PHYSICAL REVIEW B VOLUME 10, NUMBER 4 15 AUGUST 1974

Piezo-optic study of the F center in alkali halides—Evidence for structure in the F band of KCl, KBr, and NaCl†

A. Perregaux* and G. Ascarelli

Physics Department, Purdue University, Lafayette, Indiana 47907

(Received 17 July 1972; revised manuscript received 8 June 1973)

Using a piezo-optical modulation technique we studied the changes of optical absorption associated with the F band in KCl, KBr, and NaCl. Contrary to our expectations, structure is found in the piezo-optic spectrum obtained with light polarized perpendicular to the stress axis. Such a structure (F_{III} band), observed with different degrees of clarity in KCl, KBr, and NaCl, is respectively, ~140, ~110, and ~90 meV above the maximum of the corresponding F band. We have not been able to correlate this structure with spin-orbit coupling, phonon sidebands, Jahn-Teller effect, transitions to a hybrid $2s$-$2p$ state, effects due to F-center preparation, or photochemical reactions associated with the F center. It has also been empirically noticed that the energy of the F_{III}, K_1, K_2, L_1, L_2, and L_3 bands differs from the energy of the F band by a value that can be described by the relation $E_l - E_F = \epsilon_0[l(l+1)-2]$; ϵ_0 is of the order of 10 meV for all alkali halides with the NaCl structure where the L bands have been found and l is an odd integer. This relation is reminiscent of a rotational spectrum.

I. INTRODUCTION

Although the F center in alkali halides has been extensively studied,[1,2] some problems remain that, we believe, are related to the strong electron-phonon interaction. It is experimentally observed, and theoretically justified, that the shape of the F band is well described by a double Gaussian.[1] The ratio of the half-widths on the high- and low-energy sides of this curve changes slightly with temperature. It is also known[1] that the half-Gaussian representation of the high-energy side joins smoothly with that of the low-energy side.

Besides the excited state responsible for the F band, there are other excited states of the F center[3,4] giving rise to the K and L bands. There is some evidence that a large portion of the K band is due to the series limit of the excited states of the electron trapped in the negative-ion vacancy.[4] The identification of the states giving rise to the L bands as being electronic scattering states beyond the F-series limit, is based on the observed large quantum efficiency for photoconductivity[1] and on a calculation[5] for KCl whose result appears to depend on the form of the potential chosen for the F center as well as on the conduction-band parameters. In the present paper we will show that other states besides p-like excited states coupled to Γ_1^+, Γ_3^+, and Γ_5^+ vibrational modes contribute to the optical absorption in the F-band region. The coupling of the F electron with modes of such symmetries has been treated in detail by Henry, Schnatterty, and Slichter (HSS)[6] and by Schnatterly[7] using the method of moments. Gebhardt and Maier[8] measured a similar quantity by observing the shift of the half-power-absorption points with stress; they obtained values of the coupling constants of the F-center electron with modes of Γ_3^+ and Γ_5^+ symmetry that were in approximate agreement with those of Ref. 7 for NaCl. The agreement is much poorer for KCl.

As will be seen in this paper, the effect of stress on the optical absorption is much smaller when it is observed with light polarized perpendicular to the stress axis ($P_\perp$) than when it is observed with light polarized parallel to the stress axis ($P_\parallel$). This difference is a consequence of the comparable strength with which the F electron is coupled with stresses of Γ_1^+, Γ_3^+, and Γ_5^+ symmetry. As a result, dichroism measurements ($P_\parallel - P_\perp$) are heavily weighted by $P_\parallel$ except near the maximum of the F band where $|P_\parallel| \simeq |P_\perp|$. Our data show that the structure appearing in $P_\perp$ is not noticeable either in $P_\parallel$ or in ($P_\parallel - P_\perp$).

In order to obtain the coupling coefficient of the excited state of the F center with modes of Γ_3^+ and Γ_5^+ symmetry, a model for the excited states responsible for the F band is necessary. Schnatterly[7] used the logical choice of a triplet Γ_4^- split by the spin-orbit interaction into a Γ_6^- state and a Γ_8^- state. Such states are coupled mainly with vibrational modes of Γ_1^+, Γ_3^+, and Γ_5^+ symmetry. These modes also couple the F to the K band. On the basis of our results, such vibronic energy levels cannot completely describe the excited states of the F center.

II. EXPERIMENTAL

A. Experimental technique and results

The experimental technique used in this study is a modified version of the piezomodulation experiment described by Ascarelli and Barone.[9,10] The sample is a crystal having the shape of a parallelepiped $1\times1\times5$ cm in size.

A parallel-plate capacitor is formed by a piece of indium foil glued to the 1×1-cm face of the sample and an auxiliary electrode. The two plates of this capacitor are separated by a thin Mylar sheet (Fig. 1). When the frequency (~20 kHz) of an alternating voltage applied on this capacitor is equal to half the frequency of the lowest-extensional mode of the sample, this mode is excited and the amplitude of the internal alternating stress is approximately Q times that of the external applied stress. Q, the quality factor of the mechanical resonator, is of the order of 10^3. In this fashion we apply an alternating uniaxial stress ($f\simeq 40$ kHz) to the sample. This stress has a nearly constant amplitude in the central portion of the sample, where the measurements are made.

The strain is monitored by means of a vibration detector[11] which can be calibrated. The calibration sample consists of a metal rod on which a strain gauge[12] is glued. The errors in the relative measurements of the stress are estimated to be of the order of ±20%. When successive measurements are done on the same sample which has not been removed from the cryostat, the reproducibility of the magnitude of the data is of the order of ±10%. The errors of the positions of the positive and negative peaks are less than 1 nm.

The absolute values of the stresses may be affected by large systematic errors. We would not exclude a factor of 2. Such an estimate is essentially based on the discrepancy between our evaluation of the change of the F band with hydrostatic stresses and that obtained by either Jacobs[13] or Brothers and Lynch.[14] Our values are, however, close to those measured by Gebhardt and Maier.[8]

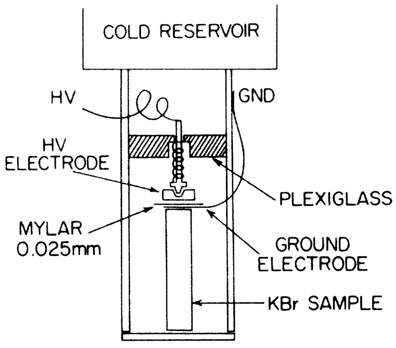

FIG. 1. Sample mounted on the tailpiece of the Dewar. The platform on which the sample is mounted is connected to the liquid-helium reservoir by a J tube so that the refrigerant liquid circulates both in the J tube and the hollow platform.

As will be seen in the following, it is likely that the apparent discrepancy between our results of the change of the F band with the Γ_1^+-like component of the strain, and those obtained by direct hydrostatic-pressure measurement, arises because the experiments refer to different weighted averages of a group of states.

Another important source of errors in the piezospectroscopic measurements arises from a baseline shift due to the periodic displacement of the image of the exit slit of the monochromator on the face of the photomultiplier used in the experiment. This shift is produced by the periodic deformation of the sample. On account of the nonuniformity of the photocathode of the photomultiplier, the illumination of different portions of the photomultiplier face gives rise to a signal whose magnitude and wavelength dependence can change with the particular region of the photomultiplier that is scanned. The magnitude of this signal was under 3% of the maximum piezospectroscopic signal observed with light polarized parallel ($P_\parallel$) to the stress axis when the optical density at the peak of the F band was about 2. However, it gave rise to a "background signal" which was relatively important for the measurements carried out with light polarized perpendicular to the stress axis ($P_\perp$). A block diagram of the apparatus is shown in Fig. 2.

All crystals were initially annealed at 450 °C for at least 12 h, in order to decrease internal strains; thereafter F centers were produced by x irradiation[15,16] at approximately −80 °C. The sample was warmed in the dark to room temperature and it was mounted in the cryostat and cooled. Red safelight ($\lambda \geq 620$ nm) was used during the mounting operation which lasted about 1 h.

The experimental results for the change of the optical absorption coefficient $\alpha(E)$ as a function of the photon energy E are given in Fig. 3 for the F and K bands in KCl at liquid-nitrogen temperature (LNT). (More detailed K-band data obtained

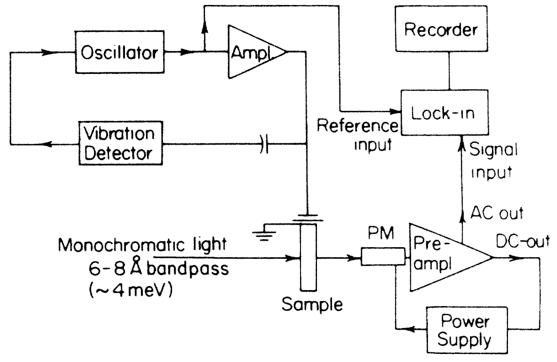

FIG. 2. Block diagram of the apparatus.

from more heavily colored samples will be discussed in a subsequent publication.) The data are reduced to those to be expected for an absorption coefficient of 1 cm^{-1} at the maximum of the F band and an applied stress of 1-Mbar rms. The maximum stress at the center of the sample was however only 5-bar rms. The data that are displayed correspond to a stress whose axis is along the principal crystallographic directions: [100], [110], and [111]. The polarization is either parallel ($P_{\parallel}$) or perpendicular ($P_{\perp}$) to the stress axis.

