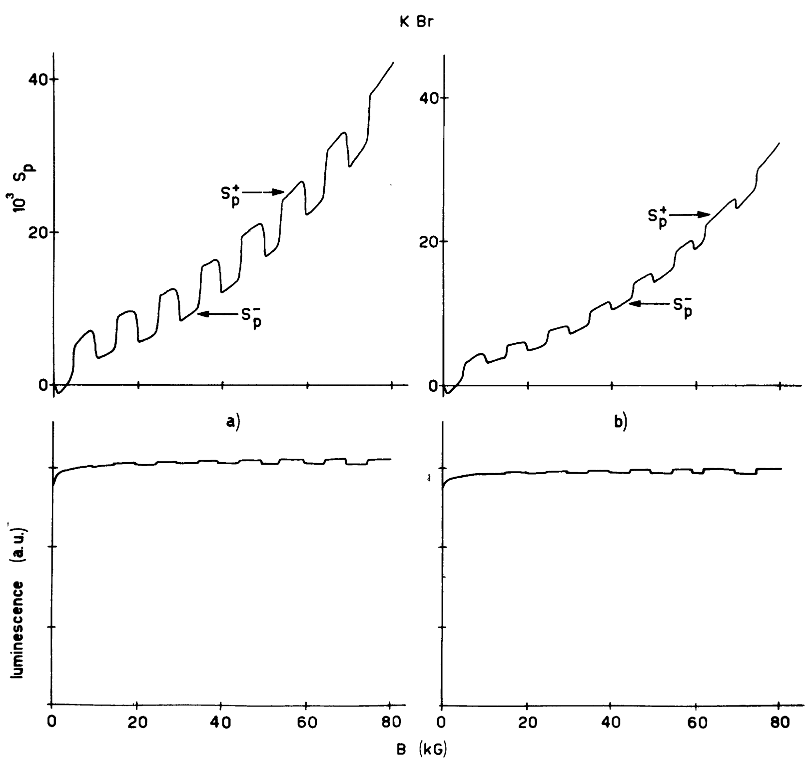

FIG. 6. The same as Fig. 5 for KBr. (a) $\nu = 15$ kHz; (b) $\nu = 16$ Hz.

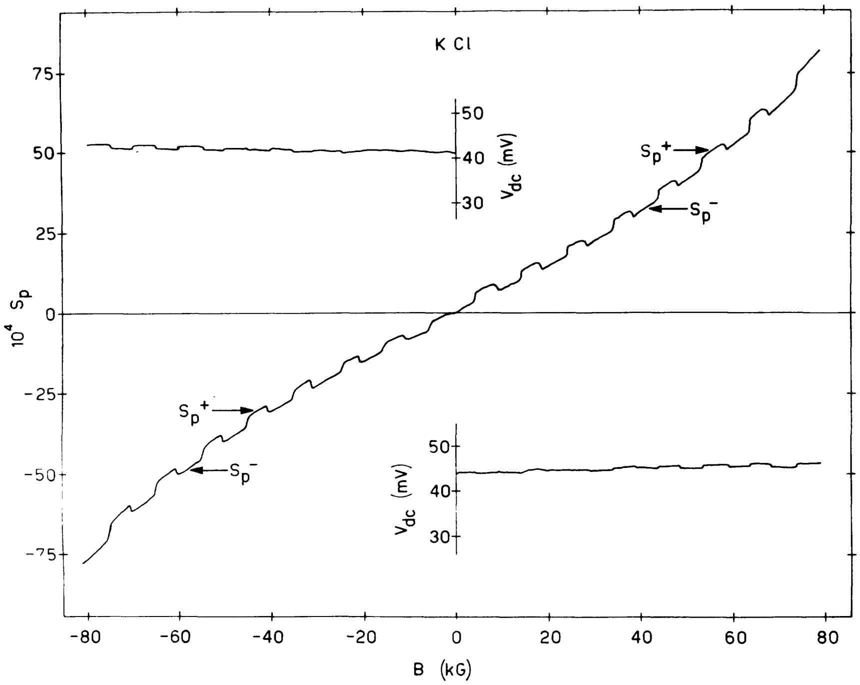

FIG. 7. The same as Fig. 5 for KCl at negative and positive magnetic field and at only one frequency $\nu = 5$ kHz.

in the figures.

