## Faraday Rotation and Spin-Orbit Splitting of the F Center in Alkali Halides\*

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The energy-level structure of the F center in alkali-halide crystals was investigated by means of the Faraday effect. It was found that the Faraday angle is composed of two parts, a small high-temperature contribution and a "paramagnetic" rotation which can be quite large at low temperatures. The results for a number of alkali halides can be consistently interpreted in terms of an energy-level diagram for the F center which includes unequal population of the ground state and a negative spin-orbit splitting of the unrelaxed excited state. The magnitudes of spin-orbit splitting are generally less than the F-band width but increase with atomic number of both the alkali and the halide ion. A comparison is made with theory. Certain additional observations are reported, for example, on the spin-lattice relaxation time of the ground state up to 50 kG.

### I. INTRODUCTION

LKALI-halide crystals colored by irradiation or A by heating in the alkali-metal vapor, exhibit the well-known F-band absorption in the visible region of the spectrum. The F band arises because of a highly allowed transition between an S-like ground state and an excited P state for an electron trapped at a negative ion vacancy. A great deal is known about the ground state from both spin resonance<sup>1,2</sup> and electron-nuclear double-resonance experiments.3 However, little is known about the excited state of the F center. A magnetic field might be used to investigate the excited state except that the Zeeman splitting in ordinary fields is very small, about  $10^{-4}$  eV, compared to an *F*-band width of 0.2 eV.

A few years ago Dexter<sup>4</sup> pointed out that Faraday rotation would be a promising technique for studying the F center and should be easily measurable because of the combined effect of a large number of F centers per unit volume. The experiment would measure the properties of the F center in absorption and reveal the character of the excited state before lattice relaxation. After lattice relaxation the excited state is apparently quite diffuse and may have very different character.<sup>5,6</sup> Results on the Faraday effect have recently been reported for the F band in KCl.<sup>7</sup> These results show the spectral dependence predicted by Dexter, as well as important new features. For example, it was found that the Faraday angle is composed of two parts, a temperature-independent part,  $\theta_{dia}$ , and a temperature-

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dependent part,  $\theta_{para}$ , which can be quite large at low temperature. At 50 kG  $\theta_{\text{para}}$  was proportional to 1/Tdown to 4.2°K, the lowest temperatures used. This "paramagnetic" contribution arises essentially because of unequal population of the two spin levels of the ground state and the existence of structure due to spin-orbit interaction in the excited state. The spinorbit splitting was found to be in the range  $10^{-3}$ - $10^{-2}$ eV for KCl and was negative indicating that for the Fcenter in KCl, the  $P_{1/2}$  level lies above the  $P_{3/2}$  level.

The existence of similar fine structure in the F band of KBr has recently been confirmed as a result of experiments using circularly polarized light and a magnetic field.<sup>8</sup> These investigators were able to study certain properties of the ground state, for example the spin-lattice relaxation time  $T_1$ , and to demonstrate the effect of optical pumping. The work on circular dichroism in a magnetic field has recently been extended to F centers in NaCl, NaBr, KCl,<sup>9</sup> and the cesium halides.10

Faraday rotation is the rotation of the plane of polarization of a plane-polarized light wave upon traversing an optical medium in the direction of an applied magnetic field. The amount of rotation depends upon the difference in phase of the two circularly polarized components of the plane-polarized wave after traversing the medium. It is not hard to show<sup>11</sup> that the Faraday angle  $\theta$  is given in terms of the indices of refraction as

$$\theta = (\omega/2c)(n_r - n_l)l, \qquad (1)$$

where  $\omega$  is the angular frequency of the light,  $n_r$  and  $n_l$ the index of refraction for right and left circularly polarized components, respectively, l the thickness of the sample, and c the velocity of light. Here right cir-

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FIG. 1. Relationship between absorption, dispersion, and Faraday rotation. The rotation due to the uncolored crystal arises from the dispersion caused, for example, by the first exciton peak. In the inset, the addition of F centers produces a change in the dispersion of the crystal and gives the spectral dependence of the Faraday rotation shown. Typical magnitudes of each parameter are given.

