Stark Effect in Color Centers of Alkali Halides*

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The stark effect of the F center in NaCl, NaBr, KCl, KBr, KI, and RbCl, the M center in KCl, and the Z_1 center in KCl:Sr was measured using an ac electric field. The fractional change of the absorption coefficient, $\Delta\alpha/\alpha$, at the peak of the F band, normalized to a Lorentz local field of 200 kV/cm, was found to be approximately 2×10^{-5} for NaCl and NaBr, 11×10^{-5} for RbCl, and 17×10^{-5} for KCl, KBr, and KI. The value of $\Delta\alpha/\alpha$ at the peak of the M band in KCl was $(3.9\pm0.4)\times10^{-5}$ for an applied electric field of 97 kV/cm. A measurement of the change in the absorption coefficient, $\Delta\alpha$, versus photon energy produced a nonsymmetrical curve. This indicates that the effect observed was not the linear Stark effect, and thus provides additional evidence that Seitz's model is incorrect. The absorption coefficient increased at energies lower than the M band, corresponding to a decrease in the absorption coefficient of the M band. The effect is attributed to the mixing of two nondegenerate energy levels of opposite parity. The optical transition to the level of lower energy is normally forbidden. The Z_1 center in KCl:Sr did not exhibit a detectable Stark effect. It was determined, however, that $\Delta\alpha/\alpha<8\times10^{-6}$ for an applied electric field of 97 kV/cm. If the Z_1 possesses a permanent dipole moment, the difference between the expectation values of dipole moment in the ground state and excited state is less than 1.0×10^{-20} cgs unit.

I. INTRODUCTION

IN 1958, Overhauser and Rüchardt[1] suggested using the linear Stark effect to determine whether a color center which exhibits dichroism has inversion symmetry. They noted that quantum states of systems which do not have inversion symmetry will generally possess dipole moments and will undergo a linear shift in energy when an electric field is applied. They attempted to detect an effect in the M and R bands using a dc electric field, but failed. This led to the conclusion that the M and R centers have inversion symmetry.

Henry, Schnatterly, and Slichter[2] analyzed the effect of external perturbations on the absorption-band line shapes using the method of moments. They considered the effect of an electric field on the absorption of the F center. Since the F center has cubic symmetry, there is no linear Stark effect; however, there should exist a quadratic effect. In 1966, Chiarotti, Grassano, and Rosei[3] reported the observation of the Stark effect of the F center in KCl.

This paper reports the measurements using an ac electric field of the Stark effect in the F centers of other alkali halides and the Stark effect in the M center in KCl. In addition, the use of the Stark effect as an aid to distinguish between the various models of the Z_1 center is described.

II. METHOD OF MOMENTS

The theoretical calculation of the optical-absorption line shape of color centers and the effect of an external perturbation on the line shape is a difficult task. However, the effects of perturbations on magnetic-resonance line shapes have been studied by Van Vleck.[4] He showed that although the exact calculation of the line shape is often impossible, the moments of the line shape could be rigorously computed and compared with experimental results. The application of the method of moments to the optical-absorption line shape was done by Lax.[5] Henry, Schnatterly, and Slichter[2] have developed a simpler, more direct method of calculation of the moments and have analyzed the effect of an electric field on the F band. The following discussion summarizes their method.

The optical-absorption coefficient $\alpha(E)$ is defined by

$$\alpha(E)=-\frac{1}{I}\frac{dI}{dx}, \tag{1}$$

where I is the intensity of the light, x is a length measured along the direction of light propagation, and E is the energy of the light photons.

A line-shape function $f(E)$ is defined which is easier to treat theoretically than is $\alpha(E)$. The line-shape function and the absorption coefficient are related by

$$\alpha(E)=CEF(E), \tag{2}$$

where C is a constant. The zeroth moment ("area") is defined as

$$A=\int f(E)dE. \tag{3}$$

The integration extends over the energy range of a single resolved line. The first moment ("center of gravity") is defined as

$$\langle E\rangle=\bar{E}=A^{-1}\int Ef(E)dE. \tag{4}$$

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[1] A. W. Overhauser and H. Rüchardt, Phys. Rev. **112**, 722 (1958).
[2] C. H. Henry, S. E. Schnatterly, and C. P. Slichter, Phys. Rev. **137**, A583 (1965).
[3] G. Chiarotti, U. M. Grassano, and R. Rosei, Phys. Rev. Letters **17**, 1043 (1966).
[4] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).
[5] M. Lax, J. Chem. Phys. **20**, 1752 (1952).

All higher moments, measured about $\bar{E}$, are defined by

$$\langle E^n\rangle = A^{-1}\int (E-\bar{E})^n f(E)dE. \quad (5)$$

The second moment $\langle E^2\rangle$ is of interest since it is a measure of the spread of the band.