The true paramagnetic effect is represented by the quantity $\Delta S_p = \frac{1}{2}(S_p^+ - S_p^-)$, whereas the quantity $S_a = \frac{1}{2}(S_p^+ + S_p^-)$ is produced, as will be explained in Sec. VI, by a differential absorption of σ^+ and σ^- pump light. In that case S_a does not correspond to an effect associated with P and it was indeed obtained directly by removing the linear polarizer plus the $\frac{1}{4}\lambda$ plate from the beam. The signal S_a, to which we will refer as an "anomalous" effect, has the same origin as the difference between the luminescence intensities, proportional $V_{dc}(+) - V_{dc}(-)$, taken with σ^+ and σ^- pumping light in the diamagnetic effect, (see Figs. 3 and 4). Since we did not use a spectrometer in our experiment, the observed effect corresponds essentially to a change in zeroth moment of the band. The question as to whether or not there are changes of the higher moments was solved previously.[15] Indeed, despite the small signal-to-noise ratio, a spectral analysis was made in both KI and KBr, and within the limits of the experimental indetermination, only a zero-order band moment change has been observed. Figure 8 shows ΔS_p as a function of the magnetic field for KI, KBr, and KCl up to 80 kG. The data refer to a modulating frequency in range (ii), i.e., $1/T_r \ll \omega \ll 1/\tau$, and they are duly normalized to the luminescence intensity. ΔS_p reaches the maximum value for $B \simeq 20$ kG and shows a clear decrease at high magnetic fields at least in KI and KBr (we will return on this important point in Sec. VII). The general behavior of ΔS_p vs B, except at low fields, is quite similar for all frequencies of modulation.

Figure 9 displays the true paramagnetic signal ΔS_p, as a function of the frequency of light modulation between σ^+ and σ^- at $B = 20$ kG for F centers in KI. Figures 10 and 11 show the same results for KBr and KCl. The measurements are taken at various pumping powers as explained in the figure captions. If ΔS_p is linearly related to the spin polarization of the RES, the previous data must reflect the behavior of P_ρ given by formula (3) or (4).

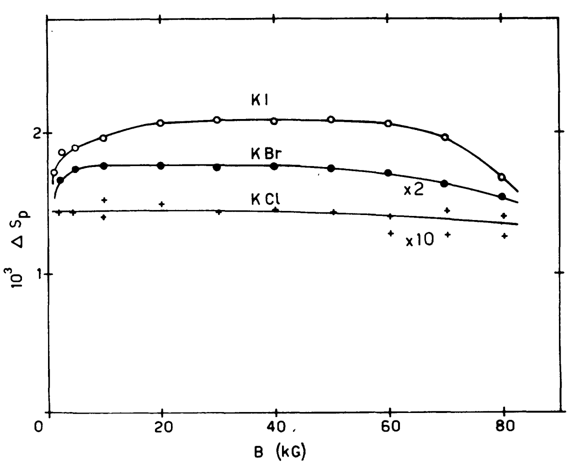

FIG. 8. ΔS_p as a function of the magnetic field up to 80 kG for KI, KBr, and KCl: the modulation frequencies are 20, 15, and 5 kHz, respectively.

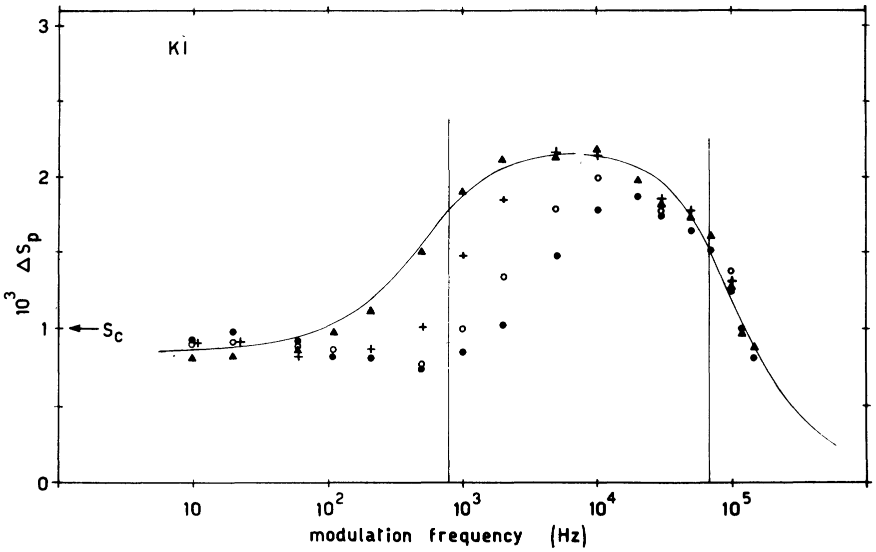

FIG. 9. ΔS_p as a function of the modulation frequency at $B = 20$ G for KI. Pumping power on the crystal surface $w_0 = 7.5$ mW for the black circles, $\frac{1}{2}w_0$ for empty circles, $\frac{1}{4}w_0$ for crosses, and $\frac{1}{10}w_0$ for triangles. The continuous curves are theoretical fittings.