cularly polarized is defined so that the electric-field vector at a fixed point on the wave rotates clock-wise as viewed looking opposite to the direction of propagation. The Faraday rotation in a colored alkali-halide crystal arises partly because of background dispersion associated with the exciton absorption and partly due to the additional dispersion introduced by F centers (see Fig. 1). We are interested in the additional rotation produced by F centers, and it is fortunate that the background can be measured in an uncolored crystal and then subtracted from the total rotation in the colored crystal.7

Results are presented in Sec. III below on the Faraday angle versus wavelength for various alkali halide crystals containing known densities of F centers. These data yield values of the spin-orbit splitting  $\Delta$ which can be compared with a recent theory for the Fcenter.<sup>12</sup> The experimental method and apparatus is described in Sec. IIA. A method of analysis of the observations appears in Sec. IIB along with some qualifying remarks concerning the effect of lattice vibrations and linewidth. It seems more appropriate to analyze Faraday rotation and the shape of the F band in terms of moments<sup>13</sup> rather than in terms of a susceptibility tensor as recently used for narrow lines<sup>14</sup> or in terms of a dielectric constant tensor as sometimes used for interband Faraday effect.<sup>15</sup>

#### **II. EXPERIMENTAL METHOD**

#### A. Apparatus

Although the expected Faraday angle is of the order of a few degrees per kilogauss per centimeter,<sup>4</sup> for a KCl crystal containing  $10^{18} F$  centers/cm<sup>3</sup>, very thin crystals would have to be used at this density of coloration. It was hoped to work with samples of low or moderate coloration and to avoid aggregate centers. A dynamical method of measurement was developed as shown in Fig. 2. The method makes use of a 1-in. i.d. superconducting solenoid<sup>16</sup> suspended in liquid helium in a stainless-steel Dewar. The solenoid is rated at 50 kG but is capable of producing fields in excess of 58 kG. A field homogeniety of 2% within a 1-cm-diameter sphere and a  $2\frac{1}{2}$ -min time constant were specified. The sample was mounted inside of a thin-wall tube into which helium exchange gas could be admitted. The sample temperature could be controlled and measured by means of a small heater and gold-cobalt normal silver thermocouple. The sample chamber was closed at



FIG. 2. Schematic diagram showing both the optical arrangement and detection system used to observe the Faraday rotation.

<sup>13</sup> M. Lax, J. Chem. Phys. 20, 1752 (1952).
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<sup>15</sup> I. M. Boswarva and A. B. Lidiard, Proc. Roy. Soc. (London) A269, 125 (1962); A278, 588 (1964).

<sup>16</sup> Westinghouse Electric Corporation, Pittsburgh, Pennsylvania.

<sup>&</sup>lt;sup>12</sup> D. Y. Smith, first following paper Phys. Rev. 137, A574 (1965).

Crystal	Method of coloration	F-center density <sup>a</sup> (cm <sup>-3</sup> )	Total Verdet constant at 4.2°K $\left(\frac{\text{deg}}{\text{G cm}}\right)$	$\begin{array}{c} \text{Diamagnetic} \\ \text{Verdet} \\ \text{constant} \\ \left( \frac{\text{deg}}{\text{G cm}} \right) \end{array}$	Half-width at 4.2°K (eV)	Spin-orbit splitting $\Delta$ (eV $\times 10^{-3}$ )	Values of $\Delta$ from circular dichroism measurements <sup>e</sup> (eV ×10 <sup>-3</sup> )	<i>m*/m</i>
NaCl	x-irradiated crystal contained U centers	8.2×10 <sup>16</sup>	4.0×10 <sup>−4</sup>	1.8×10-4	0.255ª	5.1±1.0	7.7±1.2	0.38
KCl	x-irradiated crystal contained U centers	1.1×1017	$2.4 \times 10^{-3}$	4.4×10-4	0.163	11.4±2.3	10.0±1.2	0.62
KBr	additively colored	$7.8  imes 10^{16}$	2.1×10⁻³	3.0×10 <sup>4</sup>	0.158	$19.2 \pm 3.8$	$29.8 \pm 4$	0.47
KI	x-irradiated crystal contained U centers	4.9×10 <sup>16</sup>	1.0×10 <sup>-3</sup>	1.1×10-4	0.155	30.0±3.2	57.0±8.6	0.83
RbBr	additively	$3.4  imes 10^{16}$	$2.1 \times 10^{-3}$	$1.3 \times 10^{-4}$	0.130	$32.4 \pm 6.5$	$27.2 \pm 3.7$	0.47
CsBr	x irradiated	$1.1 \times 10^{17b}$	$1.3 \times 10^{-2}$	1.1×10-3	0.135	$42 \pm 8.4$	78	0.36

TABLE I. Experimental data and resulting values of spin-orbit splitting.