Similar data are given in Fig. 4 for KCl at 20 °K stressed along [110] and are compared with the data obtained on the same sample at LNT. Some qualitative features are evident. The signal obtained with polarization parallel to the stress axis resembles what is to be expected from an external perturbation that primarily changes the position of the F-band maximum (broken line in Fig. 3). The width and the maximum absorption of the F band are only slightly changed. The signal arising from light polarized perpendicular to the stress axis suggests that the above changes take place for two bands displaced by about 150 meV from each other. The higher-energy hump appears to be due mainly to a change in transition probability.

A comparison of the data obtained with the stress axis oriented along various crystallographic directions leads to the conclusion that the center is in a cubic environment. An analysis of the coefficients describing the shifts and splittings of the F excited state under uniaxial stress[17] can justify this statement (Table I). As an example, the shift and splitting coefficients expected from a hypothetical center having ⟨100⟩ symmetry are given in the last column of Table I. Our data do not indicate the presence of centers with axial symmetry. From this information, from the F-band absorption that is undistinguishable from what is published by others,[1,2] and from the fact that neither absorption nor piezo-optic signal are

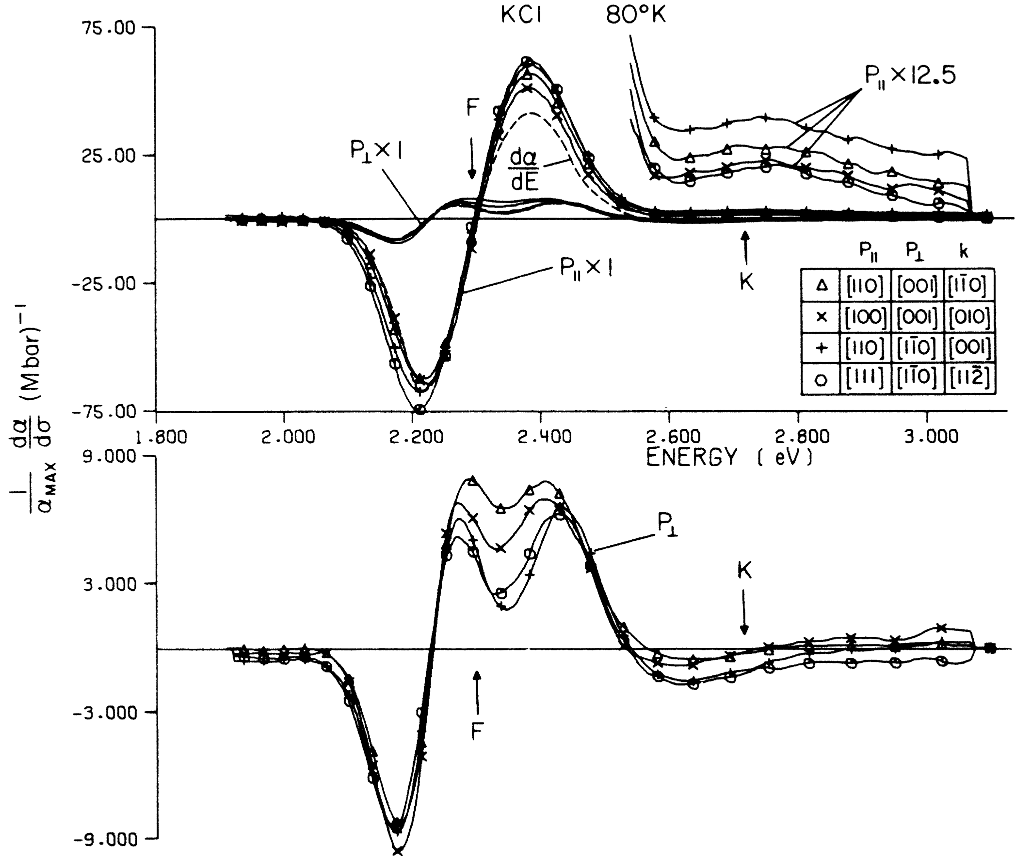

FIG. 3. Piezomodulation signal $(1/\alpha_0)$ $(d\alpha/d\sigma_3)$ for the F and the K band in KCl at 80°K. The quantity α is the absorption coefficient, α_0 is the value of α at the maximum of the F band (E_0), and σ_3 is the applied stress along the sample axis. The applied stress for all measurements was under 10- bar rms (~40 kHz) usually ~5- bar rms. In order to get good signal-to-noise ratio near E_0, α_0 had to be about 2 cm^{-1}. The broken line is an appropriately scaled plot of $(1/\alpha_0)\, d\alpha/dE$. The lower curves are an enlargement of $P_{\perp}$.

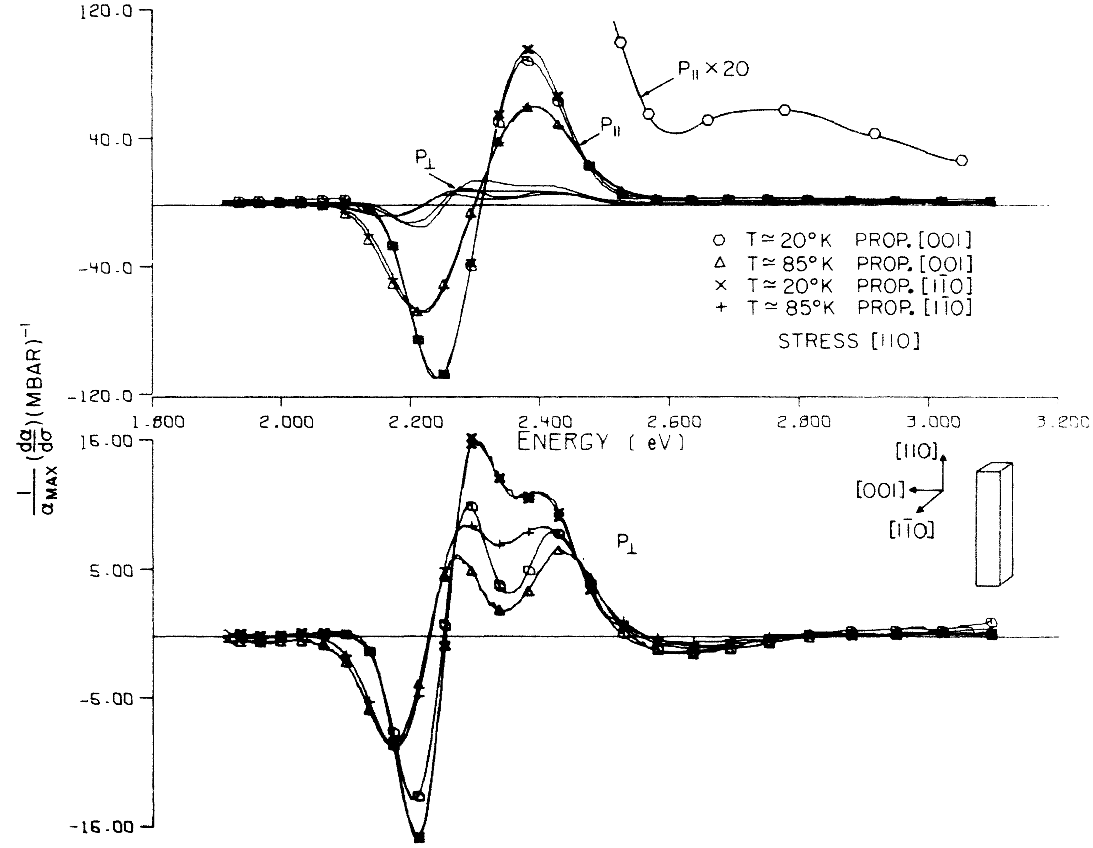

FIG. 4. Comparison of the piezomodulation spectrum of KCl at 80 °K and ~20 °K. Stress orientation [110].

detected on the low-energy side of the F band up to $\lambda = 850$ nm, we conclude that the F centers are isolated. In general, the data do not reveal any dependence on stress orientation either in the $P_{\parallel}$ signal, or on the low-energy side of the $P_{\perp}$ signal.

Some evidence of anisotropy exists in the $P_{\perp}$ signal near ~2.35 eV. $P_{\parallel}$ differs a little from the rigid-shift data ($d\alpha/dE$) described by the broken line in Fig. 3. We shall initially ignore these differences.

TABLE I. Predicted splitting of an excited state (Γ_4^-, Γ_6^-, or Γ_8^-) in a cubic environment with applied uniaxial stress (Ref. 16). The last column indicates what is expected in the case of tetragonal centers in a cubic crystal.

