13). In the case of the chlorine-doped crystal discussed in Sec. D, it appears that the impurity conductivity sets in as the chlorine level is filled. It should be remarked that the decrease in mobility as the temperature is lowered is a characteristic of CdS.[4-6] Piper and Halsted[6] have shown a direct correlation between the temperature at which the mobility decreases and the gallium donor concentration. Therefore it is not really certain that the impurity in the chlorine-doped crystal is the same as that in Group-I-doped material.

CONCLUSION

The transport properties in "storage"-type crystals of CdS indicate that electrical conduction takes place via an impurity mechanism. On comparing the situation with the better understood materials silicon and germanium, it appears that the activation energy ϵ_3 is being observed and that it is about 0.001 eV. The second energy observed at 0.0007 eV may be the contribution of a second impurity, since mass-spectrographic analysis shows several elements present in sufficient concentration to permit impurity conductivity.

The exact mechanism for the formation of the impurity band is not known even to the extent of uniquely identifying the element involved. All that is known is that Group-I atoms are necessary, but not sufficient. Further work involving crystal growth and doping techniques will be needed to more accurately characterize the crystals.

Magneto-Optic Experiments on the F Center and A Center in KCl†

Charles H. Henry*

Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois

(Received 13 May 1965)

We report the measurement of the magnetically induced circular dichroism in the optical-absorption bands of the F center and A center in KCl performed to test theoretical productions of Henry, Schnatterly, and Slichter based on the method of moments. It is found that a magnetic field can alter the area of an optical-absorption band, but only at the expense of other optical-absorption bands of the center; the total area due to all the optical-absorption bands of the center remains constant. The magnetic field causes the F band to shift in energy. The shift is found to be greater in the peak than in the tails of the F band. Depending upon the orientations of the A centers, the magnetic field causes either a shift in the $A2$ band, or an increase in the area of the $A2$ band and equal and opposite decrease in the area of the $A1$ band. These results are in good agreement with the predictions of Henry, Schnatterly, and Slichter. We show that the signals from paramagnetic circular dichroism in the K band and F band occur with the same spin-lattice relaxation time, confirming that the K band is an excited state of the F center. The ratios of the coupling to the cubic and noncubic lattice modes of the F center and the ratios of the spin-orbit coupling constants of the A center are also evaluated.

I. INTRODUCTION

RECENTLY, magneto-optic experiments on the F band have led to a determination of the spin-orbit coupling in the first excited state of the F center.[1,2] Stimulated by these experiments, Henry, Schnatterly, and Slichter (HSS) performed a detailed analysis of the effect of a magnetic field (and other perturbations) on the optical properties of color centers, applying these results to the F center and A center.[3] Calculating the optical-absorption line shape of the F center and the effect of a magnetic field on the line shape is extremely difficult owing to the large electron-lattice coupling, the

orbital degeneracy of the excited state, and the presence of a strong spin-orbit interaction. In spite of these difficulties, HSS showed that the moments of the optical-absorption band and the changes which occur in these moments when a magnetic field is applied may be computed quite simply and with rigor. Their analysis shows that by measuring the second moment and the magnetically induced changes in the first and third moments of the F band, one could evaluate not only the spin-orbit coupling constant, but also the orbital g factor of the first excited state of the F center and several parameters describing the electron-lattice interaction of this state.

HSS applied their results to analyze the magneto-optic experiments of Margerie and Romestain[4] on the F band in CsCl and CsBr. HSS found that the energy separation of the partially resolved transitions to the

* Now at Bell Telephone Laboratories, Murray Hill, New Jersey.

† This research was supported in part by the U. S. Atomic Energy Commission, Contract AT(11-1)-1198.

[1] F. Lüty and J. Mort, Phys. Rev. Letters 12, 45 (1964).

[2] N. V. Karlov, J. Margerie, and Y. Merle-d'Aubigné, J. Phys. Radium 24, 717 (1963).

[3] C. H. Henry, S. E. Schnatterly, and C. P. Slichter, Phys. Rev. 137, A583 (1965).

[4] J. Margerie and R. Romestain, Compt. Rend. 258, 4490 (1964).

$P_{1/2}$ and $P_{3/2}$ states of the F center could be explained using the spin-orbit and electron-lattice coupling parameters evaluated from the moments measurements. This demonstrated the utility of the moments method in evaluating parameters. The very success of this analysis has provided the best experimental check of the validity of the moments method itself.

Besides allowing the evaluation of parameters, the moments method leads to certain predictions regarding changes in line shapes which take place when a magnetic field is applied. The purpose of the present paper is to test these predictions through careful measurement of the magnetically induced circular dichroism of the absorptions of the F center and A center in KCl.