The curves drawn at high frequencies represent the theoretical expectation given by formulas (4a) for $|P_p|$. The agreement with the experimental points is fairly good and as expected there is not a dependence on the pumping power. The vertical line on the right-hand side of Figs. 9–11 marks out the value of the frequency for which $\omega\tau = 1$. Hence, the radiative lifetime of the RES can be obtained. The values obtained in this way are 2.5, 1.3, and 1.1 μsec, respectively, for KI, KBr, and KCl, which compare fairly well with the known values of 3.2, 1.8, and 0.8 μsec.[7,23]

The curves drawn at low frequencies are an attempt to fit the theoretical behavior expressed by formulas (4c) to the unexpected trend of the experimental points toward a well-defined limit different from zero. This situation is clearly more dramatic for KBr in Fig. 10, where the low-frequency limit is even bigger than the value of ΔS_p at intermediate frequencies, range (ii). We recall that the calculated value of $|P_p|$ for $\omega \to 0$, [Eq. (4d)] goes practically to zero for $\epsilon U T_1 \gg 1$, a condition which is satisfied in the present experiments. The existence of this low-frequency limit, independent of the pumping power, is confirmed by the signal S_c in the diamagnetic experiments (see Figs. 3 and 4). The arrows on the left-hand side of Figs. 9–11 show the values of S_c. The fact that S_c coincides with ΔS_p, when the paramagnetic effect is studied at very low frequency of modulation, is evident if we look at the symmetry existing between the diamagnetic and paramagnetic measurements.

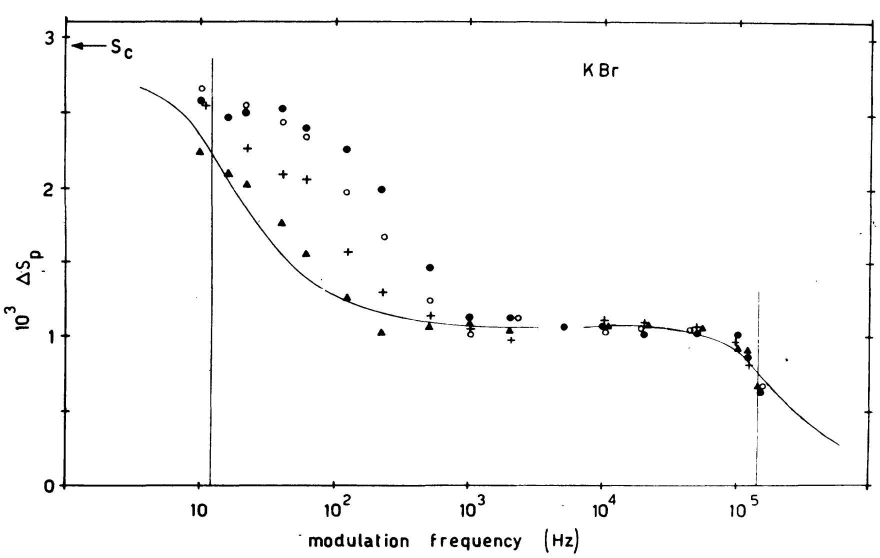

FIG. 10. The same as Fig. 9 for KBr.

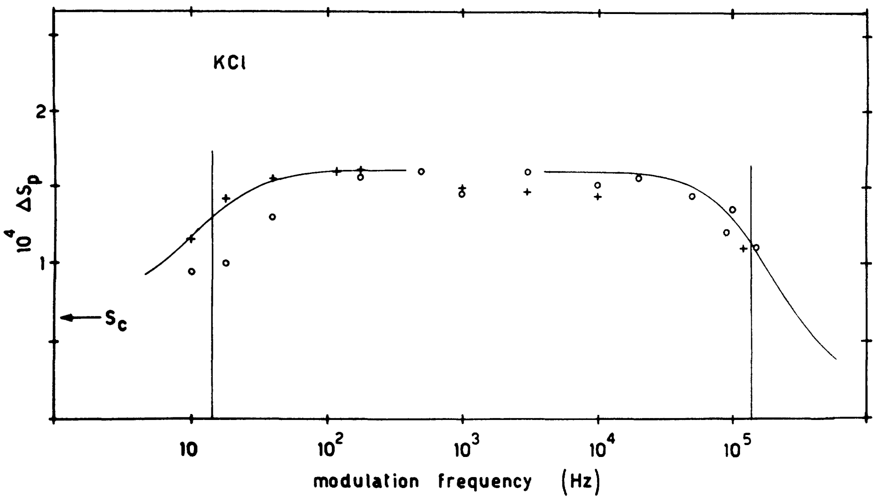

FIG. 11. The same as Fig. 9 for KCl. Pumping power on the crystal surface $w_0 = 12.5$ mW for circles and $\frac{1}{2}w_0$ for crosses.