Pressure Distortion	Γ_4^- (p state)	Polarization	Γ_6($p_{1/2}$ state)	Γ_8($p_{3/2}$ state)	Tetragonal center	Polarization
001 $\Gamma_1+\Gamma_3$	$A+2B$ $A-B$	[001] [010]	A	$A+2B$ $A-2B$	A_1+B_1 A_1+B_2	[001] [010]
110 $\Gamma_1, \Gamma_3, \Gamma_5$	$A+\frac{B+C}{2}$ $A+\frac{B-C}{2}$ $A-B$	[110] [1$\bar{1}$0] [001]	A	$A+\sqrt{B^2+\frac{C^2}{4}}$ $A-\sqrt{B^2+\frac{C^2}{4}}$	$A_1+\frac{1}{2}(B_1+B_2)$ A_1+B_2	$\left\{\begin{matrix}[110]\\ [1\bar{1}0]\end{matrix}\right.$ [001]
111 $\Gamma_1+\Gamma_5$	$A+\frac{2}{3}C$ $A-\frac{1}{3}C$	[111] [11$\bar{2}$]	A	$A+\frac{C}{\sqrt{3}}$ $A-\frac{C}{\sqrt{3}}$	A_1	any

After Kaplyanskii, Optics & Spectr. 16, 557 (1964)
16, 329 (1964)

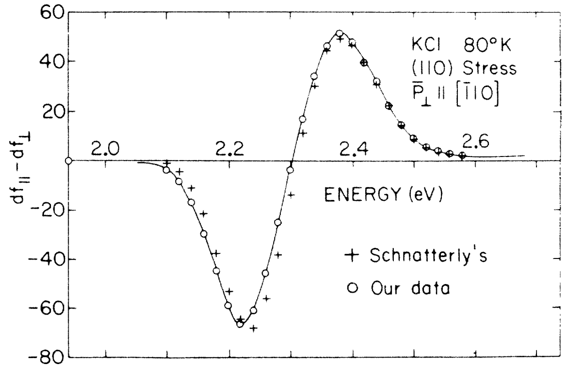

FIG. 5. Comparison of the dichroism measurements for the *F* band in KCl at LNT obtained in this work ($P_\parallel$-$P_\perp$), and those obtained by Schnatterly (Ref. 7).

A comparison of the data presented in Fig. 3 with those obtained by Schnatterly[7] is given in Fig. 5. Since we do not know the absolute scale of Schnatterly's data, and in order to take into account errors due, e.g., to the stress calibration, the data have been scaled so that both curves coincide near the positive maximum. We believe that the differences that remain are explained by difficulties in determining the base line, plastic flow effects, differences in the optical bandwidth (6 Å in our case and 25 Å in the case of Ref. 6), and finally, possible errors in the estimate of sample temperature. The latter are particularly important in our case at liquid-helium temperatures (LHeT).

The data arising in the case of KBr and NaCl are shown, respectively, in Figs. 6 and 7. In Fig. 8 our data for KBr are compared with Schnatterly's. From the raw data presented in Figs. 3–7 it is clear that structure appears in the stress-modulation signal observed with polarization perpendicular to the stress axis. This structure is approximately 140, 110, and 90 meV above the corresponding *F*-band maximum, respectively, in KCl, KBr, and NaCl. It is also clear that within experimental errors the present data for ($P_\parallel - P_\perp$) agree with those of Ref. 7, so that a moment analysis along the lines of Ref. 7 cannot but reproduce Schnatterly's results.

B. Qualitative analysis

We may expect, without considering any specific model, that in the case of a single band, the ap-

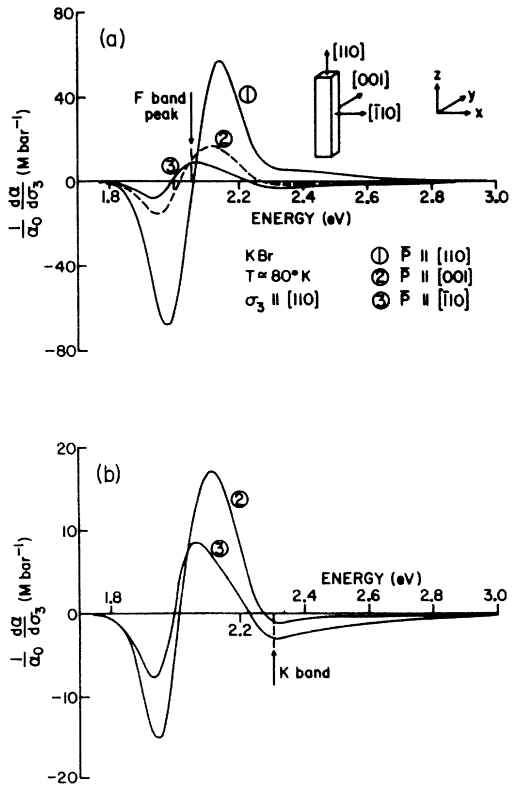

FIG. 6. Piezomodulation data for the *F* band in KBr at LNT. The stress axis is [110]. Part (b) is an enlargement of curves 2 and 3 in part (a).

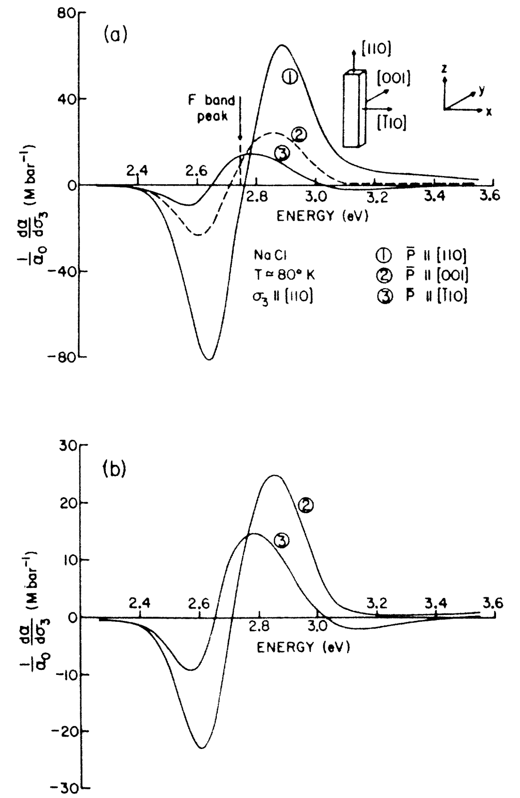

FIG. 7. Piezomodulation data for the *F* band in NaCl at LNT. The stress axis is [110]. Part (b) is an enlargement of curves 2 and 3 of part (a).

plication of an infinitesimal stress to the crystal will, in first approximation, cause a change in the position of the maximum of the optical absorption, change the magnitude of the absorption maximum, and produce a change in linewidth.[7,9,17] If we represent the absorption coefficient α by a Gaussian

$$\alpha = \alpha_0 e^{-[(E-E_0)/W]^2}, \tag{1}$$

where E is the phonon energy and E_0 is the energy separation between a ground state and an excited-state multiplet, then we have (σ being the stress)

$$\frac{1}{\alpha}\frac{d\alpha}{d\sigma} = \frac{1}{\alpha_0}\frac{d\alpha_0}{d\sigma} + \frac{2}{W^2}(E-E_0)\frac{dE_0}{d\sigma} + \frac{2}{W^3}(E-E_0)^2\frac{dW}{d\sigma}\ . \tag{2}$$

In general, $d\alpha/d\sigma$ depends on the direction of the stress and on the direction of the polarization, since the stress splits states that were degenerate in the unstressed crystal.[17] Equation (2) may be rewritten

$$\frac{1}{\alpha}\frac{d\alpha}{d\sigma} = a + b(E-E_0) + c(E-E_0)^2\ . \tag{3}$$

The value of $dE_0/d\sigma$ is related to the coupling of stresses of different symmetries with the levels in question; in general, it is different when it is observed with light of different polarizations. The value of $dE_0/d\sigma$ is equal to the appropriate combination of the coefficients A, B, and C given by Kaplianskii[17] and reproduced in Table I. The cases considered in Table I are those of transitions from a Γ_1^+ ground state to a Γ_4^- excited state, from a Γ_6^+ ground state to a Γ_6^- and Γ_8^- excited states, and finally those from an s-like to a p-like state for hypothetical centers that have their axis directed along the equivalent $\langle 100\rangle$ directions of a cubic crystal. The coefficients A, B, and C indicate the coupling of the electronic levels with stresses that are hydrostatic (A), tetragonal (B), and trigonal (C). Formally identical relations are valid for the changes in transition probability, primarily $d\alpha_0/d\sigma$ in our case. The coefficients[17,18] C_1, C_2, and C_3 describe the changes in transition probability due to stresses having, respectively, Γ_1^+, Γ_3^+, and Γ_5^+ symmetry. In order to maintain the same relation between the changes in transition probability with stress and the coefficients C_i, as between the changes in energy of the electronic states with stress and the coefficients A, B, and C of Table I, our C_3 will be chosen three times smaller than the coefficient given in Ref. 18.