One such prediction is that the application of a magnetic field will not change the total area under the optical-absorption bands of the F center (or A center), although it may transfer area from one band to another. HSS calculated the effect of a magnetic field on the A center and found that to a first approximation, depending upon the orientations of the A centers, either the $A2$ band will shift in position and remain unchanged in area or the $A2$ band will remain unchanged in shape and position, but its area will increase at the expense of the $A1$ band. HSS also predicted that a magnetic field will cause the F band in KCl to shift more in the peak than in the tails. All three of these predictions are verified in the experiments described below.

II. THEORY

A. Definition of Moments

HSS defined the optical-absorption line shape as $f_\eta(E) = C\alpha_\eta(E)/E$, where $\alpha_\eta(E)$ is the optical-absorption coefficient for light of polarization η, E is the energy, and C is a constant. $f_\eta(E)$ will be proportional to the transition probability for the absorption of a photon of polarization η and energy E. The moments of an optical-absorption band for light of polarization η, measured relative to the center of gravity $\bar{E}_\eta$ of the band, are

$$A_\eta = \int f_\eta(E)dE,$$

$$\bar{E}_\eta = A_\eta^{-1}\int E f_\eta(E)dE,$$

$$\langle E_\eta{}^n\rangle = A_\eta^{-1}\int (E-\bar{E}_\eta)^n f_\eta(E)dE,$$

$$\langle \Delta E_\eta{}^n\rangle = A_\eta^{-1}\int (E-\bar{E}_\eta)^n \Delta f_\eta(E)dE, \quad (1)$$

where A_η is the area, $\langle E_\eta{}^n\rangle$ is the nth moment, and $\langle \Delta E_\eta{}^n\rangle$ is the change that occurs in the nth moment when $f_\eta(E)$ goes to $f_\eta(E)+\Delta f_\eta(E)$ as a result of applying a magnetic field. In this paper, we will only consider the change that occurs in the line shape for right-
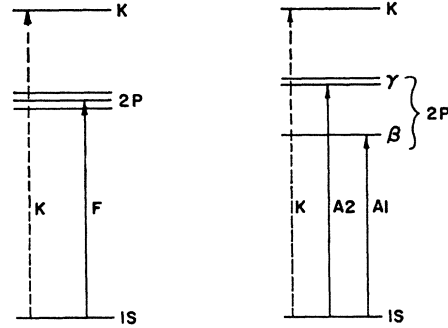

FIG. 1. Energy-level diagram showing the orbital states of the F center and the A center. The ground and first excited states of the F center are roughly hydrogenic and have been labeled $1S$ and $2P$ by analogy. The degeneracy of the states that give rise to the K band is not known. They are indicated by a single level labeled K. The $2P$ states of the A center are split by the crystal field into the orbital doublet γ and the orbital singlet β.

circularly-polarized light $\Delta f_+(E)$ when a magnetic field is applied along the direction of the light.

B. F Center

The orbital levels and the transition of the F center and A center are shown schematically in Fig. 1. The F center has two optical-absorption bands, the F and K bands.[5] The A center has three bands, called $A1$, $A2$, and K. To distinguish between the different bands, we denote the moments by the subscripts, F, K, $A1$, etc.

For the F center, HSS concluded the following:

(a) If the mixing of the nondegenerate states K and $2P$ by $\mathcal{H}_{so}$ and $\mathcal{H}_z$, the spin-orbit and Zeeman interactions, is neglected,

$$\Delta A_{+F} = 0. \quad (2)$$

That is, there is no net change in the area of the F band when a magnetic field is applied. The effect of a mixing of the $2P$ and K states by $\mathcal{H}_{so}+\mathcal{H}_z$ is to cause a small change in the area of the F band and an equal and opposite change in the area of the K band such that

$$\Delta A_{+K} + \Delta A_{+F} = 0. \quad (3)$$

(b) When a magnetic field is applied in some direction, there will be a change in the first moment given by

$$\langle \Delta E_+\rangle_F = \tfrac{2}{3}\Delta\langle S_z\rangle + g_{orb}\beta H, \quad (4)$$

where Δ is the spin-orbit splitting of the $2P$ state, g_{orb} is the orbital g factor for the $2P$ state (Δ and g_{orb} were defined in HSS), β is the Bohr magneton, and $\langle S_z\rangle$ is the component of spin polarization in the ground state along the direction of the light. The first term is called the "paramagnetic" change in the line shape, the second the "diamagnetic" change. In general, when the magnetic field is turned on, it takes a time for the electron spins to become polarized in the ground state. Denoting