One of the important results of Henry *et al.* is that the zeroth moment remains unchanged upon application of a perturbation. The line shape changes from $f(E)$ to $g(E)$.

$$A = \int f(E)dE = \int g(E)dE. \quad (6)$$

The changes in the other moments are given by the expressions

$$\langle \Delta E\rangle = \int E[g(E)-f(E)]dE, \quad (7)$$

$$\langle \Delta E^n\rangle = \int (E-\bar{E})^n[g(E)-f(E)]dE. \quad (8)$$

Further discussion of the moments will appear in the sections in which they are used.

III. APPARATUS

The measurement of the Stark effect requires apparatus which is capable of detecting a fractional change in the optical absorption coefficient of approximately 10^{-5} in the presence of noise. Such small changes can be detected with ac techniques utilizing a lock-in amplifier.

The fractional change in the absorption coefficient, $\Delta\alpha/\alpha$, can be computed from measurements of the intensity of the light passing through the crystal, I, the change in the intensity upon application of an electric field, ΔI, and the optical density of the crystal, O.D., at the wavelength of interest. These quantities are related by the following equation:

$$\frac{\Delta\alpha}{\alpha} = -\frac{1}{2.3(\text{O.D.})}\frac{\Delta I}{I}. \quad (9)$$

The magnitude of $\Delta I/I$ will depend upon the polarization of the light with respect to the applied electric field. It is greatest for light which is plane polarized parallel to the applied field and least for light which is plane polarized perpendicular to the applied field.

The light beam can be modulated for the determination of ΔI in two ways:

(1) Since the absorption of light polarized parallel to an applied electric field differs from the absorption of light polarized perpendicular to the field, the plane of polarization may be rotated and a dc field applied to the crystal.

(2) With the plane of polarization of the light remaining fixed, an ac field may be applied to the crystal.

Initially, the former method was tried. In principle, the apparatus was sufficiently sensitive to detect a $\Delta\alpha/\alpha$ of about 2×10^{-5}. A dc electric field of 10^5 V/cm was applied. However, attempts to detect the Stark effect in the F center in KCl, NaCl, and KI failed when using this technique. The absence of the effect may have been due to space charge.

To avoid the problem of space charge, the experiments were repeated using an ac electric field. The block diagram of the apparatus is shown in Fig. 1. A beam of monochromatic light was plane polarized parallel to the applied ac electric field using a Glan-Thompson prism. A lens focused the light into the crystal at liquid-nitrogen temperature (78°K) in the cryostat. A narrow aperture on the crystal holder allowed only light which has transversed the crystal between the electrodes to be detected by the photomultiplier tube (PMT). The ac portion of the signal was fed into the lock-in amplifier.

An ac electric field was applied perpendicular to the direction of light propagation (see Fig. 2). Since the change in optical absorption is independent of the polarity of the applied voltage, the frequency of the modulation will be twice that of the applied voltage. A reference signal of frequency f was obtained from the RC oscillator and fed into the reference channel of the lock-in amplifier. The lock-in amplifier contains a frequency doubler on the reference channel which produces a frequency of $2f$ for comparison with the signal. A time constant of 150 sec was used in all measurements. The output of the lock-in amplifier was recorded on a T-Y recorder (i.e., signal versus time).

The intensity of the beam passing through the crystal was measured by mechanically chopping the beam at frequency $2f$. The resulting ac signal was measured by the lock-in amplifier. When ΔI was being measured, the chopper was not operated.

The optical density was measured on a Cary 14 spectrophotometer. The optical density was measured both before and after the measurements of $\Delta I/I$.

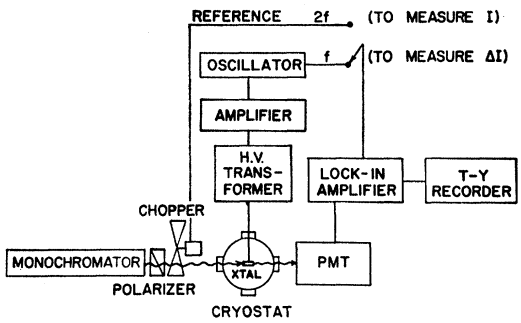

FIG. 1. Block diagram of the apparatus for the measurement of the Stark effect utilizing an ac electric field. The chopper is used to measure I but is not in the beam for measurements of ΔI.

Bleaching was slight but detectable for all the samples used.

The samples used were typically 10 mm×6 mm×0.65 mm. They were annealed 10 min in air at 400°C and quenched by placing on an aluminum block at room temperature. The color centers were produced by x irradiation. The x rays were filtered to remove low-energy x rays. The low-energy component is more efficient in coloring the crystals, but because they are more easily absorbed, a nonuniform coloration would result. As shown in Fig. 2, the crystal was colored such that the absorption of the light beam occurred only in the region between the electrodes. The remainder of the crystal received only negligible scattered radiation.

The ultimate sensitivity of the measurement of ΔI was limited by noise. The sources of noise were:

(1) dark current of the photomultiplier tube which consists of leakage currents and pulses produced by electrons which are thermionically released from the cathode or secondary electrons released by ionic bombardment of the dynodes or cathode;
(2) microphonics of the photomultiplier tube;
(3) shot noise (frequency-independent);
(4) fluctuations in the brightness of the tungsten light source ("flicker") (inverse frequency dependence).