When there are two superposed bands with absorption coefficients α_1 and α_2 such that $\alpha = \alpha_1 + \alpha_2$, $(1/\alpha)d\alpha/d\sigma$ shows a discontinuity corresponding to a transition from a region where band 1 dominates to another where band 2 dominates.[18]

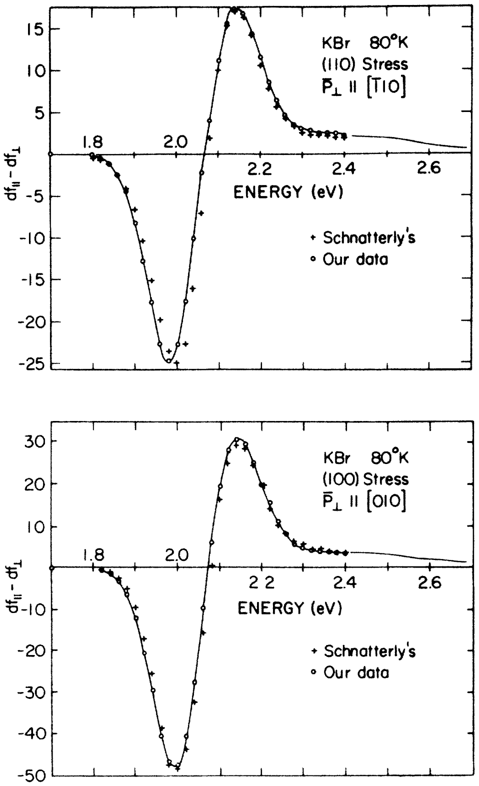

FIG. 8. Comparison of the measurements of dichroism in the F band in KBr at LNT obtained in this work ($P_{\parallel}$-$P_{\perp}$), and those obtained by Schnatterly (Ref. 7).

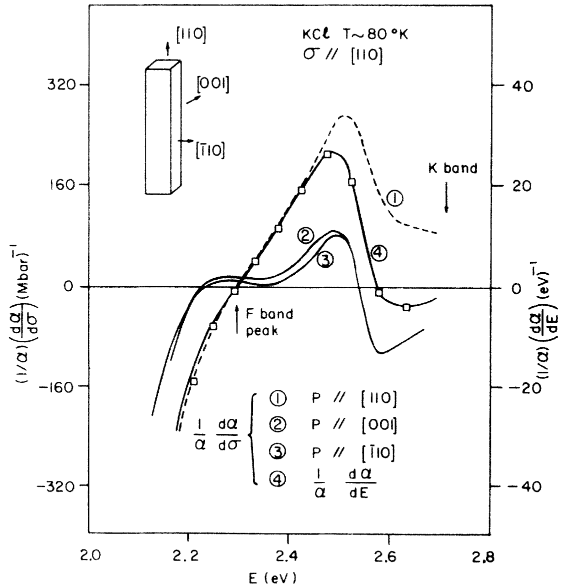

FIG. 9. Plot of $(1/\alpha)d\alpha/d\sigma_3$ for the F band in KCl at LNT stressed along [110].

The data displayed in Figs. 6 and 7 as well as the results expected from a rigid shift of the optical absorption (the latter is proportional to the derivative of the optical absorption) are shown in Figs. 9–11 in such a way as to put in evidence what is expected from Eq. (3).

In the case of KCl the $P_\perp$ signal suggests that all three coefficients a, b, and c of Eq. (3) are of comparable importance, while for $P_\parallel$ the terms containing the coefficients a and c are much smaller than the term containing b. In KBr and NaCl, $P_\perp$ gives evidence of a discontinuity in the slope of $(1/\alpha)d\alpha/d\sigma$ near the maximum of the F band. This discontinuity is an indication of structure similar to that observed in KCl in the originally recorded data, respectively, $\simeq 110$ and $\simeq 90$ meV above the maximum of the F band.

The coefficient b introduced in Eq. (3) can, in principle, be measured for each direction of stress and each direction of polarization, and the parameters A, B, and C can be calculated. We have limited ourselves to an evaluation of A, B, and C based on the part of our data that is on the low-energy side of the F band, since the curves indicate structure in the $P_\perp$ signal on the high-energy side. In the absence of theoretical guidance the assignment of the different parts of the $d\alpha/\alpha$ curves to one or the other features is completely arbitrary.

On account of the shape of the $P_\parallel$ curves, no difficulty arises in the evaluation of b for $P_\parallel$, since its value is not a strong function of the position that is chosen for the maximum of the optical absorption giving rise to the low-energy side of the F band. In the case of $P_\perp$ the choice is more difficult, and the corresponding results for the values of A, B, and C are moderately sensitive to this choice in KBr and NaCl; the largest sensitivity is found in KCl. One choice consists of extrapolating linearly the value of $d[(1/\alpha)d\alpha/d\sigma]/dE$ to the maximum of the F band. This choice was made in Ref. 15. As a consequence one may get $b>0$ from $P_\parallel$ and $b<0$ from $P_\perp$, which implies that $dE_0/d\sigma$ has opposite signs for $P_\parallel$ and $P_\perp$, contrary to the experimental results. An alternate possibility is to choose, in the case of $P_\perp$, the value of b at the zero crossing. In the first case, the values B and C for KCl are in much better agreement with those of Refs. 7, 8, and 19 than if the alternate choice is made. In either case, the values of A, B, and C obtained are rather unreliable because more than one state contributes to the piezo-optic signal. The signals due to these states overlap very much and a calculation of any coefficient is very sensitive to a somewhat arbitrary curve fitting.

In our estimates of A, B, and C we have not subtracted an extrapolation of the signal arising from the K band that might underlie the F band. The justification lies in the fact that we are considering the values of A, B, and C obtained from the data on the low-energy side of the F band where an extrapolation of the K-band signal is expected to be both small and uncertain. In order to give a basis of comparison with other workers the experimental results for the coefficients A, B, and C are nevertheless given in Table II.

To progress further we have to limit ourselves primarily to an analysis of the KCl data because the structure observed in $P_\perp$ is more prominent in this case. The results obtained with KBr and NaCl will, however, give a qualitative confirma-

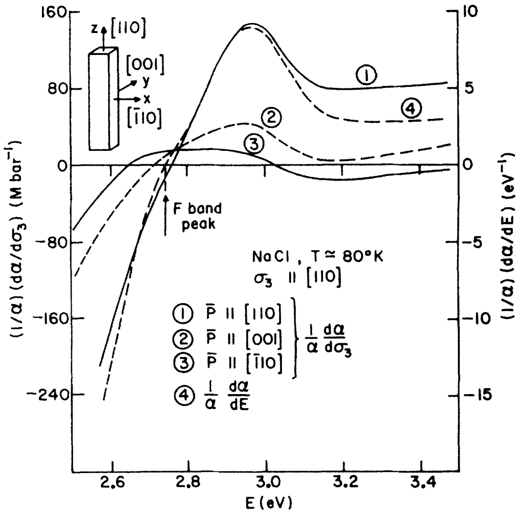

FIG. 10. Plot of $(1/\alpha)d\alpha/d\sigma_3$ for the F band in KBr at LNT stressed along [110].

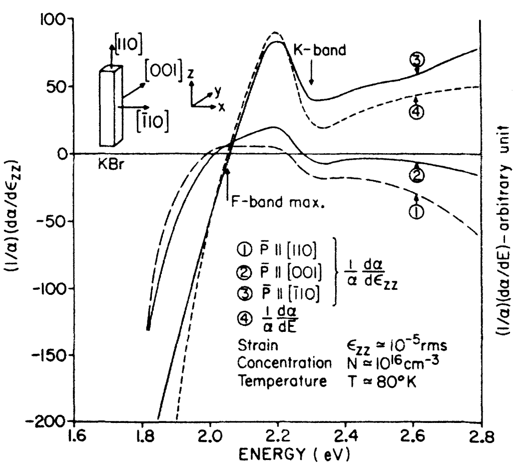

FIG. 11. Plot of $(1/\alpha)d\alpha/d\sigma_3$ for the F band in NaCl at LNT stressed along [110].

tion of the conclusions drawn on the basis of the KCl data.

We shall call F_{I} and F_{III} the two bands that appear in the F region (Fig. 3) with light polarized perpendicular to the stress axis. F_{I} is the band that corresponds to the low-energy side of the F band while F_{III} corresponds to the high-energy side (2.43 eV at LNT). We do not know where to locate F_{I}; a reasonable position is the peak of the F band (2.296 eV at LNT).

Referring to Fig. 3 one observes that the results for $P_{\parallel}$ are independent of the direction of stress while for $P_{\perp}$ they are independent of the stress axis in the F_{I}-band region only. This conclusion is also valid for the $P_{\parallel}$ signal in KBr. On the basis of this observation and from comparison with Table I, we conclude that on the low-energy side of the F band Kaplianskii's coefficients B and C are in the relation $3B = C$, indicating piezo-optic isotropy. The F_{I} band behaves as if the responsible center were embedded in an isotropic medium. In KBr the anisotropy of $P_{\perp}$ in the F_{I} region is small. The anisotropy is largest in NaCl. A similar study of the low-temperature data (~20 °K) in KCl obtained with stress in different crystal directions leads to the same conclusion regarding the F_{I} band, i.e., the piezo-optic signal is practically isotropic.

It is also immediately noticeable that the zero crossings of both $P_{\parallel}$ and $P_{\perp}$ do not occur at the maximum of the F band. On the basis of Eqs. (2) and (3) this should be interpreted as a change in α_0. The zero crossing of $P_{\parallel}$ and $P_{\perp}$ are, respectively, at energies slightly above the F-band maximum and appreciably below it.