---

[5] The Lüty bands will not be considered since they lie far away in energy from the P state and have low oscillator strength.

the spin-lattice relaxation time of the ground state as T_1, we have that $\langle S_z \rangle$ is a function of time, $\langle S_z(t) \rangle$, given by

$$\langle S_z(t) \rangle = \left[-\tfrac{1}{2} \tanh(\beta H/kT) \right]\left[1 - \exp(-t/T_1) \right] \quad (5)$$

if the magnetic field H is applied at $t=0$. In the experiments we are about to describe, T_1 was 50 to 100 sec, so that the paramagnetic changes in the line shape were easily distinguished from the "diamagnetic" changes and background effects which followed the instantaneous value of H. Only the paramagnetic changes will be discussed in this paper.

(c) The change in first moment $\langle \Delta E_+ \rangle_F$ is brought about by a shift of the F band. Previous experiments[1,2,6,7] were analyzed assuming the entire band shifts rigidly by $\langle \Delta E_+ \rangle_F$. The change in line shape for such a rigidly shifted F band is

$$\Delta f_{+FRS} = -\langle \Delta E_+ \rangle_F df(E)_F/dE, \quad (6)$$

where the subscript RS stands for rigid shift. However, HSS find that if the noncubic lattice modes are important in broadening the F band, the band will not shift rigidly but will shift more in the peak than in the tails. Hence, Δf_{+F} will be greater in the peak and smaller in the tails of the F band than Δf_{+FRS}. The change in the third moment will therefore be smaller for Δf_{+F} than for Δf_{FRS}, and it is given by

$$\langle \Delta E_+{}^3 \rangle_F = \langle \Delta E_+{}^3 \rangle_{FRS}(1+\tfrac{1}{2}x)/(1+x),$$
$$x = \langle E^2 \rangle_{NC}/\langle E^2 \rangle_C,$$
$$\langle \Delta E^3 \rangle_{FRS} = 3\langle E^2 \rangle_F \langle \Delta E_+ \rangle_F, \quad (7)$$

where $\langle E^2 \rangle_C$ and $\langle E^2 \rangle_{NC}$ are the contributions to the second moment of the F band made by the cubic and noncubic lattice modes. By measuring $\langle \Delta E_+{}^3 \rangle_F$, $\langle E^2 \rangle_F$, and $\langle \Delta E_+ \rangle_F$, we can evaluate x.

Although the F band is not rigidly shifted, it still displays a shifted appearance, for there is a sizeable change in the first moment of the F band while to a good approximation the area and the second moment of the F band remain unchanged.

C. A Center

The A center consists of an F center in KCl in which one of the nearest-neighbor potassium ions has been replaced by a sodium ion. The orbital energy levels and transitions are shown in Fig. 1, and the three possible orientations of the A center are shown in Fig. 2. The double line in Fig. 2 indicates the direction of the impurity, which is also the axis of symmetry of the center. The $A1$ band is active for light polarized along the axis of the center, while the $A2$ band is active for light polarized perpendicular to the axis of the center.

[6] R. Romestain and J. Margerie, Compt. Rend. **258**, 2525 (1964).

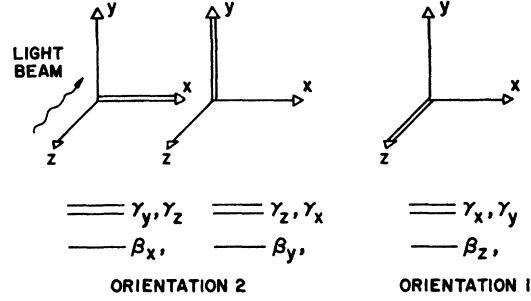[7] J. Mort, F. Lüty, and F. C. Brown, Phys. Rev. **137**, A566 (1965).

FIG. 2. Diagram showing the various orientations of the A center. The double arrow gives the direction of the axis of the center. The states are labeled with subscripts x, y, z. γ_z is a $2P$-like orbital wave function with a nodal plane normal to the x direction, etc.

In these experiments, we are using circularly polarized light, which means that two of the orientations are equivalent. They have been denoted as orientation 2 in Fig. 2.