When the light source was turned off, no noise appeared on the output of the lock-in amplifier even when a short integration time constant (5 sec) was used. This indicated that neither dark current nor microphonic noise of the photomultiplier were major sources of noise.

Shot noise is due to the statistical fluctuations in the number of photoelectrons ejected from the photocathode of the photomultiplier tube during a time equal to an integration time constant. The fluctuation is given by

$$\Delta I/I_{\text{noise}}=\Delta N/N=1/\sqrt{N}, \tag{10}$$

where N is the number of photoelectrons ejected from the photocathode during a time equal to an integration time constant. Experimentally, it was observed that a decrease in the beam intensity caused by the removal of the lens, by denser coloration of the crystal, or by decreasing the width of the monochromator slits, was accompanied by an increase in the noise. This indicates that shot noise does contribute to the observed noise.

The other major source of noise is believed to be fluctuations in the brightness of the tungsten light source. When the modulation frequency was increased, the noise was reduced, which demonstrated that there was frequency dependence.

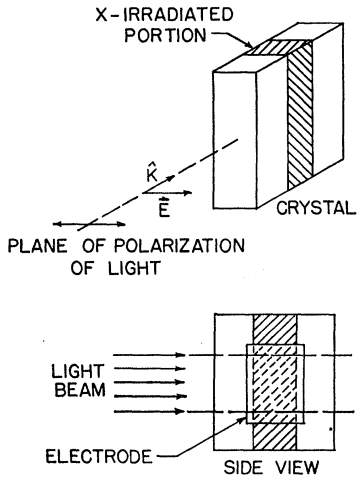

FIG. 2. Orientation of the electric field **E**, direction of light propagation $\hat{K}$, and the polarization of the light. The shaded area represents the location of the color centers.

IV. STARK EFFECT IN THE F CENTER OF ALKALI HALIDES

A. Theory

The optical absorption of the F band of the alkali halides arises from an electronic transition from a $1s$ ground state to a $2p$ excited state. The $1s \rightarrow 2s$ transition is forbidden.

Henry, Schnatterly, and Slichter[2] calculated the change in the zeroth, first, and second moments of the F band which occurs upon application of an electric field. The perturbation H_p to the Hamiltonian is

$$H_p=-ez\mathcal{E}, \tag{11}$$

where e is the charge of the electron and $\mathcal{E}$ is the electric field in the z direction. Their results are summarized in the following discussion.

As previously mentioned, the zeroth moment remains unchanged. The first moment also does not change, indicating that the "center of gravity" does not shift. For light which is polarized parallel to the applied electric field (z direction), the change in the second moment is

$$\langle \Delta E_z^2 \rangle = (e\mathcal{E})^2 |\langle z|z|\gamma\rangle|^2. \tag{12}$$

The $2s$ state is denoted by $|\gamma\rangle$ and the $2p_z$ state by $|z\rangle$. The x and y components of the change in the second moment, $\langle \Delta E_x^2 \rangle$ and $\langle \Delta E_y^2 \rangle$, vanish, indicating that no Stark effect occurs for light which is polarized perpendicular to the electric field.

When Henry *et al.* assumed that the $2s$ and $2p$ states were nearly degenerate (i.e., $E_{2p}-E_{2s}$ is less than a linewidth), they found the following expression for the fractional change in the optical-absorption coefficient:

$$\frac{\Delta\alpha}{\alpha}=-\frac{\langle \Delta E_z^2 \rangle}{2\langle E^2 \rangle}=-\frac{(e\mathcal{E})^2|\langle z|z|\gamma\rangle|^2}{2\langle E^2 \rangle}. \tag{13}$$

The effect of the electric field is to mix the $2s$ and $2p$ states. The $1s \rightarrow 2s$ transition is now partially allowed at the expense of the $1s \rightarrow 2p$ transition. If the $2s$ and

$2p$ states are nearly degenerate, the zeroth and first moments of the band remain unchanged. The electric field causes a broadening of the band.

However, if the $2s$ and $2p$ states were resolved (i.e., $E_{2p}-E_{2s}$ is greater than the linewidth of the band), the $1s \rightarrow 2s$ transition becomes partially allowed and the area of the $1s \rightarrow 2p$ band decreases. The conservation of area requires

$$\Delta A_{1s\rightarrow 2s} = -\Delta A_{1s\rightarrow 2p}. \tag{14}$$

Since the center of gravity does not change, $\langle \Delta E \rangle = 0$, the band associated with the $1s \rightarrow 2p$ transition must shift slightly. The expression for the fractional change in the absorption coefficient at the peak of the band is

$$\frac{\Delta\alpha}{\alpha} = -\frac{\langle \Delta E_z^2 \rangle}{(E_{2p}-E_{2s})^2}. \tag{15}$$

There is also a mixing of higher p states with the $2s$ state. Since the higher p states are responsible for the K band which is resolved from the F band, an exchange of areas between these two bands occurs. The K band will decrease and the F band will increase by a corresponding amount.