Estimated using Smakula formula N<sub>f</sub> =8.7 ×10<sup>16</sup>n(n<sup>2</sup>+2)<sup>-2</sup>α<sub>max</sub>W<sub>1/2</sub>.
<sup>b</sup> Assuming an oscillator strength of unity.
<sup>c</sup> See Refs. 8, 9, 10, and 29.
<sup>d</sup> W. Gebhart and H. Kühnert, Phys. Letters 11, 15 (1964).

the bottom by a fused quartz window at liquid-helium temperatures employing a special O-ring seal.<sup>17</sup>

Light from a tungsten source and a Leiss double monochromator passed through polarizer I and was focused upon the sample. The transmitted light passed through polarizer II which was rotated by a synchronous motor<sup>18</sup> at a frequency of 1800 rev/min. This transmitted light, modulated at twice the rotational frequency, was detected by a photomultiplier. The photomultiplier output passed through a narrow band amplifier and was compared in phase with the signal from detector II and a reference light source. Thus the problem of measuring the rotation of a plane of polarization was converted into the measurement of the relative phase of two electrical signals. The phase measurement was accomplished by the use of an amplitude insensitive phase meter of the coincidence type.<sup>19</sup> Faraday rotations as small as 0.03 deg could be observed and recorded on a strip chart recorder. One advantage of the system was that noise due, for example, to misalignment or vibration of the rotating polarizer could be filtered out since detection occurred at twice the rotation frequency. The method of measurement was a dynamical one in that the phase angle was continuously recorded at a fixed wavelength of light as the magnetic field was programmed from zero to full or to a selected constant value. Records were taken as the wavelength was varied point by point. The magnetic field was determined by the current flowing through the solenoid but was checked against a magnetometer of the magnetoresistance type. In all the measurements made, the Faraday angle was found to be linear or almost in magnetic field.

Crystals obtained from various sources were colored by additive coloration, x irradiation at room temperature, or by irradiating crystals containing U centers at room temperature.<sup>20</sup> The various coloration techniques led to similar Faraday rotation results as long as reasonable care was taken to produce an isolated Fband. We turn next to the observations and their analysis. Optical density measurements were made using either a Cary Model 14 or 15 spectrophotometer. The half-width for the F band at 4.2°K in each crystal was also obtained and these are listed in Table I.

#### B. Method of Analysis

The spectral dependence of the Faraday rotation for KCl is shown in Fig. 1 of Ref. 7 and for KBr and RbBr in Figs. 4 and 5 of the present article. When the background, as observed in an uncolored crystal, is subtracted off, these curves display nearly the spectral dependence of the derivative of the index of refraction with respect to photon energy. This leads one to interpret the data in the case of the F centers by means of an approximation first introduced by Becquerel.<sup>21</sup> That is, we rewrite Eq. (1) as

$$\theta = (\omega l/2c) (dn/dE) \Delta E, \qquad (2)$$

where dn/dE is the derivative of the index of refraction and  $\Delta E$  is the energy shift for right and left circularly

<sup>&</sup>lt;sup>17</sup> Viton O-rings under strong spring compression.
<sup>18</sup> Type NYC-34, Bodine Electric Company, Chicago, Illinois.
<sup>19</sup> Phasemeter Type 405, Ad-Yu Electronic, Passaic, New Jersey.

<sup>&</sup>lt;sup>20</sup> W. Martienssen and H. Pick, Z. Physik 135, 309 (1953).