Just as in the case of the F center, we expect in general that there will be no net change in the area of all the bands. As we will see, the circular dichroism of the K band is quite small, so we expect to good approximation that

$$(\Delta A_+)_{A1} + (\Delta A_+)_{A2} = 0. \quad (8)$$

The individual areas of the $A1$ and $A2$ bands will not be conserved, however, because there will be a strong mixing by $\mathcal{3C}_{so} + \mathcal{3C}_z$ of the degenerate γ states with the β state. Depending upon the orientation of the A centers, there will be two distinct effects. For orientation 1, only the $A2$ band will be present and the paramagnetic change in first moment will be

$$\langle \Delta E_+ \rangle_{A2} = \tfrac{2}{3}\Delta_2 \langle S_z \rangle, \quad (9)$$

where Δ_2 is defined as

$$\Delta_2 = (e\hbar/2m^2c^2)\langle \gamma_y | (\mathbf{E} \times \mathbf{p})_z | \gamma_x \rangle \quad (10)$$

and is just the matrix element between the states γ_x and γ_y of the spin-orbit interaction thus associated with S_z,

$$\mathcal{3C}_{so} = (e\hbar/2m^2c^2)(\mathbf{E} \times \mathbf{p}) \cdot \mathbf{S}. \quad (11)$$

This change in first moment arises from a shift of the $A2$ band. (Just as in the case of the F band, this will not be a rigid shift.) There are no area changes of the $A1$ and $A2$ bands.

For orientation 1, the change in first moment is

$$\langle \Delta E_+ \rangle_{A1A2} = \tfrac{4}{3}\Delta_{12}\langle S_z \rangle (A_{A1}A_{A2})^{1/2}/(A_{A1} + A_{A2}), \quad (12)$$

where

$$\Delta_{12} = (e\hbar/2m^2c^2)\langle \gamma_y | (\mathbf{E} \times \mathbf{p})_z | \beta_x \rangle. \quad (13)$$

This change in first moment arises from an increase in the area of the $A2$ band and an equal and opposite decrease in the area of the $A1$ band.
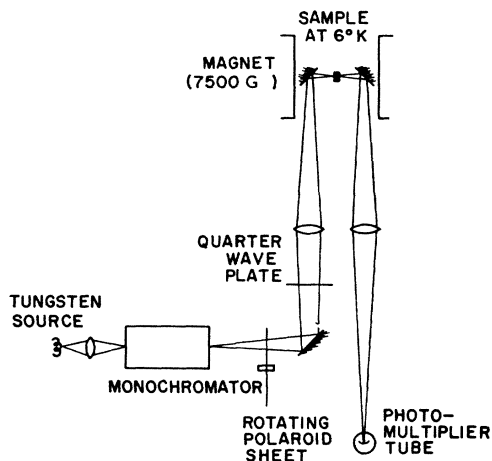
FIG. 3. Schematic diagram of apparatus.

III. EXPERIMENT

The circular dichroism of the A center and F center were measured by ac method shown in Fig. 3. Light from a grating monochrometer was consecutively passed through a polaroid sheet rotating at 17 cps through a mica quarter-wave plate, through the sample held near liquid-helium temperature (about 6°K) in an optical cryostat, and finally focused onto a 1P21 photomultiplier tube. The polarization of the light passing through the sample was alternately right circular, linear, left circular, and linear during each half-cycle of rotation. Thus, a circular dichroism induced by the magnetic field produced a signal at 34 cps at the photomultiplier tube. This signal was detected by a lock-in amplifier tuned to this frequency.

The two metallic reflections as well as the quarter-wave plate influenced the light polarization passing through the sample. This turned out to be an advantage because it was found that small rotations of the optic axis of the quarter-wave plate (cut for a wavelength of 5500 Å) with respect to the direction of the mirror axes allowed the combination of the two mirrors and the fixed quarter-wave plate to be tuned to produce perfectly circular polarized light over the entire range of measurement (4200 to 6200 Å). The spectrometer could detect changes in $\alpha_+(E)$ of less than 10^{-4}.

IV. RESULTS

A. F Center

The solid curve in Fig. 4 shows the measured circular dichroism of the F band $\Delta f_+(E)_F$.[8] The dashed curve in Fig. 4 is a plot of $\Delta f_+(E)_{FRS} = [df/dE(E)_F]\langle\Delta E_+\rangle_F$

adjusted to have the same first moment as the solid curve. As predicted, $\Delta f_+(E)_F$ is smaller in the wings than $\Delta f_+(E)_{FRS}$ and thus $\langle\Delta E_+^3\rangle_F < \langle\Delta E_+^3\rangle_{FRS}$.[9] Measurement of $\langle\Delta E_+^3\rangle_F$, $\langle E^2\rangle_F$, $\langle\Delta E_+\rangle_F$, and the use of Eq. (7) gives

$$\langle E^2\rangle_{NC}/\langle E^2\rangle_C = x = 1.10\pm0.11.$$

Hence, the rms interaction with the noncubic lattice modes is about 10% larger than the interaction with the cubic lattice modes. This is in slight disagreement with the measurement of Schnatterly,[10] who finds $x = 0.90\pm0.05$ from stress experiments at liquid-nitrogen temperature. It is possible that this disagreement is due to a temperature dependence of x. An increase of $\langle E^2\rangle_C$ by 20% as the temperature changes from 6 to 77°K would explain the two different values of x, and would also be consistent with the observed broadening of the F band in this temperature range.[11]