HSS[6] have shown that the invariance of the zeroth moment of the shape function (defined in Ref. 6) under external perturbations is an important limitation of the method of moments. Schnatterly extended this study to the case where a small exchange of area takes place between the F and the K bands, by introducing additional constants describing, among other things, this exchange of area. From our data a calculation of the changes in zeroth moment of the shape function obtained from the combined F- and K-band data ($P_{\perp}$) in-

TABLE II. Comparison of the coefficients A, B, and C obtained in this work (on the low-energy side of the F band) with those of other workers. The symbols * and ** indicate that the value of b used in the calculation comes, respectively, from the zero crossing of $P_{\perp}$ for $P_{\perp}$ and the maximum of the F band for $P_{\parallel}$, or, from the maximum of the F band for both $P_{\parallel}$ and $P_{\perp}$. All units are meV/Mbar.

Crystal	T	Stress axis	A	B	C	A [a]	B [b]	C [b]	A [c]	B [c]	C [c]	B [d]	C [d]
KCl	80 °K	[100]	3.2*	1.2*									
			0.75**	2.5**									
		[111]	3.0*		4.5*								
			1.0**		7.5**	4.5	2.1	8.8	3.72	2.63		2.1	8.3
		[110]	3.4*	1.5*	3.6*								
			0.55**	2.2**	7.3**								
	20 °K	[100]	4.4*	2.2*									
			1.8**	5.1**									
		[110]	4.3*	1.7*	6.4*							1.97	8.0
			1.6**	3.2**	10.4**								
KBr	80 °K	[100]	3.5*	1.75*									
			2.7*	1.5**									
		[111]	4.4*		8.3*								
			3.1**		7.0**	5.4	1.5	6.4					
		[110]	4.7*	1.9*	6.5*								
			2.4**	1.3**	6.8**								
	20 °K	[110]	4.0*	1.9*	6.0*								
			2.1**	1.3**	5.9**								
NaCl	80 °K	[110]	9.5*	2.9*	12.5*								
			5.4**	1.4**	12.2**	5.4	0.82	6.8	4.3	1.24	8.75		

[a] Reference 12.

[b] Reference 6.

[c] Reference 7.

[d] Reference 17.

dicates a notable change in the transition probability, i.e., there is a large interaction with states outside the F and K bands.

The positive and negative contributions to the change in zeroth moment of the shape function are given in Table III for KCl. They were computed on the basis of the combined signal arising from the F_{I}, F_{III}, and K bands. As could be foreseen from our previous discussion, the positive and the negative contributions to the zeroth moment obtained from $P_{\parallel}$ nearly cancel each other. The largest net change in zeroth moment arises in the case of $\langle 100 \rangle$ stress. The contribution of the signal in the K-band region (after a judicious extrapolation of the F-band signal in the K-band region) is estimated to be of the order of 1.5% of the area arising from the positive signal.

With the possible exception of the $P_{\parallel}$ signal obtained with $\langle 100 \rangle$ stress, we can conclude that there is no experimentally observed change in transition probability in the F- and K-band region.

The situation is, instead, completely different in the case of light polarized perpendicular to the stress axis. The changes in zeroth moment calculated from the $P_{\perp}$ signal are appreciable; the difference between the magnitudes of the positive and the negative contributions are of the order of 25% of the latter. In the case of $P_{\perp}$ the K band contributes from 20 to 30% to the magnitude of the negative signal. If the signal arising from the K band were subtracted, the net change in the zeroth moment would be nearly doubled with respect to those given in Table III. Errors caused by the background signal (e.g., from inhomogeneities in the photomultiplier cathode) cannot account for such changes in zeroth moment.

TABLE III. Experimental changes of the shape function calculated from the data of Figs. 3 and 4. The terms A_+ and A_- (Mbar^{-1}) correspond to the positive and negative contributions to the change of the shape function. Both signals arising from the F and the K bands are considered in the integrals. The background was subtracted assuming it varied linearly between 3.1 and 1.9 eV. Note that in the case of $P_{\perp}$ its maximum value is less than 10% of the maximum value of $P_{\perp}$, and in the case of $P_{\parallel}$ its maximum value is less than 3% of the maximum value of $P_{\parallel}$. In both cases its contribution is particularly small in the F-band region. The background is shown in Figs. 3 and 4.

T	Stress	Polarization	A_+	A_-
80 °K	[111]	[111]	2.87	3.01
	[111]	$[1\bar{1}0]$ or $[11\bar{2}]$	0.42	0.31
	[110]	[110]	3.7	3.6
	[110]	$[1\bar{1}0]$	0.53	0.46
	[100]	[100]	3.0	3.3
	[100]	[010]	0.60	0.46
20 °K	[110]	[110]	3.9	3.9
	[110]	$[1\bar{1}0]$	0.51	0.54
	[110]	[001]	0.84	0.49
	[100]	[100]	4.3	4.6
	[100]	[001]	0.76	0.49

Under the assumption that the high-energy hump of $P_{\perp}$ is caused only by a change in transition probability of F_{III}, one could locate the peak of the F_{III} band in KCl at 2.43 ± 0.01 eV and estimate its $1/e$ width to be roughly 0.14 eV. Since the change in zeroth moment is predominantly observed with light polarized perpendicular to the stress axis, we conclude that the most important state giving rise to F_{III} has Γ_5^- symmetry[17] (f like). Furthermore, the change in zeroth moment was observed despite the fact that both F and K bands were taken into account. It implies that the oscillator strength induced by the stress must arise primarily from states outside the F and K bands. On the assumption that the signal in the F_{III} band region is due only to a change in area, we can assign 15% of that change as arising from the F_{I} band, and about as much from the K band.

From the changes in the zeroth moment of the shape function given in Table III, we estimate that at LNT the values of the coefficients C_i are [in units of 1/Mbar, referring to the $(1/\alpha)d\alpha/d\sigma$ curves] for KCl

$$C_1 = 0.07\,, \quad C_5 = -0.11\,, \quad C_3 = -0.12\,.$$

Errors are estimated of the order of 30%. The results at 20 °K are consistent with the same values of C_i although a slightly better agreement is found if $C_3 = -0.2$ Mbar^{-1}.

On account of the large values of both the changes in area and the coefficients C_i, it appears unlikely that the changes in transition probability in the F_{III} band reflect a decrease in the intensity of the L bands.[19] It is a well-known fact[2] that the L bands are removed by more than 1 eV from both the F_{I} and F_{III} bands and that their oscillator strengths are much smaller than that of the K band. Therefore, the limited size of the contribution from the F_{I} and K bands to the changes in zeroth moment makes it unlikely that the L bands play an important role.

It is also empirically observed (Fig. 12) that the energies E_l of the peaks of the F_{I}, F_{III}, K_1, K_2, L_1, L_2, and L_3 bands[20-22] in KCl can be described by the expression

$$E_l - E_1 = \epsilon_0 l(l+1) - 2\epsilon_0\,, \tag{4}$$

where l is an odd integer and ϵ_0 is a parameter determined experimentally. If, based on this empirical relation, we assign the K_1 band (or the peak of the usual K band) to $l = 5$, Eq. (4) describes well the positions of the F, K_1, L_1, L_2, and L_3 bands in RbI, RbBr, KI, RbCl, and LiCl (Fig. 12). The L bands have clearly been observed by optical absorption measurements in all these crystals.[10] Except for the case of RbCl,[18] the K_2 band has not been observed in the above crystals and accordingly, for the other crystals, a band corresponding to $l = 7$ is missing in Fig. 12.

The L bands have not been found by direct optical absorption in both NaCl and LiCl, and the K band is difficult to separate from the F band in both these crystals. The K bands observed either by photoconductivity or photoluminescence[23,24] may again be described by a relation of the form of Eq. (4). In the case of KBr, NaCl, and LiCl, a slightly better agreement is obtained if the L_1, L_2, L_3, and possibly L_4 bands are assigned to values of l that are, respectively, 11, 13, 15, and 17 with a corresponding decrease of about 20% in the value of ϵ_0. It implies that the $l = 9$ band is hidden in the tail of the K_2 band.[22] In view of its position, the K band of NaCl cannot justifiably be assigned to the $l = 5$ state; its assignment to $l = 7$ is the only reasonable one, independently of the identity of the L bands. It is interesting to note that an equation of the type of Eq. (4) is reminiscent of the energy spectrum of a rigid rotator that is known to describe well the rotational spectrum of diatomic molecules.[25]

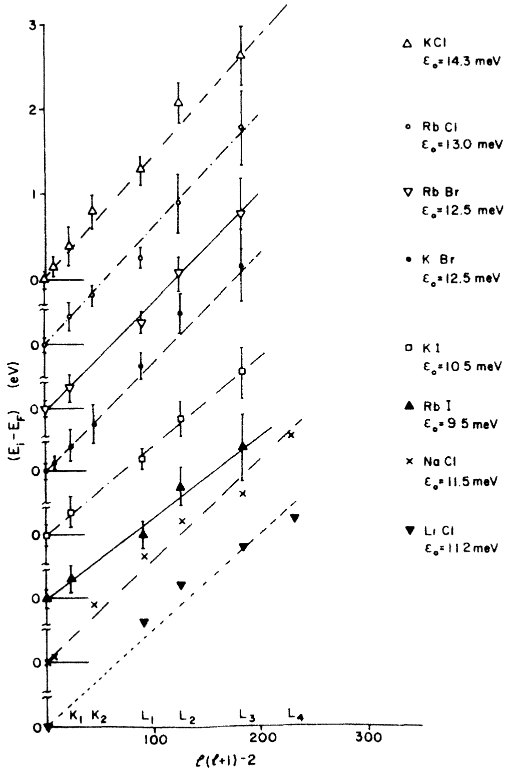

FIG. 12. Observed and calculated positions of the F, K, and L bands in different alkali halides. The error bars correspond to the width of the appropriate band as experimentally observed. They are missing for the L bands in NaCl and LiCl because they are unknown. The data for different crystals have been displaced by 0.75 eV for clarity. The straight lines are not chosen according to a least-square-fit method.