<sup>&</sup>lt;sup>21</sup> H. Becquerel, Compt. Rend. 90, 992 (1897).

polarized components brought about by the magnetic field. This approximation is valid because of the great width of the F band and small Zeeman splitting. An analytic expression can be obtained for dn/dE in Eq. (2) if one uses the Kramers-Kronig relation and assumes a Gaussian shape for the F absorption band. A Gaussian shape is a fairly good approximation for most of the alkali halides but certainly a poor one for the cesium salts.<sup>22</sup> This was the approach used by Dexter<sup>4</sup> who pointed out that the width of the F band results from a large number of oscillators having slightly different frequencies because of interaction with lattice vibrations. Although the broadening effect of lattice vibrations is large, it is remarkable that the much smaller effects of spin-orbit and Zeeman interaction can be interpreted to a first approximation in terms of an energy level diagram similar to that for an alkali atom.<sup>7</sup> The energy levels of such a diagram are imagined to be at the center of gravity of each of the many components which constitute the F band. It is assumed that the magnetic field and spin-orbit interaction affect the degeneracy of each component in the same way. A rigid shift of the F band results.

The difficulty with such an alkali atom model is that because of the large effect of lattice vibrations one expects the character of the excited P state to be considerably altered. For example, noncubic lattice vibrations will lift the orbital degeneracy of the Pstate and cause the orbital angular momentum to be quenched. This has been pointed out by Henry, Schnatterly, and Slichter<sup>23</sup> in an article on the effect of applied fields on the optical properties of color centers. These authors take the electron-lattice interaction into account and rigorously compute the changes in the moments of an absorption line brought about by an applied field. They give a simple expression for the change in the first moment and show that the change in the second moment is zero to first order. The area of the line does not change under any condition. These results suggest a rigid shift of the absorption line and therefore also of a plot of the index n versus photon energy. This would allow us to use Eq. (2), where dn/dE is calculated from the line shape in the absence of an external applied field. Actually Henry et al. give an expression for the Faraday angle which is nearly the same as that obtained from an atomic model neglecting the lattice. We will present the simple alkali-atom model below because of the physical insight which it provides.

In order to obtain an explicit expression for dn/dE, it is convenient to assume a Gaussian shape for the F band as mentioned above. We take the absorption constant  $\alpha(E)$  to be

$$\alpha(E) = \alpha_{\max} \exp[-(E - E_0)^2 / W^2],$$
 (3)

where  $\alpha_{\max}$  is the maximum absorption constant at energy  $E_0$ , and W is a measure of the width of the band. More specifically if  $W_{1/2}$  is the full width at halfmaximum  $W = W_{1/2}/2$  ln2. In Eq. (2) the index *n* refers to the index associated with the additional absorption due to the *F* band. The total index  $n_t$ , is given in terms of the absorption constant by the Kramers-Kronig relation.<sup>24</sup>

$$n_t(E) - 1 = \frac{\hbar c}{\pi} P \int_0^\infty \frac{\alpha(E') dE'}{E'^2 - E^2},$$
 (4)

where P indicates the principal value of the integral. Absorption over the entire range of the spectrum including the exciton region contributes to  $n_t$ . The index  $n_0$  of an uncolored crystal would be given by a similar equation except that there is little or no contribution in the visible or F band region of the spectrum. Thus it can be seen that the change in index  $n=n_t-n_0$  produced by F centers is of the form

$$n(E) = \frac{\hbar c}{\pi} P \int_0^\infty \frac{\alpha(E') dE'}{E'^2 - E^2},$$
(5)

where now  $\alpha$  refers only to the additional absorption produced by the *F* band. Substituting Eq. (3) into Eq. (5) and using the approximation  $E' + E \approx E_0 + E$  since  $W \ll E_0$  we have

$$n(E) = \frac{\hbar c \alpha_{\max}}{\pi(E_0 + E)} P \int_0^\infty \frac{\exp[-(E' - E_0)^2 / W^2] dE'}{E' - E} \,. \tag{6}$$

This integral can now be evaluated and shown to be given by

$$n(E) = \frac{2\hbar c \alpha_{\max}}{\pi^{1/2} (E_0 + E)} \exp\left[\frac{-(E - E_0)^2}{W^2}\right] \times \int_0^{(E - E_0)/W} \exp(y^2) dy. \quad (7)$$