Equation (3) predicts that there will be no net change in the sum of the areas of the F band and K band. The measurement of $\Delta f_+(E)$ in the K band is shown in
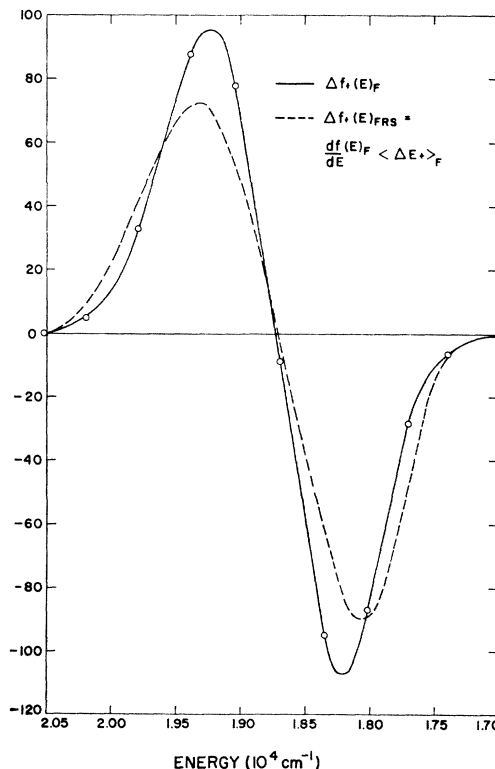

FIG. 4. The solid curve is a plot of the measured values of $\Delta f_+(E)_F$. The dashed curve is a plot of $\Delta f_+(E)_{FRS}$. Both curves have the same first moment.

---

[8] Actually, $\Delta f_+(E) - \Delta f_-(E)$ is measured. It is assumed that $\Delta f_+(E) = -\Delta f_-(E)$, so that $\Delta f_+(E) - \Delta f_-(E) = 2\Delta f_+(E)$. This assumption is true if $\Delta f_+(E)$ is linear in $\langle S_z\rangle$, as was observed. In any case, this assumption does not change any of the results reported here.

[9] J. Margerie (private communication) has also found this result for the circular dichroism of the F center in a number of different alkali halides.

[10] S. E. Schnatterly, Phys. Rev. (to be published).

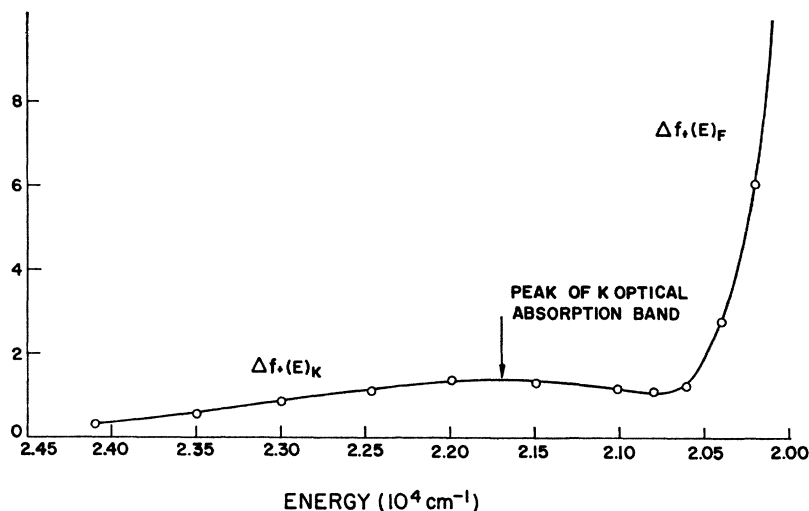[11] J. D. Konitzer and J. J. Markham, J. Chem. Phys. 32, 843 (1960).

FIG. 5. $\Delta f_+(E)_K$ and $\Delta f_+(E)_F$ plotted at 10 times the scale of $\Delta f_+(E)_{FRS}$ in Fig. 4.