We would like to conclude this section by excluding the possibility that the observed F_{III} structure arises either from spurious effects or from other well-known states. Spin-orbit splitting of the p-like states[1,26,27] may be excluded. Not only is the spin-orbit splitting too small to be directly observable (11.4 meV for KCl, 19.2 meV for KBr, and 5.1 meV for NaCl, but from an observation of the data we would conclude that the separation between F_{I} and F_{III} is larger in KCl than in KBr, which is exactly the opposite of what is observed for the spin-orbit splitting in magnetic-circular-dichroism experiments. Furthermore, the state whose change of energy per unit stress is expected to be isotropic (Γ_6^-) should give rise to an optical transition that is at a higher energy than that caused by the Γ_8^- state. This is contrary to the fact that the most "isotropic" band (F_{I}) is below the F_{III} band.

We may exclude the possibility that F_{I} and F_{III} are phonon replicas of each other. The characteristic phonon energies, as obtained from the variation of the half-width of the F band with temperature,[1] are 11.5 meV for KBr, 12.2 meV for KCl, and 18.1 meV for NaCl. Not only are these energies at least five times smaller than the F_{I}-F_{III} separation that we estimate from our experimental data, but the relative magnitudes of the F_{I}-F_{III} separation in KCl, KBr, and NaCl do not support such an assignment. An assignement to LO phonons is equally unrealistic.

We exclude that the F_{III} structure is due to a transition to a 2s state mixed with a 2p state by odd vibrational modes.

Stark measurements by Grassano *et al.*[28] indicate that the 2s level in KCl, KBr, and NaCl is, respectively, $E_{sp} = 110$ meV, $E_{sp} = 70$ meV, and $E_{sp} = 170$ meV above the corresponding 2p level. At first sight the values of E_{sp} for KCl and KBr do not appear to conflict with the value of the energy difference (Δ) between F_{III} and F_{I}. Such an assignment would, however, require that Δ for NaCl should be nearly 1.5 times as large as for KCl contrary to the experimental result.

The mixing between the 2s and 2p state by Γ_4^- lattice vibrations is expected to be characterized by the quantity $|\langle 2s|z|2p\rangle|/E_{sp}$. In the absence of dynamic effects the matrix element $\langle 2s|z|2p\rangle$ characteristic of the Stark effect should be similar to that describing the mixing by Γ_4^- modes. This matrix element is 1.5 times as large in KBr as in KCl so that the $2s$-$2p$ mixing should be more important in the former than in the latter. The width of the $2s$ band[28] is 20% larger in KBr than in KCl. Accordingly, if the F_{III} structure arose from a transition into a $2s$ state it should be about equally important in both KBr and KCl. The experimental results do not support this conclusion.

Bogan and Fitchen,[29] Stiles *et al.*,[30] Honda and Tamura,[31] Kojima and Kojima,[32] and Hamm[33] estimated the $2s$-$2p$ mixing of the states that contribute to the F center emission. In this case the $2s$ state is assumed below the $2p$ state. In the case of emission of F centers in KCl the $2s$-$2p$ admixture is estimated as ~40% in Refs. 29 and 30, 10% in Ref. 31, 15% in Ref. 32, and 8% in Ref. 33. The matrix elements $\langle 2s|z|2p\rangle$ are estimated[31] to be about three times larger in the case of emission than in the case of absorption[28] while $|E_{sp}|$ is nearly identical. The admixture of the $2p$ state into the $2s$ state in the case of absorption should be, therefore, even smaller than in the case of emission.

The small piezo-optic signal observed when light is polarized perpendicular to the stress axis arises because the cubic and noncubic deformations gave nearly equal and opposite contributions to the energy shifts of the F band (Table II).

In the case of the $2s$ state in which there is a small $2p$ admixture the coupling with noncubic modes can only arise from the latter. The magnitude of this coupling can be estimated as equal to the coupling of the "pure" $2p$ state times the admixture of the latter into the $2s$ state. The resulting coefficients B' and C' that describe the coupling to nonhydrostatic stresses are expected to be much smaller than in the case of a predominantly $2p$ state. The resulting piezo-optic signal should, therefore, be nearly independent of the direction of polarization contrary to the experimental result and about five times larger than observed.

The $2s$-$2p$ mixing should increase with increasing temperature,[31] implying a progressive increase in the importance of F_{III}. This appears to be supported by the experimental data. It should, however, be realized that any other mechanism that relies on lattice vibrations in order to make transitions to F_{III} allowed would give rise to the same qualitative behavior.

We can finally exclude spurious effects related to the production of the F centers: aggregation of F centers among themselves or aggregation with other defects. In the case of KBr, F centers were produced both by x irradiation and by conversion of U centers.[34] The stress-modulation results were undistinguishable. Our F bands in the case of KBr and KCl were undistinguishable from others published in the literature. The widths at half-maximum at 90 °K were 195 meV for KCl, 190 meV for KBr, and 310 meV for NaCl. At 20 °K, the widths were 170 meV for KCl and 163 meV for KBr. The position of the F-band maxima were, respectively, 2.296, 2.055, and 2.745 eV for KCl, KBr, and NaCl at 80 °K. The positions of the band maximum at 20 °K were 2.307 and 2.068 eV, respectively, for KCl and KBr. The KCl and KBr data are in excellent agreement with those of the narrowest F bands observed by others. The piezo-optic signal scales with the F-band absorption coefficient in the range of $1\ \text{cm}^{-1} \lesssim \alpha_0 \lesssim 8\ \text{cm}^{-1}$, indicating isolated F centers; furthermore it is linear in stress. We have not detected any F-aggregate centers (M or R) in the optical absorption ($400 < \lambda < 850$ nm, 950 nm for KBr) and the dependence of the stress-modulation signal on the stress axis does not give any indication of a systematic axis of the defect. The absence of F-aggregate centers is indeed expected on account of the low relatively uniform, F-center densities used.

We exclude that the structure is due to Petroff's B band.[1] If this were the case, some indication should have been seen in $P_{\parallel}$ as well as in $P_{\perp}$. The B band is ~25 meV above the F band in KCl while the maximum of the extra structure is ~140 meV above the peak of the F band. Furthermore, if the B band had been produced by a photochemical reaction when the sample was being mounted, KBr should have been more sensitive than KCl; instead, F_{III} is more prominent in the latter than in the former. Finally, when the F centers were produced in KCl at -80 °C, and the sample was cooled and measured at LNT without being warmed to room temperature (RT), the stress-modulation spectra had the same shape[35] as in Fig. 3.

From these considerations we conclude that observed structure does not arise from impurities, F aggregates, phonon replicas, spin-orbit splitting or an eventual mixture of $2s$ and $2p$ states. In all likelihood it is due to another state of the F center whose symmetry is probably primarily Γ_5^-, i.e., it arises from an f-like state.

III. EFFECT OF ELECTRON-PHONON INTERACTION

A. Coupling with even modes

O'Brien[36] concluded that, in the strong coupling limit, the Hamm reduction factors[37] K_3 and K_5 that describe the coupling of the trigonal and tetragonal components of the stress to the Γ_4^- states are equal to $\frac{2}{5}$ when both Jahn-Teller energies $V_3^2/2\mu_3\omega_3^2$ and $2V_5^2/3\mu_5\omega_5^2$ are equal, and when the frequencies characteristic of the Γ_3^+ and Γ_5^+ local modes of vibrations, ω_3 and ω_5, are the same. The quantities V_i and μ_i are, respectively, the coupling constants of the electronic state with the distortions of the Jahn-Teller complex that have Γ_i symmetry and the vibrational effective masses of the complex.

Whenever the above conditions are satisfied, the Hamiltonian that describes the coupling of a p state with lattice distortions transforming as Γ_3^+ and Γ_5^+ is soluble.[36] The energy minima that correspond to trigonal or tetragonal distortions are on the same equipotential surface.[36]

When we have either

$$\Delta' = [(V_5^2/\mu_5\omega_5^2)/(V_3^2/\mu_3\omega_3^2)] - \tfrac{3}{4} \neq 0 \tag{5}$$

or

$$\Delta'' = 2(\omega_3^2 - \omega_5^2)/(\omega_3^2 + \omega_5^2) \neq 0 \, , \tag{6}$$

the equienergetic surfaces (that were spheres in the five-dimensional space of the distortions Q_i) distort and the energy corresponding to either a trigonal or a tetragonal deformation of the Jahn-Teller complex is lowered. O'Brien[36] treated departures from $\Delta' = 0$ and $\Delta'' = 0$ with perturbation theory and showed that the form of either one of the above perturbations is the same. It implies that perturbations arising from $\Delta' < 0$ and $\Delta'' > 0$ partially compensate each other. O'Brien also showed that the perturbations due to the fact that either Δ' or Δ'' is different from zero have the form of a cubic potential. When the trigonal or tetragonal distortions of the Jahn-Teller defect are favored, the Hamm reduction factors, K_3 or K_5, corresponding to the unfavored distortion, tend to zero.