We are interested in the derivative of this last expression and especially in its minimum value at  $E = E_0$ . Only the variable end point of the integral in Eq. (7) contributes with the result that for  $E = E_0$ 

$$\left(\frac{dn}{dE}\right)_{\min} = -\frac{\hbar c \alpha_{\max}}{\pi^{1/2} W E_0}.$$
(8)

Using Eq. (2) the magnitude of the Faraday angle at its minimum can be shown to be

$$\theta_{\min} = -\frac{\alpha_{\max}l}{2\pi^{1/2}W} \Delta E \tag{9}$$

<sup>&</sup>lt;sup>22</sup> H. Rabin and J. H. Schulman, Phys. Rev. **125**, 1584 (1962). <sup>23</sup> C. H. Henry, S. E. Schnatterly, and C. P. Slichter, second following paper Phys. Rev. **137**, A583 (1965). See also Phys. Rev. Letters **13**, 130 (1964).

<sup>&</sup>lt;sup>24</sup> See for example the article by F. Stern in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963).



FIG. 3. Energy-level diagram used to interpret the results, showing the allowed transitions with their weightings taken from the atomic case. The number of electrons in the spin levels  $-\frac{1}{2}$  and  $n_2$ , respectively. In Fig. 3(A),  $n_1=n_2$  and represents the diamagnetic case while in Fig. 3(B)  $n_1 > n_2$  corresponding to the paramagnetic case. Note that the energy separation between the S and P states is about 2.3 eV whereas  $\Delta$  is only about  $10^{-2}$  eV. In the case of the F center  $\Delta$  is negative so that the  $P_{1/2}$  levels lie above the  $P_{3/2}$  levels.

or in terms of the width at half-maximum  $W_{1/2} = 2(\ln 2)^{1/2}W$ 

$$\theta_{\min} = -\left(\frac{\ln 2}{\pi}\right)^{1/2} \frac{\alpha_{\max}l}{W_{1/2}} \Delta E.$$
 (10)

The effective energy shift  $\Delta E$  can now be evaluated with the aid of the energy level diagram given in Fig. 3. It should be emphasized that this diagram is drawn with the following experimental facts in mind (1) the Faraday angle is almost linear in H up to the highest fields used. (2) A high-temperature diamagnetic and a low-temperature paramagnetic contribution occur. (3) The diamagnetic contribution is independent of temperature and the paramagnetic contribution is proportional to 1/T down to  $4.2^{\circ}$ K (see Fig. 3 of Ref. 7). It is apparent that one cannot neglect spin and unequal population of the sublevels of the ground state.

The energy shift  $\Delta E$  in Eqs. (2) and (10) should be a mean value for all pairs of transitions corresponding to right and to left circular polarization. Each transition must be weighted properly, and in our alkali atom model we use the customary values,<sup>25</sup> one, two, and three, as shown in Fig. 2. If there are  $n_1$  electrons in the lower state and  $n_2$  electrons in the upper state, there are  $(n_1+n_2)/2$  pairs of electrons altogether. However, using the weighting factors shown a total of six transitions are accessable to a pair. The total number of transitions is  $6(n_1+n_2)/2$  and the average energy difference is obtained by working out a sum of the form

$$\Delta E = \frac{1}{3(n_1 + n_2)} \sum_j n_j \Delta E_j, \qquad (11)$$

<sup>25</sup> L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), p. 292.

where  $\Delta E_j$  is the energy difference for the *j*th pair and  $n_j$  is the number of possible transitions for this pair. At high temperature  $n_1 = n_2$  and it is not difficult to see from Fig. 3(A) that the diamagnetic contribution  $(\Delta E)_{\text{dia}}$  is given by

$$(\Delta E)_{\rm dia} = \frac{1}{3} [\beta H(g_2 + 5g_3)], \qquad (12)$$

where  $\beta = e\hbar/2mc$ , *H* is the magnetic field, and  $g_2$  and  $g_3$  are the *g* values of the  $P_{1/2}$  and  $P_{3/2}$  states, respectively. In the free atom  $g_2 = \frac{2}{3}$  and  $g_3 = \frac{4}{3}$  as given by the Landé formula. Notice that only the *g* values of the excited state enter in Eq. (12).