Indeed, the paramagnetic case, for $\omega \rightarrow 0$, coincides with successive pumping σ^+ and σ^- as used in the diamagnetic case. Moreover, the detection frequency ω_0 of the stressplate modulation can be ideally lowered to any value down to the manual switching from σ^+ to σ^- transmitted light, as we use for the paramagnetic case. The identity of S_c and $\Delta S_p(\omega \rightarrow 0)$ is revealed also by their behavior as a function of small magnetic fields, (see Figs. 12 and 13). The values of S_c for KCl are not reported in Fig. 13 because the results, qualitatively similar to those of ΔS_p of Fig. 12, present large experimental errors. The experimental points of ΔS_p are taken with a frequency of light modulation included in range (iv) for KI and KBr, and between range (iii) and (iv) for KCl. Unfortunately we can offer no convincing explanation for the signal S_c [or $\Delta S_p(\omega \rightarrow 0)$]. We expect that any instrumental effect can be excluded. The fact that S_c dips to zero for zero field would seem to indicate that it is correlated with P or P_ρ or both, even if P_ρ is supposed to be nearly zero for the conditions of pumping. Furthermore, ΔS_p reaches half of its maximum value for $B \simeq 700$ G for KI and KBr, which is well above the known RES linewidth[16] for the same colored crystals. Furthermore, P could affect the luminescence only through a Porret-Lüty effect[22] or exchange effects,[24] both of which are strongly dependent on the F center concentration. In previous measurements[15] it was found that S_c is almost independent of the concentration of F centers up to $10^{17}/\text{cm}^3$, while a slight dependence is present (S_c decreases in KBr and increases in KI) above this value up to $10^{18}/\text{cm}^3$. In conclusion the origin of S_c [or $\Delta S_p(\omega \rightarrow 0)$] remains a mystery, even if the polarization of the ground state P, which reaches its maximum value just for $\omega \rightarrow 0$, is strongly suspected to play some role.

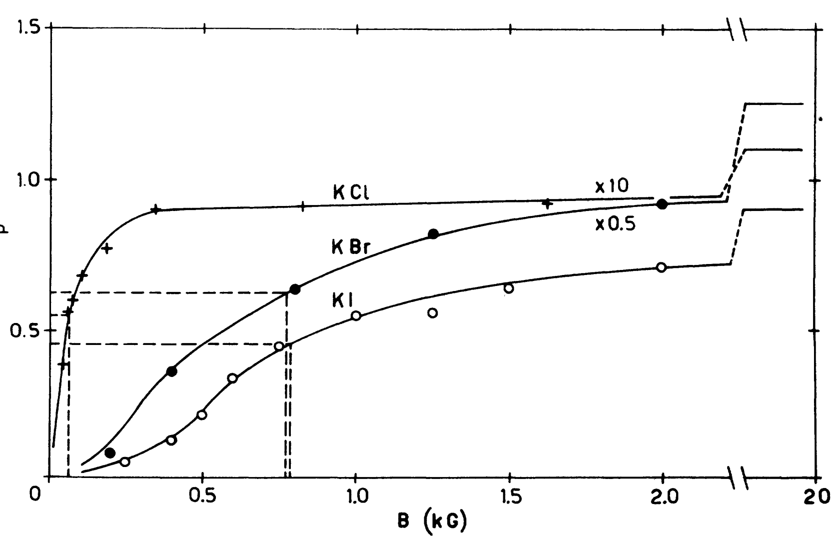

FIG. 12. ΔS_p as a function of small magnetic field taken at a modulation frequency of 70, 16, and 10 Hz for KI, KBr, and KCl, respectively. The value at 20 kG is also shown on the right.

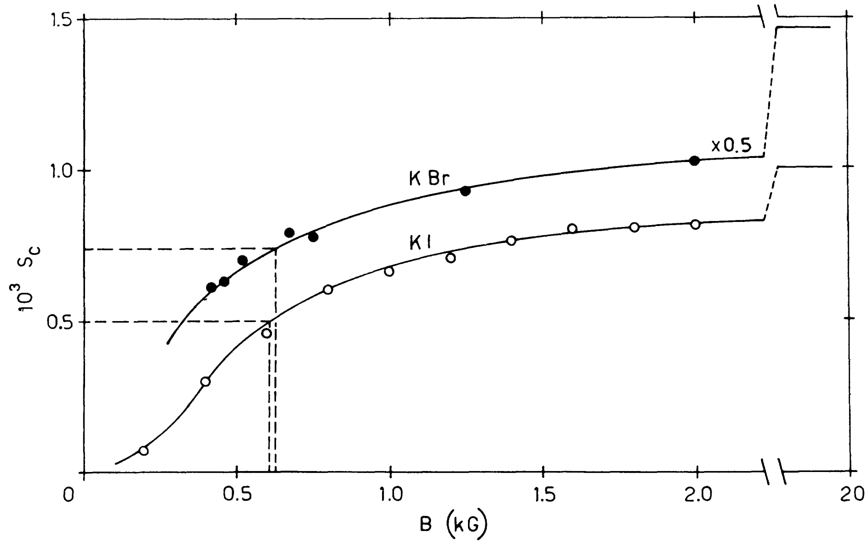

FIG. 13. S_c as a function of small magnetic fields. The maximum value at 20 kG is also shown on the right.

Returning to Figs. 9–11, the curves on the low-frequency side represent the behavior of P, Fig. 10, and P_ρ, Figs. 9 and 11, as in formulas (4c). The agreement with the experimental points is fairly good for KI and KCl and a little less for KBr. The same type of curves can fit all the data taken at different powers. The vertical line on the left-hand side gives the value of frequency for which $\omega T_p = 1$ at the lowest pumping power. The frequency so determined is proportional to the pumping power as predicted by the rate equations [see formulas (4c)]. Furthermore, from the known spot of the laser beam on the sample (diam. of $\simeq 100\ \mu$ for He-Ne laser and $\simeq 50\ \mu$ for Ar^+ laser) it is possible to calculate the total pump rate out of the ground state U, which is always much smaller than $10^6\ sec^{-1}$. Hence, the value of the spin mixing parameter ϵ is easily extracted from the previous fittings: 0.3, 0.02, and 0.005, respectively, for KI, KBr, and KCl. These numbers compare well with 0.24, 0.04, and 0.01, given by Mollenauer and Pan,[16] keeping in mind that the true value of U is only approximatively known.