Fig. 5. The change in area $\Delta A_+ = f \Delta f_+(E)dE$ is only about 10^{-4} the area of the F and K bands given by

$$A_+ = \int f_+(E)dE. \qquad (14)$$

However, since ΔA_+ is proportional to $\mathfrak{K}_{so}$, while A_+ is independent of the spin-orbit interaction, the comparison of ΔA_+ and A_+ does not have much meaning. A better and more severe test of area conservation is to compare the net change in area ΔA_+ with the total change (regardless of sign) $|\Delta A_+|$, given by

$$|\Delta A_+| = \int |\Delta f_+(E)| dE, \qquad (15)$$

since both ΔA_+ and $|\Delta A_+|$ are proportional to $\mathfrak{K}_{so}$. The change in area of the K band is $0.02 |\Delta A_+|$, and that of the F band is $(0.01 \pm 0.04)|\Delta A_+|$. The errors are due to the subtraction of two areas, each nearly equal to $\frac{1}{2}|\Delta A_+|$, in evaluating the contribution of ΔA_+ made by the F band. Adding these two contributions, we obtain

$$\Delta A_+ = (0.03 \pm 0.04)|\Delta A_+|. \qquad (16)$$

Thus, within experimental error, we find that the area of the superposition of the F band and K band is conserved.

The paramagnetic signals of the F and K band are proportional to $\langle \Delta S_z(t) \rangle$, which grows to its equilibrium value with the spin-lattice relaxation time of the ground state T_1, as indicated by Eq. (5). Figure 6 shows a measurement of $(1 - \Delta f_+(E,t)/\Delta f_+(E)_{max})$ for the F band and K band. It confirms that $\Delta f_+(E,t)$ does increase exponentially. Within experimental error, both bands give the same value of T_1. This is another confirmation that the K band is indeed an absorption band of the F center.

B. A Center

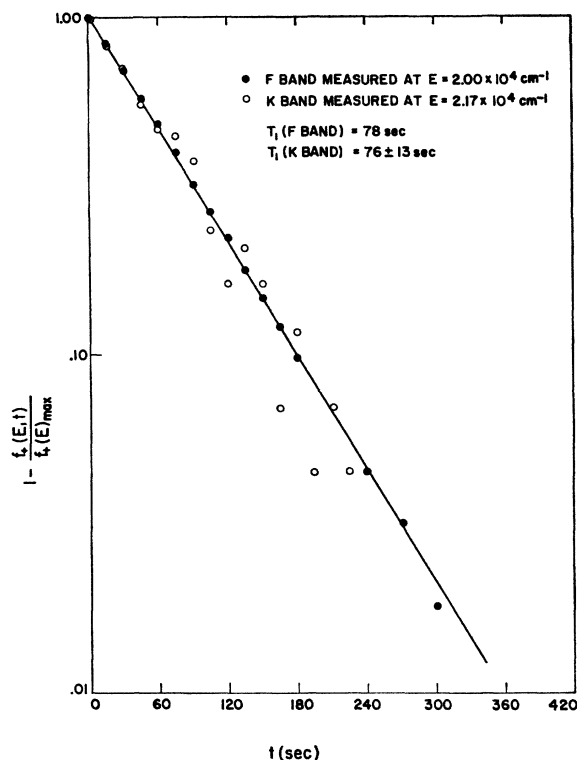The A-center optical-absorption and circular-dichroism data are shown in Figs. 7 and 8.[12] The A

FIG. 6. Growth of the signals from paramagnetic circular dichroism in the F band and K band.