We now evaluate the energy shift at low temperature when  $n_1 > n_2$ . Five terms in the sum of Eq. (11) can be evaluated with the help of the weighting factors shown in Fig. 3(B). Notice that although there is unequal occupation of the ground state, the right and left circularly polarized transitions pair off so that there is no net absorption of one polarized component over the other. There is an average energy shift however containing two terms as follows:

$$\Delta E = \frac{(g_2 + 5g_3)}{3} \beta H - \frac{2}{3} \left( \frac{n_1 - n_2}{n_1 + n_2} \right) \Delta.$$
(13)

Boltzmann statistics apply since electrons on F centers are in principle distinguishable. The weighting factor in the second (paramagnetic) term of Eq. (13) is therefore given by

$$\frac{n_1 - n_2}{n_1 + n_2} = \tanh\left(\frac{g_1\beta H}{2kT}\right),\tag{14}$$

where  $g_1=1.995$  is the g value of the ground state. A linear dependence on 1/T was found so that, at not too low temperatures or too high fields, it is possible to make the following approximation:

$$\tanh \frac{g_1 \beta H}{2kT} \simeq \frac{g_1 \beta H}{2kT}.$$
 (15)

Combining Eqs. (10), (13), (14), and (15) we have an expression for the minimum Faraday angle at low temperature:

$$\theta_{\min} = -\left(\frac{\ln 2}{\pi}\right)^{1/2} \frac{\alpha_{\max} l\beta H}{W_{1/2}} \left(\frac{g_2 + 5g_3}{3} - \frac{g_1 \Delta}{3kT}\right). \quad (16)$$

This relation has been used by the French group<sup>26</sup> to interpret some of their recent results. The first term in Eq. (14) is the so-called diamagnetic contribution which is small at low temperatures and in any case can be measured at high temperature and subtracted. The second term is of opposite sign and depends upon the spin-orbit splitting  $\Delta$ . Our elementary derivation of

<sup>&</sup>lt;sup>26</sup> J. Margerie (private communication).



FIG. 4. Spectral dependence of Faraday rotation for the F band in KBr. The crystal contained  $7.8 \times 10^{16}$  F centers/cc and with a field of 50 kG gave a maximum rotation at  $4.2^{\circ}$ K of 5°.

Eq. (14) must be corrected slightly even within the alkali atom framework. We have neglected a small contribution made by the Zeeman-spin term in the perturbation treatment because of mixing of the  $P_{1/2}$  and  $P_{3/2}$  states due to the magnetic field. This changes the diamagnetic term slightly so that the factor  $(g_2+5g_3)/3=22/9$  should be replaced by exactly two. Our simple derivation has its advantages since it illustrates how the Faraday effect at low temperature arises primarily because of unequal occupation of the ground states and it illustrates the origin of the term dependent upon  $\Delta$ .

An alternative derivation for the Faraday angle is given by Henry *et al.* as mentioned above.<sup>23</sup> Their result which takes the lattice and its vibrations into account is

$$\Delta E = 2\beta H |\langle x | L_z | y \rangle| - \frac{4}{3} \Delta \langle S_z \rangle.$$
(17)

Here  $\langle S_z \rangle$  is the average value of the ground-state spin or just one-half the value given by Eq. (14), and  $|\langle x|L_z|y \rangle|$  is an angular momentum matrix element between the excited states  $\langle x \rangle$  and  $\langle y \rangle$ . For the alkali atom  $|\langle x|L_z|y \rangle| = 1$ , but this is not so in the crystal. By analogy with the effective mass theory for shallow donors<sup>27</sup> we are inclined to write this as a kind of effective mass correction to the g values for the excited state. That is, if we write

$$\langle x | L_z | y \rangle = (m/m^*), \qquad (18)$$

then Eq. (17) becomes

$$\Delta E = 2\beta H (m/m^*) - \frac{2}{3} \Delta \tanh(g_1 \beta H/2kT). \quad (19)$$