We have also measured ΔS_p in range (ii), i.e., at intermediate frequencies, and the signal is essentially a constant for $|B| \geq 1$ kG. The behavior of ΔS_p for small fields is shown in Fig. 14. ΔS_p decreases for $B \to 0$ as expected from the behavior of P_ρ; in fact also P_ρ become small at $B \to 0$. If we take the value of B at which ΔS_p is reduced by a factor of two as a measure of the width of the dip, we obtain ~340, ~170, and ~40 G for KI, KBr, and KCl, respectively. These numbers are of the same order of magnitude as $\frac{1}{2}\Delta B$, where ΔB is the known ESR linewidth in RES ($\Delta B = 575$, 270, and 55 G for KI, KBr, and KCl).[16] At this point it is in-

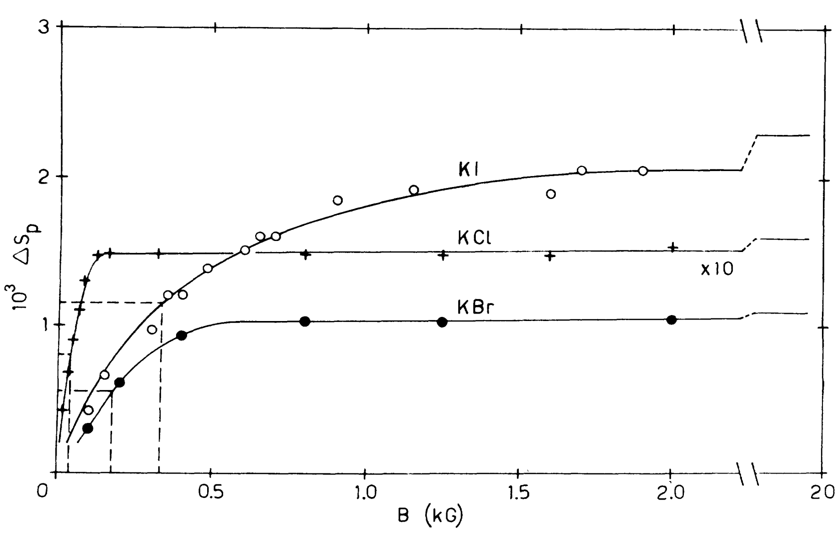

FIG. 14. True paramagnetic effect ΔS_p as a function of small magnetic fields. The frequencies of modulation are 20, 15, and 5 kHz for KI, KBr, and KCl, respectively. The maximum value at 20 kG is also indicated.

TABLE II. Summary of the true paramagnetic effect and relative polarization P_ρ.

Crystal	$\lvert P_\rho \rvert$	$10^3 \lvert \Delta S_p \rvert$ Baldacchini and Mollenauer Reference 15	$10^3 \lvert \Delta S_p \rvert$ This work
KCl	0.05	...	0.16 ± 0.02
KBr	0.14	1.27 ± 0.1	1.1 ± 0.1
KI	0.21	2.16 ± 0.2	2.1 ± 0.2

teresting to compare the behavior of ΔS_p as a function of magnetic field in the frequency range (ii) (Fig. 14) and (iv) (Fig. 12). The comparison suggests for the paramagnetic signal at $\omega \to 0$ a different origin other than P_ρ, which we believe to be responsible for the true paramagnetic effect ΔS_p at higher frequencies. ΔS_p in range (ii) was also measured as a function of F center concentration and it was found to be essentially constant.[15]

In conclusion we are of the opinion that aside from the low-frequency anomalous values, the general behavior of ΔS_p versus frequency is well described by the function $P_\rho(\omega)$ as given by Eqs. (3) and (4). This is a further proof of the origin of the paramagnetic effect as due to the spin polarization of the RES. Values of ΔS_p in the frequency range (ii) have been determined in several experimental runs. Table II shows the average values for KI, KBr, and KCl compared with previous results,[15] along with the values of $|P_\rho|$ as obtained from the rate equation in the same range of frequencies of modulation.