[12] The plot of $(\Delta f_+)_{after}$ shown in Fig. 8 is the raw data multiplied by a constant factor which corrects for differences in the circular-dichroism measurements made before and after alignment. These differences were due to changes in the gain of the detector and changes in the sample temperature. The factor was chosen so that the ratio of $(\Delta f_+)_{before}$ to $(\Delta f_+)_{after}$ in the region of the $A1$ band is equal to N_2'/N_2. These corrections (which were mainly due to changes in sample temperature) were about 10–15%.
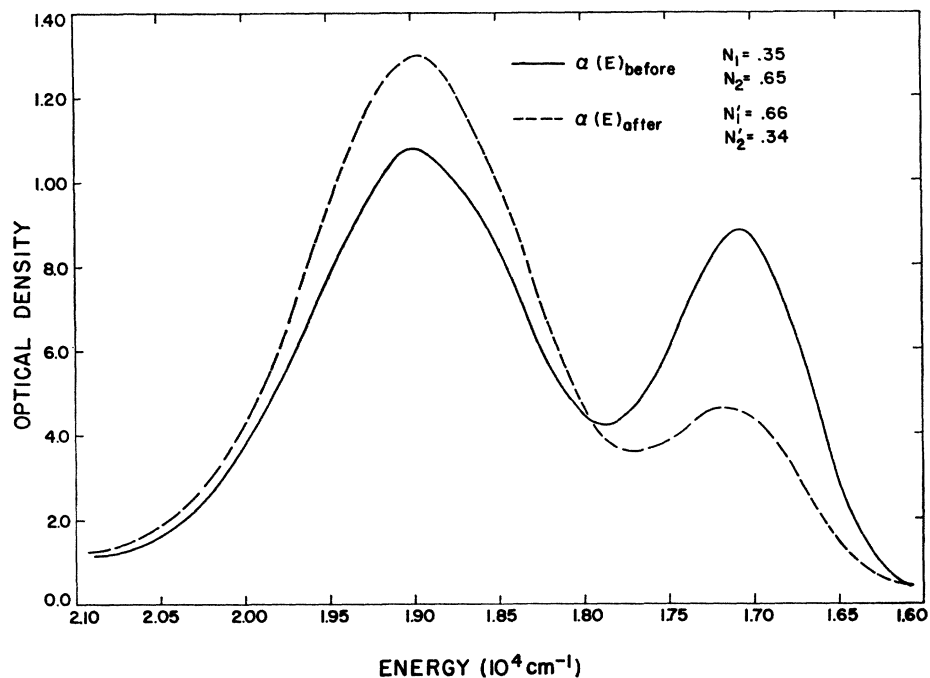
FIG. 7. The $A2$ and $A1$ optical-absorption bands before and after partial alignment of the A centers.

centers were produced by bleaching in the F band at $-30°C$ in additively colored KCl crystals doped with 1% NaCl. The centers were partially aligned in orientation 2 by bleaching in the $A1$ band at $-170°C$. The numbers $N1, N2, N1', N2'$, refer to the fraction of the A centers in orientations 1 and 2 before and after alignment. The numbers of orientation 1 and orientation 2 were determined from the ratios of the optical-absorption peaks of the $A1$ and $A2$ bands using the results of Lüty.[13] As already discussed, if the centers

FIG. 8. The A center circular dichroism before and after the partial alignment of the A centers.

[13] F. Lüty, Z. Physik 165, 17 (1961).

are completely aligned in orientation 2, the circular dichroism would be $(\Delta f_+)_{A2}$, in which the change in the first moment is brought about by the shifting of the $A2$ band; if the centers are in orientation 1, the circular-dichroism function would be $(\Delta f_+)_{A1A2}$, in which change in the first moment is due to an increase in the absorption of the $A2$ band and an equal and opposite decrease in the absorption of the $A1$ band. For incomplete alignment, the curves in Fig. 8 should be able to be fitted with

$$(\Delta f_+)_{\text{before}} = N_1(\Delta f_+)_{A1A2} + N_2(\Delta f_+)_{A2},$$
$$(\Delta f_+)_{\text{after}} = N_1'(\Delta f_+)_{A1A2} + N_2'(\Delta f_+)_{A2}. \quad (17)$$

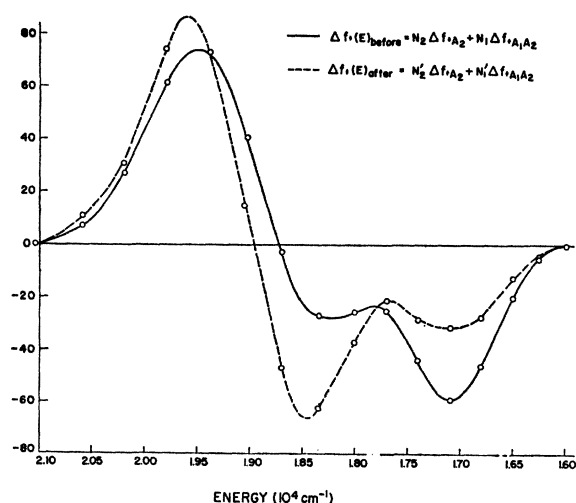Figure 9 shows the curves $(\Delta f_+)_{A2}$ and $(\Delta f_+)_{A1A2}$ which are obtained from subtractions of the curves in Fig. 8. $(\Delta f_+)_{A2}$ is an antisymmetric curve that resembles the derivative of $(f_+)_{A2}$ and in the first approximation causes a shift at the $A2$ band with no change in half-width or area. $(\Delta f_+)_{A1A2}$ is an antisymmetric curve whose positive and negative peaks roughly follow the $A1$ and $A2$ bands. In the first approximation, therefore, $(\Delta f_+)_{A1A2}$ will merely increase the area of the $A2$ band and decrease the area of the $A1$ band without changing the shape or positions of these bands.