TABLE I. Parameters of the F band in alkali halides at 78°K. The values of $\langle E^2 \rangle$ were calculated assuming a Gaussian shape for the F band.

Crystal	Peak of F band (nm)	(eV)	Half-width (eV)	$\langle E^2 \rangle$ (10^{-2}eV^2)
NaCl	449	2.76	0.28[a]	1.40
NaBr	525	2.36	0.35[b]	2.20
KCl	539	2.30	0.20[a]	0.72
KBr	604	2.06	0.20[a]	0.72
KI	663	1.87	0.21[a]	0.80
RbCl	608	2.04	0.19[c]	0.65

[a] J. J. Markham and J. D. Konitzer, J. Chem. Phys. 34, 1936 (1961).
[b] G. E. Sturgis, J. J. Markham, and G. A. Noble, J. Chem. Phys. 40, 3634 (1964).
[c] Measured by the author.

In the approximation of Henry *et al.*, the Stark effect depends only upon $|\langle z|z|\gamma \rangle|$ and $\langle E^2 \rangle$. The values of $\langle E^2 \rangle$ can be calculated by assuming that the F band has a Gaussian shape. They are given in Table I. The value of $|\langle z|z|\gamma \rangle|$ ought to roughly scale with the $2p$ wave function and thus vary with the lattice constant.

B. Experimental

The F-band Stark effect in KCl[6] was used in this investigation to verify that the apparatus was operating properly and had sufficient sensitivity. The initial measurements with the apparatus were performed by applying an electric field with a frequency of 41 Hz.

[6] The alkali-halide crystals on which the measurements were performed were obtained from the Harshaw Chemical Co., Cleveland, Ohio, with the exception of RbCl, which was obtained from Vinor Laboratories, Medford, Mass.

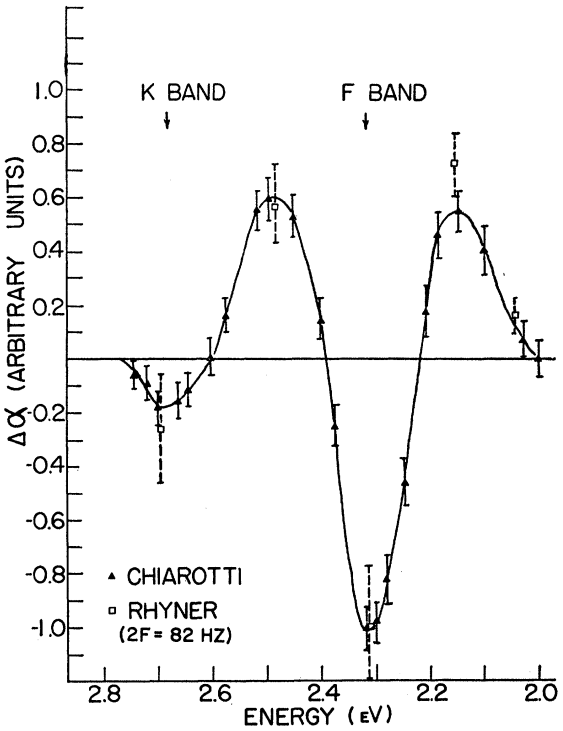

FIG. 3. Change of the absorption coefficient of KCl (78°K) versus photon energy. The triangles are obtained from the work of Chiarotti, Grassano, and Rosei. The squares are obtained from this investigation.

The Stark effect in KCl was measured as a function of the wavelength. Measurements of $\Delta\alpha$ were made at wavelengths which correspond to the maxima and minima of the plot of Chiarotti *et al.* of $\Delta\alpha$ versus photon energy.[3]

The value of $\Delta\alpha$ is obtained from $\Delta I/I$ by the equation

$$\Delta\alpha = -(1/x)(\Delta I/I), \tag{16}$$

where x is the length of the absorption path (which is a constant for a given crystal). However, $\Delta\alpha$ is dependent upon the coloration of the crystal, so that arbitrary units were used in comparing data. Both the Chiarotti *et al.* data[3] and the data of this investigation were normalized such that at the peak of the F band, $\Delta\alpha = -1.0$. The results are shown in Fig. 3. The dashed error bars are estimates of the maximum error likely to be present in the measurements. The agreement was sufficiently good so that they were not repeated later when the modulation frequency was increased to 700 Hz. The wavelength dependence of $\Delta\alpha$ shown in Fig. 3 demonstrates that the energy difference between the $2s$ and $2p$ states is less than the absorption linewidth, since the bands are not resolved.