Finally, inserting into Eq. (10) and making an approximation for the tanh we obtain an expression very similar to Eq. (16) but one which we prefer to use

$$\theta_{\min} = -\left(\frac{\ln 2}{\pi}\right)^{1/2} \frac{\alpha_{\max} l\beta H}{W_{1/2}} \left[\frac{2m}{m^*} - \left(\frac{g_1 \Delta}{3kT}\right)\right]. \quad (20)$$

Our data will be compared with this equation in the next section in order to obtain values for  $\Delta$  and for  $m^*/m^{27a}$ 

#### **III. EXPERIMENTAL RESULTS**

#### A. Faraday Rotation for Several Alkali Halides

Analogous studies to those reported earlier for<sup>7</sup> KCl have been made for the *F*-band Faraday rotation in NaCl, KBr, KI, RbBr, and CsBr. Since the spectral dependence of the rotation for all crystals is very similar, only two examples, those for KBr and RbBr are given in Figs. 4 and 5.

As in the case for KCl two rotations are observed which have essentially the same spectral shape. These sit on a background rotation caused by the dispersion of the uncolored crystal in this wavelength region. At high temperatures ( $\sim 70-80^{\circ}$ K) only the temperatureindependent or diamagnetic rotation occurs, while at low temperatures the paramagnetic contribution grows proportional to 1/T. One notes from Figs. 4 and 5 the important experimental fact that the diamagnetic and paramagnetic rotations have the same sign. From Eq. (20) it is clear that this means that  $\Delta$  is a negative



<sup>27a</sup> In Ref. 7, the spin-orbit splitting was obtained from the observed ratio  $\theta_{\text{para}}/\theta_{\text{dia}}$ , and the mean effective splitting of the excited state  $(\Delta E)_e$ . This latter quantity was estimated from experimental results and formulas from Ref. 4 which contained numerical errors. Consequently the previously reported (Ref. 7) values of  $\Delta$  for KCl is in error and considerably smaller than that given in Table I of the present article.

<sup>&</sup>lt;sup>27</sup> W. Kohn and J. M. Luttinger, Phys. Rev. 97, 883 (1955).



FIG. 6. Schematic representation of the measurement of the spin-lattice relaxation time  $T_1$  as a function of temperature and magnetic field.

number, i.e., for the case of the unrelaxed excited F center the  $P_{3/2}$  and  $P_{1/2}$  levels are inverted with respect to the case for the free alkali atom.

Using the analysis outlined in the preceding section, the values for the spin-orbit splitting for the various crystals were obtained and are summarized in Table I. The Verdet constants given are not normalized to a given F-center density but refer to the density given in column 3. It is evident therefore that the ratio of the total rotations for RbBr and NaCl is even bigger when allowance is made for the difference in *F*-center density. Equation (20) was used to give values for  $\Delta$  and for comparison, data of the French workers are given. One of the major uncertainties which led to the error estimate given was the fact that the optical density of the crystals could not be measured during the experiment. Measurements before and after an actual rotation run indicated some loss in F centers. In the last column of the table estimates of the ratio  $m^*/m$  are given. These were obtained from Eq. (20) by using the experimentally observed values of  $\theta_{dia}$ .

## B. Spin-Lattice Relaxation

Since the paramagnetic Faraday rotation is directly related to the population difference in the *F*-center ground state, it can be used for the direct observation of the spin-lattice relaxation time  $T_1$ . Figure 6 shows in a schematic form how the measurements of  $T_1$  were made. A Faraday rotation was first attained with a constant magnetic field at 4.2°K and then a thermal pulse raised the crystal temperature to 12.7°K. The rotation decreased in a time less than the rise time of the thermal pulse ~4 sec. When the thermal pulse ended, the rotation relaxed back to its original value at 4.2°K with an exponential time constant. This time constant is a direct measure of the spin-lattice relaxation time at 4.2°K. By pulsing the crystal to different temperatures  $T_1$  was measured as a function of temperature. Similarly  $T_1$  could be measured at 4.2°K as a function of H by operating at different constant magnetic fields. Figure 7 shows the variation of  $T_1$  with both H and T. At small relaxation times  $T_1$  approaches and merges with the response time of the apparatus.