VI. ANOMALOUS EFFECTS

As indicated previously in Sec. V, the anomalous paramagnetic signal $S_a(B)$ can be explained in terms of a differential absorption of σ^+ and σ^- pump light. The argument goes as follows: assuming 100% quantum efficiency, the luminescent intensity ought to be proportional to the fraction of pump light absorbed by the crystal. In terms of pump intensities, the absorbed light is

$$I_+^{\text{abs}} = i_+(t)(1 - e^{-\alpha_+ x}), \tag{13}$$

where α_+ is the absorption coefficient for σ^+ light and x is the thickness of the crystal. A similar expression one obtains for I_-^{abs}. With the incident intensities $i_\pm(t)$ as given in Eq. (7) $I^{\text{abs}}(t)$ should be given by the following:

$$I^{\text{abs}}(t) = \tfrac{1}{2} i_0 (2 - e^{-\alpha_- x}) - \tfrac{1}{2} i_0 (e^{-\alpha_+ x} - e^{-\alpha_- x}) a_1 \sin(\omega t) . \tag{14}$$

Thus, S_a, as measured by a lock-in tuned to the modulator frequency will be given by the ratio of the $\sin\omega t$ to the dc term in Eq. (14). If we further assume that $(\alpha_+ - \alpha_-)x \ll 1$, S_a can be written as follows:

$$S_a = a_1 \left(\frac{\alpha_+ - \alpha_-}{\alpha_+ + \alpha_-} \right) \left[\frac{\alpha x}{e^{\alpha x} - 1} \right] . \tag{15}$$

Note that the quantity in square brackets in Eq. (15) approaches unity for $\alpha x \ll 1$, and approaches zero for $\alpha x \gg 1$. Thus, S_a is predicted to become small for optically dense crystals, as has been observed in both KI and KBr samples.[15]

Now, it has been shown elsewhere[16,25] that the first fraction in Eq. (15) can be written as follows:

$$\frac{\alpha_+ - \alpha_-}{\alpha_+ + \alpha_-} = P f_p + \frac{B}{B_d} , \tag{16}$$

where P is the ground-state spin polarization, where f_p, the paramagnetic dichroic fraction, is equal to P_s and given in Sec. II, and where the term B/B_d represents the diamagnetic effect in the absorption. From Ref. 25, we calculate $B_d \simeq 3.6 \times 10^6 G$ for KI, $\simeq 4.3 \times 10^6 G$ for KBr, and $\simeq 10 \times 10^6 G$ for KCl.

Even though the pump light is very intense, the polarization of the ground state will always contain a small time-independent term given by Eq. (2a). So inserting Eqs. (2a) and (16) into Eq. (15) we finally obtain:

$$S_a = a_1 \left(\frac{\alpha x}{e^{\alpha x} - 1} \right) \left(\frac{B}{B_d} + \frac{f_p P_0}{\epsilon U T_1 + 1} \right) . \tag{17}$$

The function $T_1(B)$ is well known[19] empirically and thus all quantities entering into Eq. (17) are known or calculable. We obtain an excellent fit of Eq. (17) to the $S_a(B)$ of Fig. 5(b) for a value of $U \simeq 2 \times 10^4/\text{sec}$; this value of U is the same, within the limits of experimental error, as that deduced from a measurement of the absolute light intensity. Also, the empirical behavior of S_a as a function of U agrees well with the predictions of Eq. (17).[15] Thus, for KI, S_a would seem to be well understood.

But Eq. (17) can also explain the more complex behavior of $S_a(B)$ in KBr, at least qualitatively. That is, in the presence of intense optical pumping, cross relaxation between F centers in the RES and those in the ground state makes the effective value of T_1 much shorter at low fields, where the difference in magnetic splittings of the RES and ground states is small; the cross relaxation is extremely sensitive to that difference. Thus, in KI, where the difference in g factors is much greater, and also where the T_1 of the unperturbed ground state is approximately ten times shorter at any given field B, the effect of the cross relaxation on the curve of $S_a(B)$ is hardly noticeable.

For KCl a smaller value of S_a is expected since B_d is bigger and f_p is much smaller than in KI or KBr. In fact the experimental value of S_a (see Fig. 7) is about an order of magnitude smaller than in KI, (Fig. 5) or KBr, (Fig. 6).

Perhaps it should be emphasized that S_a, at least as explained above, is not a quantity of truly fundamental interest; as stated previously, ΔS_p is the important quantity. We have devoted much space to the explanation of S_a mainly to avoid the possibility of future misinterpretations.

The small increase in the luminescence of the diamagnetic effect in KI near zero field (see Fig. 3) when pumped with σ^+ or σ^- light can easily be explained as follows. The luminescence intensity, assuming 100% quantum efficiency, is given simply by

$$I \propto (n_+u_+ + n_-u_-)\,, \tag{18}$$

and in a more explicit form,

$$I \propto \frac{NU}{2}\left(1 - \frac{u_- - u_+}{u_- + u_+}P\right). \tag{19}$$