Measurements of $\Delta\alpha/\alpha$ were performed on NaCl, NaBr, KCl, KBr, KI, and RbCl. The data on F-center parameters are given in Table I. Attempts to color pure NaI and NaI(Tl) by x irradiation failed. Didyk,

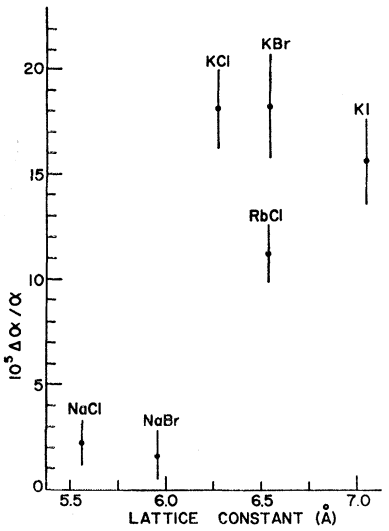

FIG. 4. Measured fractional change in the absorption coefficient at the peak of the F band for various alkali halides versus lattice constant. The data are normalized to a Lorentz local field of 200 kV/cm.

Poshkovskii, and Tsal[7] were also unable to color pure NaI. Two samples of each material were used to ensure that the results were not anomalous. Approximately six determinations of $\Delta\alpha/\alpha$ were obtained for each material. The values of $\Delta\alpha/\alpha$ were normalized to the same Lorentz local field. The correct local field is unknown; however, the Lorentz field $\mathcal{E}_L$ provides a reasonable approximation and is given by

$$\mathcal{E}_L=\tfrac{1}{3}(K_s+2)\mathcal{E}_A\,, \tag{17}$$

where K_s is the static dielectric constant and $\mathcal{E}_A$ is the applied electric field. The values of $\Delta\alpha/\alpha$ were normalized to a Lorentz local field of 200 kV/cm and are plotted versus lattice constant in Fig. 4.

C. Discussion

The data shown in Fig. 4 suggest that $\Delta\alpha/\alpha$ may be related to the alkali ion of the salt. For a Lorentz local field of 200 kV/cm, $\Delta\alpha/\alpha$ is roughly 2×10^{-5} for the two sodium salts, 11×10^{-5} for RbCl, and 17×10^{-5} for the three potassium salts. This empirical observation might be strengthened if measurements of $\Delta\alpha/\alpha$ on the remainder of the alkali halides were available. These are difficult to obtain for several reasons:

(1) The F band occurs in spectral regions which are not accessible with this apparatus.

(2) The hygroscopic properties of many of the salts make them difficult to handle.

(3) The F centers are not readily formed in some crystals.

It is unlikely that the exchange of areas of the F band and K band could account for the differences in $\Delta\alpha/\alpha$. If the energy separation of the $2s$ and $3p$ states is considered the same as the F- and K-band separation, the area exchange would be least for the sodium salts. This is obtained from Eq. (16), provided that $|\langle z|z|\delta\rangle$ is assumed constant, where $|\delta\rangle$ is the $3p_z$ orbital. Since area exchange tends to reduce $\Delta\alpha/\alpha$ in the F band, the greater effect should occur for closely spaced F and K bands. This may account for RbCl, which has a smaller separation between the F and K bands, having a smaller $\Delta\alpha/\alpha$ than the potassium salts.

V. STARK EFFECT IN THE M CENTER OF KCl

A. Theory

In 1958, Overhauser and Rüchardt[1] attempted to detect a Stark effect in the M center in KCl and NaCl. Quantum states of systems which do not have inversion symmetry will generally possess dipole moments and will undergo a linear shift in energy when an electric field is applied. The change in the transition energy, w, between the ground state and the first excited state is given by

$$w=-\Delta\mathbf{p}\cdot\mathcal{E}\,, \tag{18}$$

where $\Delta\mathbf{p}$ is the difference in the dipole moments of the ground and first excited states and $\mathcal{E}_L$ is the local electric field. By using the wave functions of Gourary and Luke[8] for Seitz's model of the M center[9] (shown in Fig. 5), they obtained an estimate for $\Delta\mathbf{p}$. For color centers with a dipole moment oriented in the [110] directions, the absorption coefficients for light polarized parallel and perpendicular to the electric field are

$$\alpha_{||}(E)=\alpha(E)+\tfrac{1}{4}w^2\alpha''(E)\,, \tag{19}$$

$$\alpha_{\perp}(E)=\alpha(E)+\tfrac{1}{8}w^2\alpha''(E)\,, \tag{20}$$

where $\alpha_{||}(E)$ and $\alpha_{\perp}(E)$ are the absorption coefficients for light polarized parallel and perpendicular to the electric field, respectively, $\alpha(E)$ is the absorption coefficient in

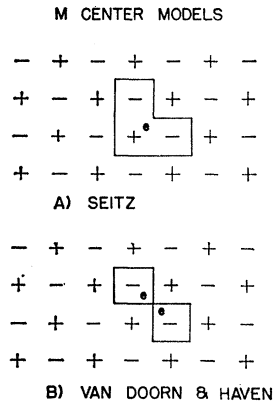

FIG. 5. Models of the M center proposed by (A) Seitz and (B) VanDoorn and Haven.