Experimentally, for KCl neither the coefficients B or C are particularly small. Their values are nearly the same when obtained either by a moment analysis or Eq. (3). From a comparison of Eq. (7) of Ref. 17 with Eq. (4.2) of Ref. 29 we get

$$B = \tfrac{1}{2} K_3 V_3^s (s_{11} - s_{12}) \, , \tag{7}$$

$$C = K_5 V_5^s s_{44} \, . \tag{8}$$

The coefficients s_{ij} and V_i^s are, respectively, the compliance coefficients and the coupling constants between the Γ_4^- state and the ith strain component. We shall take $V_i = V_i^s/a$ (where a is the nearest-neighbor distance). This relationship between V_i and V_i^s implies that both a static and a dynamic displacement of the ions surrounding the F center are equally coupled to the vibronic wave function.

From our measurements of the coefficients b for KCl at LNT we get (Table II, coefficients B^* and C^*)

$$V_5/V_3 = (C/2B)(s_{11} - s_{12})/s_{44} \simeq 0.24 \, .$$

We assumed that the values of s_{ij} proper to the vicinity of the F center are the same as in the bulk. Using B^{**} and C^{**} (Table II) we get $V_5/V_3 = 0.30$; from a moment analysis, Schnatterly[7] obtained $V_5/V_3 \simeq 0.33$. From the temperature variation of the second moments of the distribution due to vibrations having Γ_1^+, Γ_3^+, and Γ_5^+ symmetry, Hetrick[19] found for KCl

$$\omega_1 = 2.3 \times 10^{13} \text{ sec}^{-1} \, ,$$

$$\omega_3 = 1.95 \times 10^{13} \text{ sec}^{-1} \, ,$$

$$\omega_5 = 1.4 \times 10^{13} \text{ sec}^{-1} \, .$$

Using the observed values for ω_i and V_i (from B^* and C^*), assuming that $K_3 = K_5$, and that $\mu_3 = \mu_5$, we get for KCl at LNT $\Delta' = -0.63$ and $\Delta'' = 0.6$. We are thus close to the special case calculated by O'Brien.[36]

With the previous estimates of V_i we may calculate the Jahn-Teller energies for either a trigonal or a tetragonal distortion, if we make some assumption regarding the effective masses of the Γ_3^+ and Γ_5^+ vibrations. If the effective mass is taken as equal to that of the four-nearest K ions, one obtains for the tetragonal distortions of the F center in KCl

$$E_{\text{JT}} = \frac{V_3^2}{2\mu\omega_3^2} = \left(\frac{2B}{(s_{11} - s_{12}) a K_3} \right)^2 \frac{1}{2\mu_3\omega_3^2} = \begin{cases} 67 \text{ meV} & * \\ 200 \text{ meV} & ** \end{cases} \tag{9}$$

Here $K_3 = K_5$ was assumed equal to $\frac{2}{5}$. The single and double asterisks refer to the corresponding choice of B in Table II. The Huang and Rhys factor defined as $S_3 = E_{\text{JT}}/\hbar\omega_3$ would be about 6.8 in the first case and about 20 in the second. Similar Huang and Rhys factors are obtained in the case of the Γ_5^+ mode. Lemos and Markham[38] estimate $1 < S_3 < 10$. Experimentally, from a comparison of the energies corresponding to absorption and emission, one obtains $S_1 + S_3 + S_5 \simeq 50$.

Grasso *et al.*[39] observed a magnetic-circular-dichroism (MCD) signal in the C band of Tl^+ in KBr. The energy dependence of this signal has a small resemblance with stress-modulation spectra that we obtained when the light was polarized perpendicular to the stress axis. Grasso *et al.* explained their results in terms of a dynamic Jahn-Teller effect and based their conclusion on the result of a calculation by Cho[40] that had predicted the observed line shape. Cho's calculation for both the MCD and the stress dichroism were carried out in the strong-coupling limit ($S_i \gg 1$). The kinetic energy of the ionic motion was neglected. Although under certain conditions the calculation predicts the observed double-humped curve for the MCD signal, such a shape is not predicted for the case of stress dichroism (SD). Except for a larger coupling to the Γ_1^+ modes, the case of Tl^+ should not differ significantly from that of the F center.

Washimiya[41] calculated the MCD for a band arising from a transition to a doubly degenerate state which is coupled to doubly degenerate even modes of vibration, in an axial surrounding whose symmetry is, e.g., C_6, D_6, or D_{3d}. The interesting result is that the MCD is an oscillating function of photon energy, and that the optical absorption is double humped. The expectation value of L_z, corresponding to vibronic states that contribute to different parts of the MCD line shape, is a result of contributions of terms arising from an electronic transition associated with either an even or odd number of phonons. The terms associated with an even number of phonons give a contribution to L_z that has a sign opposite to that of terms associated with an odd number of phonons. As a result, the MCD line shape may be an oscillating function of energy.

Such a sign change is not expected when one calculates the expectation value of an operator that transforms as Γ_3^+ or Γ_5^+ of O_h. We do not expect, therefore, an oscillating reduction factor that might explain the shape of our piezo-optic signal obtained with light polarized perpendicular to the stress axis. Finally, although the interaction with the Γ_1^+ modes might smear out the double hump calculated by Washimiya, no hint of its existence is found in the alkali halides, nor is there any hint of an oscillating MCD dignal.[26] We conclude that none of the theories of which we are aware[36,37,40,41] that consider a p-like multiplet coupled to Γ_1^+, Γ_3^+, and Γ_5^+ vibrations describe the shape of the observed piezo-optic effect in the perpendicular polarization.

B. Coupling with odd "rotational modes"

The previous discussion indicated that the known calculations based on the Jahn-Teller effect cannot account for our observations. Neither a $2s$ state with appropriate admixture of a $2p$ state nor spin-orbit effects can account for the experimental results. Phonon sidebands appear equally unlikely. The only observation that appears to have any relation with the present results is the rigid-rotator-like spectrum described by Eq. (4). It appears to describe exceptionally well the relative positions of the F_I, F_{III}, K_1, K_2, L_1, L_2, and L_3 bands in all the alkali halides where they have been measured.

At this point we may only speculate on the origin of Eq. (4). A more detailed justification requires a complete study of the different local modes of the F center, taking into account anharmonic effects. Such a task is outside the scope of this work.

It is easy to convince oneself that on account of the strong coupling with even modes anharmonic effects will be important.

Based on the previous discussion of the Jahn-Teller effect we may calculate the hypothetical lattice distortion associated with a zero-phonon transition (the zero-phonon transition is not observed in the F center in alkali halides) for the case of coupling with Γ_3^+ modes.

The relation between the generalized coordinate Q_θ associated with a Γ_3^+ distortion and the corresponding Jahn-Teller energy is[36]

$$E_{JT} = \tfrac{1}{2}\omega^2 Q_\theta^2 \mu , \qquad (10)$$

where

$$Q_\theta = (12)^{-1/2}(2Z_3 - 2Z_6 - X_1 + X_4 - Y_2 + Y_5) . \qquad (11)$$

The quantities X_i, Y_i, $Z_i (i = 1 \cdots 6)$ are the displacements of the six ions neighboring the F center and μ is the mass characteristic of the motion. In the case of a dilation in the xy plane $2z_3 = -2z_6 = x_1 = -x_4 = y_2 = -y_5$. For KCl,[19] $\omega = 2\times 10^{13}\ \mathrm{sec}^{-1}$, μ is equal to the mass of four K ions, and $67 \leq E_{JT} \leq 200$ meV. From this result we get for the amplitude of the motion in the xy plane $2.4\times 10^{-9}\ \mathrm{cm} \lesssim X \lesssim 7.2\times 10^{-9}$ cm. This value must be compared with the characteristic length ρ appearing in the Born-Mayer repulsive potential[42] $Ae^{-r/\rho}$. In the case of KCl, $\rho_0 = 3.24\times 10^{-9}$ cm. Anharmonic effects are accordingly expected to be important even for the zero-phonon line.

The actual transition giving rise to the F band has many Γ_3^+ phonons associated with it and the amplitude of vibration of the Γ_3^+ distortions must be larger than what has been calculated above. The anharmonic effects must accordingly also be larger. Similar results are valid for the Γ_5^+ and Γ_1^+ phonons.