We expect the sum of the areas of the A bands and K band to be conserved. If we estimate the area of the K band of the A center at $0.02|\Delta A_+|$ (the value of $(\Delta A_+)_K$ for the F center), and add to $0.02|\Delta A_+|$ the areas under the curves in Fig. 8, we find

$$(\Delta A_+)_{\text{before}} = (+0.03 \pm 0.04)|\Delta A_+|,$$
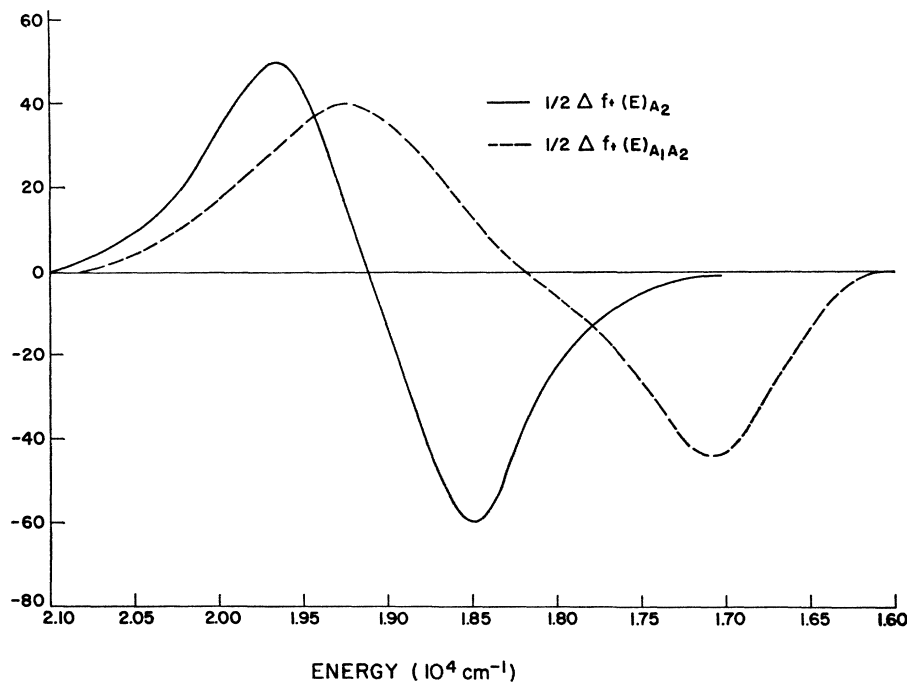$$(\Delta A_+)_{\text{after}} = (-0.02 \pm 0.04)|\Delta A_+|, \quad (18)$$

FIG. 9. $(\Delta f_+)_{A1A2}$ and $(\Delta f_+)_{A2}$ found from subtractions of the curves in Fig. 8.

so that the area is conserved within experimental error. It is interesting to note that if we had defined $f_+(E)$ proportional to $\alpha_+(E)$, instead of $f_+(E)$ proportional to $\alpha_+(E)/E$, there would have been an increase in the positive values of Δf_+ and a decrease in the negative values of Δf_+ leading to an additional area change of about 0.05 $|\Delta A_+|$. In this case, the area would not have been conserved within experimental error.

By taking the ratios of the first moments of the curves shown in Fig. 8 and using Eqs. (9), (12), and (17), we find

$$\Delta_{12}/\Delta_2 = (1.13\pm0.30).\qquad(19)$$

The large error in this ratio arises because the ratio is quite sensitive to errors in the determination of $N1'$ and $N2'$.

V. SUMMARY

These experiments have verified three results of the HSS paper. First, the area under $f_+(E)$ is not altered by a magnetic field. Second, for the F center $\Delta f_+(E)_F$ is larger in the peak and smaller in the tails than $\Delta f_+(E)_{FRS}$. Third, upon application of a magnetic field, the first moment of the A bands changes in either of two ways. For centers in orientation 2, the change arises from a shift (nonrigid) of the $A2$ band. For centers in orientation 1, the change is due to the $A2$ band increasing in area and the $A1$ band decreasing in area.

The moments measurements also allowed the evaluation of $\langle E^2 \rangle_{NC}/\langle E^2 \rangle_C$ for the F center and the evaluation (with rather poor accuracy) of Δ_{12}/Δ_2 for the A center. Measurements of the time dependence of the paramagnetic signals of the K and F bands show that these bands arise from centers with the same spin-lattice relaxation time. This helps to confirm that the F and K bands belong to the same center.

ACKNOWLEDGMENTS