[7] R. I. Didyk, M. V. Pashkovskii, and N. A. Tsal, Opt. i Spektroskopiya **20**, 832 (1966) [English transl.: Opt. Spectry. (USSR) **20**, 462 (1966)].

[8] B. S. Gourary and P. J. Luke, Phys. Rev. **107**, 960 (1957).

[9] F. Seitz, Rev. Mod. Phys. **18**, 348 (1946).

the absence of the applied field, and $\alpha''(E)$ is its second derivative. Since $\alpha''(E)$ for a symmetric curve is also symmetric, the effect of the electric field is to broaden the band. The difference between $\alpha_{||}$ and $\alpha_{\perp}$ at the peak of a Gaussian band is

$$\Delta\alpha=\alpha_{\perp}-\alpha_{||}=0.69\, w^2\alpha/W^2, \tag{21}$$

where W is the full width at half-maximum of the absorption band. The relative change in the absorption coefficient is

$$\Delta\alpha/\alpha=0.69\, w^2/W^2. \tag{22}$$

Overhauser and Rüchardt applied a dc electric field and rotated the plane of polarization of the light in an attempt to detect this effect. No effect was observed when a voltage of 30 kV was applied to a 1-mm-thick crystal (applied electric field of 300 kV/cm). They concluded that

$$\Delta\alpha/\alpha<3\times10^{-5} \tag{23}$$

for this field. They estimated the size of the effect based on the wave functions of Gourary and Luke for the Seitz model of the M center to be 6×10^{-3} for the electric field which they applied. The absence of an effect has often been cited as evidence ahat Seitz's model is incorrect.[1,10,11]

Since a dc electric field was used, there is a possibility that the lack of an effect was due to the reduced electric field in the crystal caused by space-charge polarization. This possibility was demonstrated in this study by the initial experiments on the F-center Stark effect using a dc electric field for which the upper limit attributed to $\Delta\alpha/\alpha$ was a factor of 10 smaller than the magnitude later observed.

B. Experimental

The M band in KCl is located at a wavelength of 805 nm (photon energy of 1.54 eV). After the crystal was quenched from 400°C and x-irradiated, the M and R centers were enhanced by bleaching the crystal with F light (560 nm) at room temperature for 1 h. After bleaching, the optical density of the M band was 0.38.

An RCA 7102 photomultiplier tube with an S-1 response was used. The noise at the output of the lock-in amplifier was lower than that observed when operating the apparatus in the visible region. This is attributed to the greater infrared energy output of the monochromator using a tungsten light source. The greater intensity would result in lower shot noise.

Since the M centers are oriented in the [110] directions, there was no advantage in using a polarizer. It was removed for these experiments. It is true that if the M centers possess permanent dipole moments, then by Eqs. (20) and (21), $\alpha_{||}-\alpha(=\Delta\alpha_{||})$ is twice as large as $\alpha_{\perp}-\alpha(=\Delta\alpha_{\perp})$. However, even if the centers have inversion symmetry, it is expected that any effect will be twice as large for $\Delta\alpha_{||}$ as for $\Delta\alpha_{\perp}$. This is deduced from the fact that light polarized parallel to the electric field excites centers in the A and B directions indicated in Fig. 6. This field also acts on these centers. For light polarized perpendicular to the field, centers in the A and C orientations will be excited; however, the electric field will only have an effect on the A-oriented ones. Thus, only half as many centers exhibit an effect with light polarized perpendicular to the field as with light polarized parallel to the field. The removal of the polarizer had the advantage of doubling the light beam.

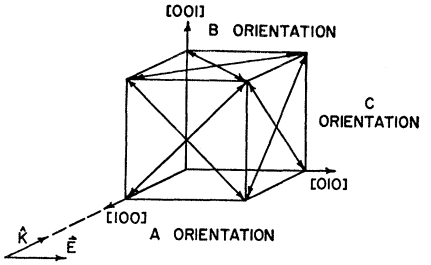

FIG. 6. The six different orientations of the principal axes of the M centers, the electric field **E**, and the direction of light propagation $\hat{K}$.

The change in the absorption coefficient, $\Delta\alpha$, was measured as a function of photon energy with an applied field of 97 kV/cm. The results are shown in Fig. 7. The error bars on the data for energies greater than 1.53 eV are the standard deviations for two or three measurements. The errors at the lower energies are estimates of the probable error. Measurements in this region had previously been performed with wider slits on the monochromator and therefore had a greater wavelength spread. These earlier measurements were consistent with the values shown.