When the pump light is circularly polarized, it has been shown[16] that $P = \pm P_s$ and $(u_- - u_+)/(u_- + u_+) = f_p = \pm P_s$, where the sign $+(-)$ holds for σ^+ (σ^-), so we have:

$$I \propto \tfrac{1}{2}NU(1 - P_s^2)\,. \tag{20}$$

From Eq. (20) we expect an effect which is decreasing going from KI, KBr, to KCl. Indeed $I(0)/I(B)$ varies as 1.19, 1.02, 1.00 for the above crystals. The agreement with the experimental values is excellent in KI (In KBr and KCl the effect is hardly noticeable). Furthermore, the increase in the luminescence near zero field can be masked by the Porret-Lüty[22] effect which gives a simultaneous decrease of the luminescence. The competition between the two effects has been observed by increasing the concentration of F centers,[15] on which the Porret-Lüty effect is strongly dependent. Eq. (19) can explain the result contained in Fig. 5(a) also. In fact in the paramagnetic effect at very low frequency both the polarization of the ground state, P [see Eq. (4d)] and the dichroic fraction $(u_- - u_+)/(u_- + u_+)$ oscillates between $+P_s$ and $-P_s$; so their time-average product will be $\frac{1}{2}P_s^2$. So a smaller effect is expected in the paramagnetic intensity, as is obtained experimentally in Fig. 5(a) and analogous measurements.

VII. MEASUREMENT OF $T_{1\rho}$ AT HIGH FIELD

In Sec. V B we have shown the behavior of the true paramagnetic signal S_p as a function of the magnetic field up to 80 kG (Fig. 8). The signal shows a clear decrease for fields higher than $\simeq 50$ kG for KI and KBr. In the case of KCl the signal-to-noise ratio is so low that it is hard to say whether ΔS_p changes at all at high fields. This behavior is not contained in Eq. (3) from which we expect no dependence on the magnetic field. However the solutions (2) and (3) of the rate equations are obtained by supposing $\tau/T_{1\rho} \ll 1$. If such approximation is not made the rate equations are more complicated to solve, but it can be shown that in region (ii), i.e. $1/T_r \ll \omega \ll 1/\tau$, the polarization of the RES is given by

$$|P_\rho| \equiv (1 - 2\epsilon)\frac{P_s}{[1 + (\tau/T_{1\rho})]}\,. \tag{21}$$

Clearly, Eq. (21) reduces to (4b) if $\tau/T_{1\rho} \ll 1$. Because we expect $T_{1\rho}$ to be strongly dependent on the magnetic field, it seems logical to associate the decrease of ΔS_p with a variation of $T_{1\rho}$. From the data of Fig. 8 and other similar results we have obtained the values of $T_{1\rho}$ reported in Fig. 15 for KI and KBr. The point at 30 kG has been taken from Ref. 16; the arrow pointing down indicates

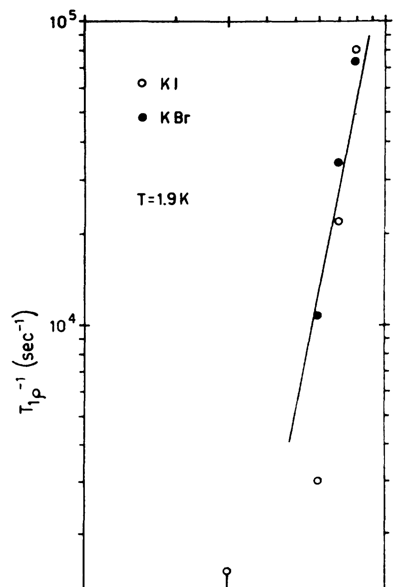

FIG. 15. Experimentally measured relaxation time in the RES for KI and KBr (see text).

that it represents an upper limit. The line drawn to fit the experimental points reflects a dependence on the fifth power of field, i.e., $1/T_{1\rho} \propto B^5$, which would indicate in the Kronig[26]–Van Vleck[27] mechanism the origin of such short relaxation time. The same mechanism was found in the relaxation time of the ground state[19] for high magnetic field, so its existence in the RES is not a surprise. We would like to stress the point that the values of $T_{1\rho}$ have an error that can be, in some cases, larger than 50%. This is clearly a consequence of the nonresonant method we have followed to measure $T_{1\rho}$. Nevertheless, this is the only measurement ever made at such low temperature, $T \simeq 1.9$ K, and high magnetic fields. We will show in the next section how the knowledge of $T_{1\rho}$ can add a useful information to the RES.

VIII. DISCUSSION AND CONCLUSION

As stressed in the introduction, knowledge of the diamagnetic effect C_d and of the paramagnetic effect ΔS_p enables us to make important progress in clarifying the nature of the RES. In fact such effects have been calculated as a function of fundamental parameters of the RES. As an example we will use the results of the theory outlined by Ham and Grevsmühl,[11,12] which at the moment is the only one that gives analytical formulas for almost all the various effects. In the weak-coupling limit the total circular polarization of the luminescence is given by

$$\frac{I^+ - I^-}{I^+ + I^-} = -\frac{2(g_L \mu_B B + \lambda \langle S_z \rangle)}{|E_{sp}| + \hbar\omega}, \qquad (22)$$