The technique has severe limitations because of the long time constant of the apparatus and the fact that both the relaxation time and the rotation depend on the magnetic field; the rotation decreasing and  $T_1$  increasing with decreasing H. For these reasons the number of experimental points obtainable was very limited so that no quantitative analysis or comparison with theory of the data has been attempted, although the data is not inconsistent with the recent extensive work of Feldman,



FIG. 7.  $T_1$  given as a function of magnetic field and temperature.

Warren, and Castle.<sup>28</sup> Within the limitations outlined above, the method has some merit and could be refined to allow the study of a wider range of relaxation times.

# IV. DISCUSSION OF RESULTS

In the following paper,  $\text{Smith}^{12}$  explains in some detail the nature of the interactions which result in the spin-orbit splitting of the unrelaxed excited state of the F center. This calculation can predict both the sign and magnitude of the splitting although it has only been carried out quantitatively for the case of NaCl. Some qualitative predictions about the dependence of  $\Delta$  on ion size is also made.

From the experimental point of view several facts can be deduced. In the first place for all crystals studied the spin-orbit splitting was negative, i.e., the *P* levels are inverted with respect to the free alkali atom case. As can be seen in Table I, the present data and those of the French groups are only in order-of-magnitude agreement. There is some justification for believing that the value of  $\Delta$  obtained for CsBr may be an underestimate. In CsBr, the  $P_{1/2}$  and  $P_{3/2}$  levels are partially resolved in absorption<sup>22</sup> so that  $\Delta$  may be suspected to be large. In this case the validity of the Becquerel relation seems in question since  $\Delta E$  is not small compared with linewidth, or in other words, within the energy change  $\Delta E dn/dE$  cannot be considered constant.

Generally speaking,  $\Delta$  for the potassium halides is determined about equally by interaction of the *F* center electron with both the nearest alkali and halogen ions. However in the case of the cesium halides, the work of Margerie and Romestain<sup>10</sup> indicates that the important ion determining  $\Delta$  is the cesium ion. This of course confirms earlier evidence<sup>22</sup> that the structure in the *F* band of these salts arises because of some characteristic of the cesium ion. Recent work<sup>29</sup> also suggests that in the rubidium halides  $\Delta$  is predominantly determined by the rubidium ion. It appears therefore that in going from the lithium to the cesium halides there is a definite tendency for the importance of the halogen ion to decrease and that of the alkali ion to increase. Henry, Schnatterly, and Slichter<sup>23</sup> have shown by the method of moments that the observed splitting in the cesium halides arises partially from a spin-orbit interaction but also from a mutual repulsion of the split P states due to the presence of perturbing noncubic lattice vibrational modes. They show from the circular dichroism data<sup>10</sup> that the shift in the first moment or  $\Delta$  is about 340 cm<sup>-1</sup> for CsBr. The Faraday rotation which we have analyzed, assuming only a change in the first moment, should therefore give a value close to this, so that the experimental value of 340 cm<sup>-1</sup> for CsBr appears to be an independent check on their theory. Such good agreement however is considered to be fortuitous.

It does appear that the data, at least in the case of NaCl and probably in the other alkali halides as well, are in fairly good agreement with the alkali atom model, although one is forced to consider the influence of the surrounding ions on the *F*-center electron. The lattice manifests itself primarily through the values of  $m^*/m$  given in Table I. These values are in fair agreement with estimates for a conduction band electron mass in the alkali halides from electron transport studies.<sup>30,31</sup>

Although a very detailed spectral dependence of the Faraday rotation was not undertaken in this work, it is possible that such a study could prove of great value. It has been pointed  $out^{23}$  that changes in the third moment, which would be apparent in the wings of the rotation pattern, would allow an estimate of the relative contribution of cubic and noncubic modes to the lattice vibrations which interact with the F center.

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<sup>&</sup>lt;sup>29</sup> Y. Merle-d'Aubigné (private communication). See also J. Gareyte and Y. Merle-d'Aubigné, Compt. Rend. **258**, 6393 (1964).

<sup>&</sup>lt;sup>30</sup> R. Ahrenkiel and F. C. Brown, Phys. Rev. **136**, A223 (1964). <sup>31</sup> It should be pointed out that there is no reason to expect good agreement here. The validity of an effective-mass approximation has not been demonstrated for energy levels as deep as the excited *F* center.