Measurements of $\Delta\alpha/\alpha$ were performed to determine its dependence upon the electric field. It was desirable to do these measurements at the peak of the M band; however, as the electric field was reduced, the effect

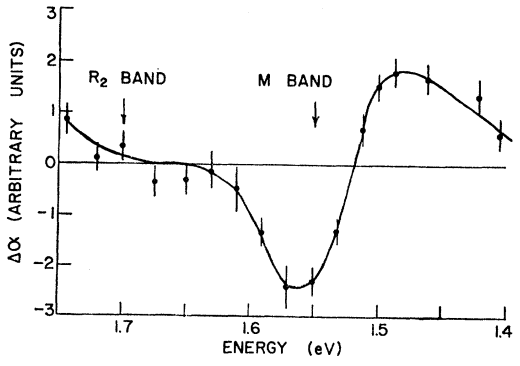

FIG. 7. The Stark effect in the region of the M band of KCl (78°K) versus photon energy.

[10] B. S. Gourary and F. J. Adrian, Solid State Phys. **10**, 127 (1960).

[11] W. D. Compton and H. Rabin, Solid State Phys. **16**, 121 (1964).

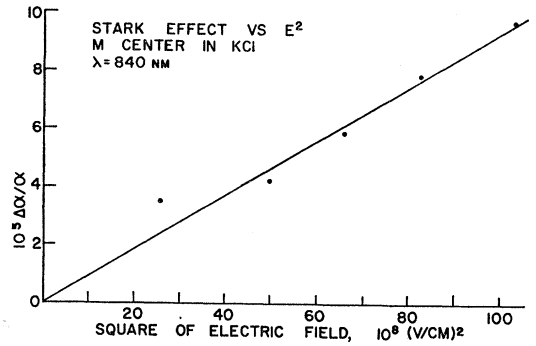

FIG. 8. Fractional change of the absorption coefficient at $\lambda=840$ nm (1.47 eV) versus the square of the applied electric field measured at 78°K.

became too small to be accurately measured. The data were taken at $\lambda=840$ nm because the observed ΔI was largest at this wavelength. In Fig. 8, the measured $\Delta\alpha/\alpha$ is plotted versus the square of the applied field, yielding a straight line.

It is noted that the data presented above have not been corrected for (1) the use of an electric field which is oriented at an angle of 45° to the axes of the centers in which the effect occurs; (2) the fact that only two-thirds of the centers are oriented such that they can exhibit a Stark effect. The orientation of the M centers is shown in Fig. 6. The electric field along the axes of the centers in the A orientation [parallel to the (100) plane] or the B orientation [parallel to the (001) plane] is $\mathcal{E}\cos 45°$. The centers in the C orientation [parallel to the (010) plane] are unaffected by the application of the field.

The correction for $\Delta\alpha/\alpha$ can be obtained by noting that only two-thirds of the centers contribute to the observed effect and only two-thirds of the measured optical density should be substituted into Eq. (9). For an applied field of 97 kV/cm (component along the major axis of the centers is 69 kV/cm), the corrected $\Delta\alpha/\alpha$ at the peak of the M band is

$$\Delta\alpha/\alpha=3.9\pm0.4\times10^{-5}. \tag{24}$$

C. Discussion

From the plot of $\Delta\alpha$ versus energy it is evident that the effect observed is not the linear Stark effect. As mentioned previously, the linear effect should produce a broadening of the absorption band with a decrease at the peak. The corresponding plot of $\Delta\alpha$ versus energy would look similar to that of the F band shown in Fig. 3 in contrast to the nonsymmetrical curve observed. The lack of a linear effect provides additional evidence that Seitz's model of the M center is incorrect and would favor VanDoorn and Haven's model[12] (Fig. 5). It is also evident that the absence of an effect reported by Overhauser and Rüchardt was erroneous. For the fields which they applied, they should have seen an effect that was about 10 times greater than the upper limit which they placed on the effect.

It is observed that the data fluctuate in the region of the R_2 band. The data are not sufficiently good to justify drawing a curved line through the average values. However, the fact that the maximum occurs at the energy of the R_2 absorption band indicates that the fluctuation may be more than coincidental and that a small effect may occur in the R_2 band. The curve also rises for energies greater than 1.7 eV, suggesting that an effect might be found for the R_1 band.

The curve in Fig. 7 may be the result of mixing two resolved energy levels which are separated by slightly more than 0.05 eV. Within experimental error, the decrease in the area (zeroth moment) of the M absorption band is compensated by an increase in the area in the region of 1.5 eV. This is consistent with the conservation-of-area rule. Since no optical absorption band is observed near 1.5 eV, it is evident that the transition which is responsible for the increased absorption is normally forbidden.

VI. STARK EFFECT IN THE Z_1 CENTER IN KCl:Sr

A. Theory

The Stark effect may provide additional information to aid in distinguishing among the various models of the Z_1 center. As discussed previously, the presence of a linear Stark effect indicates that the center possesses a permanent dipole moment. There is also interest in attempting to observe a linear effect, since no observations of it have been reported.