where g_L is the orbital g factor of the electronic p states μ_B the Bohr magneton, λ the spin-orbit splitting, $\langle S_Z \rangle$ the spin polarization, $2\langle S_z \rangle = P_\rho$, $|E_{sp}|$ the energy separation between the $2p$ and $2s$ states in a cubic configuration, and $\hbar\omega$ is in practice the energy of the longitudinal phonon, 18, 21, 27 meV, respectively, for KI, KBr, and KCl. Equation 22 contains both the diamagnetic and the paramagnetic effect, so we can obtain $|E_{sp}|$ and λ by using our values of $|C_d|$ and $|\Delta S_p|$ given in Tables I and II. Assuming $g_L = 1$ (the same as that measured in absorption) we get for $E_{sp} + \hbar\omega$ the values 60, 70, and 100 meV for KI, KBr, and KCl. Analogously using for P_ρ the numbers given in Table II, the values for $|\lambda|$ are, 0.6, 0.6, and 0.4 meV. If we observe that we do not pump exactly at the maximum of the dichroic absorption peak, in KBr and KCl, (see Fig. 2), we conclude that the true value of the polarization P_ρ to insert in (22) has to be smaller than that previously used. So for KBr and KCl the value of $|\lambda|$ is somewhat underestimated in the previous calculation. However, such low values for $|\lambda|$ seem to be in contrast with the spin-orbit parameter in the absorption, -26, -15, and -9 meV for KI, KBr, and KCl.[28] Recently, it has been shown[10] that the choice for g_L of the same value as in the absorption is not justified. On the contrary a partial quenching of the spin-orbit interaction seems to be more consistent with other parameters. However the spin-orbit coupling remains always of the order of ~1 meV.

We can also determine the values of $|\lambda|$ using the results of Sec. VII on the relaxation time $T_{1\rho}$. Until now a proper calculation of the Kronig mechanism has not been outlined for the F center, but as shown by Panepucci and Mollenauer[19] for the ground state, the following expression for T_1 can be written at high magnetic fields:

$$\frac{1}{T_1} \cong A \frac{\delta^2}{\Delta^4} B^5, \qquad (23)$$

where δ is the spin-orbit parameter, Δ the energy of the first excited state in respect to the ground state, and A is a constant for a given crystal. Now we suppose Eq. (23) to be valid for the RES also, as it seems from the behavior of $T_{1\rho}$ versus the magnetic field, with the same A. From the ratio of the two expressions, we obtain

$$\lambda \simeq \frac{\delta}{\Delta^2} \left(\frac{T_1}{T_{1\rho}}\right)^{1/2} \Delta_\rho^2, \qquad (24)$$

where λ and Δ_ρ are the quantities analogous to δ and Δ, for the RES. Assuming $\Delta_\rho = E_{sp} + \hbar\omega$, as measured in the previous dichroic effect, since all the other parameters are known, the calculated values of $|\lambda|$ are $\simeq 0.5$ meV for KI and 0.6 meV for KBr. It is gratifying that these numbers are of the same order of magnitude as those obtained from the paramagnetic effect. However a strong indication remains for a low value of $|\lambda|$.

At this point it seems difficult to match the theoretical expectation with the experimental results. On the other hand we are reluctant to admit a failure of the rate equations which seem to explain much experimental results. We do not see at present how to get out of this vicious circle. It is our opinion that only from a more complete theory can we expect a better understanding of the RES problem.

Note added in proof. Following completion of this work our attention was drawn to the work of A. Winnacker, K. E. Mauser, and B. Niesert Z. Phys. B 26, 97 (1977) on the optical cycle of the F center. Arguing on the possible mechanisms of the spin mixing parameter ϵ, they concluded that the choice of a unique value of ϵ can be justified only in special cases. Their idea seems to be well supported by some experimental results.

It is clear that this would have important implications for interpretation of our measurements. In practice the introduction of two different spin mixing parameter, ϵ^+ and ϵ^- for $M_s = \frac{1}{2}$ and $M_s = -\frac{1}{2}$ state respectively, changes drastically the rate equations[16] from which the solutions (2) and (3) are derived.

Unfortunately, the new equations are much more difficult to solve than the previous ones. However, in a first approach we found two interesting properties for the polarization of the RES. First of all, a well-defined value of P_ρ, independent from U, is found for a stationary pumping or a modulated pumping between σ^+ and σ^- in the limit $\omega \to 0$, contrary to the previous findings [see for instance formulas (3b) and (4b)]. This fact can explain the signal S_c in the diamagnetic effect and the signal ΔS_p $(\omega \to 0)$ in the paramagnetic effect (see Sec. V). Furthermore, it seems that the introduction of the two spin mixing parameters does not affect appreciably the solutions (2) and (3) for $\omega > 1/T_r$. So the value of $|P_\rho|$ in region (ii) remains practically unchanged, i.e., $P_\rho = (1-2\epsilon)P_s$, however, with $\epsilon = \frac{1}{2}(\epsilon^+ + \epsilon^-)$. This means that the conclusions drawn in Sec. VIII remain substantially valid.

In any case, the knowledge of the "exact" solutions for P_ρ and P in the new case, $\epsilon^+ \neq \epsilon^-$, is of great importance to clarify the optical cycle of the F center, and intense efforts are being made in such a direction. Indeed, a comparison of such solutions with our experimental data could prove of critical importance to confirm the idea of Winnacker and coworkers.

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