Polarization experiments[13] and ESR measurements[14,15] indicate that the Z_1 centers should be isotropic. Also, dielectric loss measurements of Bucci, Capelletti, and Pirola[16] failed to detect impurity-vacancy dipoles during the formation of Z_1 centers. These results favor Seitz's model[17] (Fig. 9). However, Bushnell's ENDOR measurements[18] failed to detect the hyperfine structure which Seitz's model would imply. He concludes from these data also that Pick's model cannot be correct. Bushnell proposed the models shown in Fig. 10 which are consistent with his measurements. His measurements favored models (a) and (b). Although model (c) could not be ruled out completely, he believed that it was unlikely.

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[16] C. Bucci, R. Cappelletti, and L. Pirola, Phys. Rev. **143**, 619 (1966).

[17] F. Seitz, Phys. Rev. **83**, 134 (1951).

[18] J. C. Bushnell, Ph.D. thesis, University of Illinois, 1964 (unpublished).

If the dipole moment of the center is not oriented along the [100] directions, then a Stark effect should be observed both for light polarized parallel and perpendicular to the applied electric field but with different magnitudes. Models (a) and (c) were expected to possess an off-axis dipole moment. On the other hand, model (b) should possess little or no dipole moment. The axis of model (b) is oriented along the [100] directions. If an effect, linear or quadratic, is observed, it should occur only for light polarized parallel to the field.

B. Experimental

The measurements were performed on KCl:Sr (0.02 molar %).[19] After quenching the crystals from 400°C, the samples were x-irradiated, then bleached with F light ($\lambda=560$ nm) at room temperature for 45 min at the exit lens of the monochromator. The Z_1 band was formed at $\lambda=595$ nm (78°K). The optical density of the band was 0.62.

The same apparatus arrangement was used as for the F center. All attempts to detect an effect failed, both using light polarized parallel to the electric field and using unpolarized light. An ac field of 97 kV/cm was applied to the crystal. An upper limit can be placed on $\Delta\alpha/\alpha$ of

$$\Delta\alpha/\alpha<8\times10^{-6}. \tag{25}$$

C. Discussion

Since no effect was detected, the various models of the Z_1 center cannot be distinguished by comparing effects for light polarized parallel and perpendicular to the electric field as described. An upper limit can be placed on the difference in the expectation values of the permanent dipole moments in the excited and ground states, Δp. If a linear effect does exist, it is largest for light polarized parallel to the electric field when the dipoles are oriented in the [100] directions. Assuming a Gaussian band and using Eqs. (19) and (20), one obtains

$$\Delta p<1.0\times10^{-20} \text{ cgs unit}, \tag{26}$$

where the following experimental values have been substituted: $W\sim0.3$ eV, $\mathcal{E}_L=216$ kV/cm (Lorentz local field), and $\theta=45°$, where θ is the angle between the dipole moment and the electric field.

Both models (a) and (c) have roughly the same effective charge configuration as Seitz's model of the M center. A rough approximation for the value expected for Δp is that calculated by Overhauser and Rüchardt for the M center, which is

$$\Delta p\sim5\times10^{-18} \text{ cgs unit}. \tag{27}$$

Comparing expressions (26) and (27), it appears that the upper limit on Δp is about an order of magnitude smaller than the value expected for models (a) and (c). Since model (b) would have only a small dipole moment, if any, the absence of an effect would favor this model. It must be noted that the reliability of the estimate of Δp for the M center is questionable; however, estimates based on wave functions calculated for the Z_1 center would be of uncertain reliability.

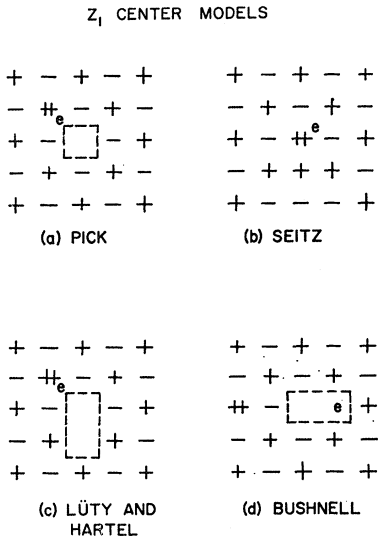

FIG. 9. Models of the Z_1 center proposed by (a) Pick, (b) Seitz, (c) Lüty and Hartel, and (d) Bushnell.

[19] Obtained from J. C. Bushnell, Sandia Corporation, Albuquerque, N. M.

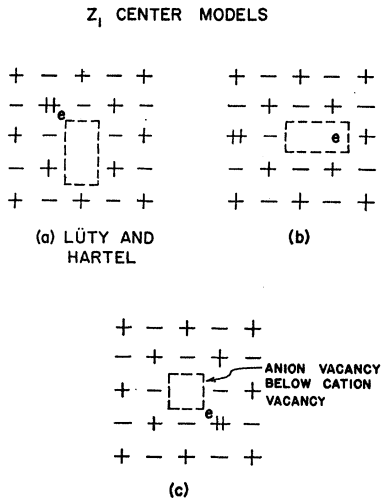

FIG. 10. Models of the Z_1 center which are consistent with ENDOR measurements by Bushnell. Models (b) and (c) were proposed by Bushnell.

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