Based on the above qualitative arguments we speculate that the rigid-rotator spectrum described by Eq. (4) arises on account of a rotational motion of the center of mass of the nearest-neighbor ions around the geometrical center of the vacancy. At least the lowest levels of such a motion should arise on account of the increase of radial force constants and an eventual decrease of tangential force constants that should accompany the large outward motion of the nearest-neighbor ions due to the coupling of the electron to the even distortions. As is evidenced by the approximate validity of Cauchy's relations in alkali halides[43] the tangetial force constant is much smaller than the radial one.[44]

A change of the radial force constants accompanies the introduction of an F center in the lattice.[44,45] In the case of KI there is a decrease of the nearest-neighbor constant[43] by about 1% that gives rise to a local decrease of c_{11} by ~30% and a corresponding increase of c_{12} by ~50%. The lattice relaxation is instead outwards[44,45] in the case of KBr just as we expect on account of the coupling of the electron with Γ_3^+ and Γ_5^+ modes.

In order to provide an order of magnitude we can calculate the radius of gyration R_0 of our hypothetical rigid rotator on the assumption that the effective "rotating" mass is that of two positive ions. From Eq. (4) we get

$$\epsilon_0 = \hbar^2/2I = \hbar^2/2MR_0^2 .$$

In the case of KCl, $\epsilon_0 = 14$ meV and $R_0 \simeq 6\times 10^{-10}$ cm, confirming the hypothesis that the displacements required for the "rotational" mode should be much smaller than those required for the even modes.

On the assumption that the speculation of a rotational motion of the center of mass of the nearest-neighbor ions is correct we may expect changes of the "rotational" quantum number just like in a diatomic molecule.[25] In the latter case the selection rules associated with spherical harmonics limit $|\Delta l|$ to one. In a cubic field the group representations corresponding to odd spherical harmonics with $l > 1$ always contain at least one Γ_4^- and one Γ_5^- representation of O_h. Consequently the cubic field relaxes the molecular selection rule allowing transitions such that Δl is odd. The transition to the Γ_4^- state should contribute to the K_1, K_2, L_1, L_2, and L_3 bands.

In the case of the $F_{\rm III}$ band, on account of its vicinity to the F band, the Γ_4^- "rotational" state is likely to be in the same region of the F band and will be difficult to recognize. Stress, however, will make transitions to the Γ_5^- component of the $l = 3$ "rotation state" allowed, justifying the piezo-optic observations of the $F_{\rm III}$ band.

IV. CONCLUSIONS

In KBr, KCl, and NaCl we have detected unexpected structure in the stress-modulation signal observed with light polarized perpendicular to the stress axis. From this observation we conclude that this signal is due to transitions to a Γ_5^- state whose transition probability is induced by both a Γ_3^+ and a Γ_5^+ deformation. The oscillator strength appears to arise from energy levels lying outside the F and K absorption bands. We have named this new band the $F_{\rm III}$ band. It lies at an energy slightly higher than the F band (~140 meV in KCl, ~110 meV in KBr, and ~90 meV in NaCl. We considered the possibility that the shape of the piezo-optic signal might arise from a Jahn-Teller effect associated with the $2p$ state, from a transition to a mixed $2p$-$2s$ state, from spin-orbit effects, or from phonon sidebands, and concluded that none of these assignments were plausible. It is empirically observed that the energy differences between the $F_{\rm III}, K_1, K_2, L_1, L_2, L_3$, bands and the F band form a series of the type

$$E_i - E_F = \epsilon_0 l(l+1) - 2\epsilon_0 ,$$

where 9 meV $< \epsilon_0 <$ 15 meV for all the alkali halides in which the L bands have been observed. The quantity l is an odd integer equal to 1 for the F band, 3 for the $F_{\rm III}$ band, 5 for the K_1 band etc., for the remaining bands related to the F center.

The above equation is reminiscent of a rigid-rotator spectrum. We speculate that it describes a rotation of the center of mass of the nearest-neighbor ions around the geometrical center of the the vacancy. The appropriate potential might arise as a consequence of the large lattice distortion associated with the even distortions, which through anharmonic coupling, could increase the force constants for radial distortions and decrease the already weak force constants associated with tangential distortions. Evidence for the weakness of the latter arises from the fact that Cauchy's relations, i.e., radial forces, predict the correct relation between C_{12} and C_{44} in alkali halides.[43]

If the above speculation has merit, the rigid-rotator states corresponding to $l > 1$ and odd are split by the cubic field into different irreducible representations that always contain Γ_4^- and Γ_5^-. We assign the newly found $F_{\rm III}$ band to a transition in which the electronic state is p like and associated with a Γ_5^- rotational state arising from an $l = 3$ rigid-rotator level. It is not to be excluded that higher rigid-rotator states might coincide with higher electronic states as, e.g., the F-center series limit assigned to the K band.[5]

Little support has been found for alternative explanations based on the hypothesis that Eq. (4) is purely fortuitous.

A final advantage of this model is that the photoconductivity that is observed in the K_2 and L bands arises in a natural way (it may be, however, increased by a corresponding anomalous density of states in the conduction band). The $l \geqslant 7$ rotational states are degenerate with states in which the electron is excited into the conduction band with the eventual contemporary creation of free phonons. A transition from the localized to the free states is then likely. Similar but not identical effects have been found in polar semiconductors.[46,47]

The F-center potential is expected to give rise to localized states pulled out from subsidiary minima of the conduction band, e.g., at the point X of the conduction band.[48] The symmetry of such states can be easily calculated in the effective mass approximation.[49] It can be shown that p-like states would give rise to Γ_5^- states. Although the effective mass approximation will certainly be a poor approximation for the calculation of the energy of the proposed state, the above model should appropriately represent the overall symmetry of the wave function. We are, however, at a loss on how to associate the F_{III} band with such a state.

A third alternative could be considered. A comparison of the results of Table III for the case in which the light is polarized parallel and perpendicular to the stress axis indicate that the data cannot exclude a possibility of area exchange between the $P_{\parallel}$ and the $P_{\perp}$ spectrum. If this is interpreted as excluding the "rotational-states" model suggested by Eq. (4) it is difficult to explain the shape of the stress-modulation spectrum as arising from the accepted p states giving rise to both F and the K band interacting with appropriate lattice vibrations. We are thus unable to bring any support to this third alternative.

ACKNOWLEDGMENTS

The authors would like to thank Dr. J. J. Markham, for the comments on a previous version of this manuscript, Dr. Y. Toyozawa, Dr. A. E. Hughes, and Dr. M. C. M. O'Brien for suggesting the possibility of a Jahn-Teller effect, and Dr. Y. Merle d'Aubigné and Dr. R. Romenstain for enlightening discussions. One of us (A. P.) would like to thank the Purdue Research Foundation for a fellowship. Finally, we wish to warmly thank Professor F. Lüty for hydrogenating some KBr samples.

---

*Present address: Brown Boveri and Cie, Baden, Switzerland.

†Supported by the National Science Foundation Grants No. GP7021 and GP12757.

[1] J. J. Markham, *F Centers in Alkali Halides* (Academic, New York, 1966).

[2] J. H. Schulman and W. D. Compton, *Color Centers in Solids* (Pergamon, New York, 1963).

[3] G. Chiarotti and U. M. Grassano, Phys. Rev. Lett. 16, 124 (1966).

[4] D. Y. Smith and G. Spinolo, Phys. Rev. 140, A2121 (1965).

[5] L. J. Page, J. A. Strozier, and E. H. Hygh, Phys. Rev. Lett. 21, 348 (1968).

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

[7] S. E. Schnatterly, Phys. Rev. 140, A1364 (1965).

[8] W. Gebhardt and K. Maier, Phys. Status Solidi 8, 303 (1965).

[9] G. Ascarelli and A. Barone, Nuovo Cimento 37, 818 (1965).

[10] G. Ascarelli, Phys. Rev. 179, 797 (1969).

[11] M. Nuovo, Ric. Sci. 31, 212 (1961).

[12] Strain gauge FAE-06N-35S13, obtained from BLH Electronics Inc. Waltham, Mass.; glued to a metal sample with Eastman 910 adhesive.

[13] I. S. Jacobs, Phys. Rev. 93, 993 (1954).

[14] A. D. Brothers and D. W. Lynch, Phys. Rev. 164, 1124 (1967).

[15] A. Perregaux, thesis (Purdue University, 1970) (unpublished). 150-kV x rays filtered by 1 mm of Cu were used. The tube current was 12 mA. The width at half-maximum of the F band in KCl quoted therein is in error on account of the excessive absorption coefficient near the maximum of the F band ($\alpha x \simeq 5$).

[16] Samples obtained from the Harshaw Chemical Co., Cleveland, Ohio. The samples were in the shape of a parallelepiped $1 \times 1 \times 5$ cm.

[17] A. A. Kaplianskii, Opt. Spectrosc. 16, 557 (1964).

[18] K. Maier and W. Gebhardt, Phys. Status Solidi 27, 713 (1968).

[19] R. E. Hetrick, Phys. Rev. 188, 1392 (1969).

[20] F. Lüty, Z. Phys. 160, 1 (1960).

[21] F. Nakazawa and H. Kanzaki, J. Phys. Soc. Jap. 22, 844 (1967).

[22] R. S. Crandall and M. Mikkor, Phys. Rev. 138, A1247 (1965).

[23] C. C. Klick, Phys. Rev. 137, A1814 (1965).

[24] R. Fieschi and P. Scaramelli, Phys. Rev. 145, 622 (1966); R. Petrescu, Phys. Status Solidi 23, K105 (1967).

[25] G. Herzberg, *Molecular Spectra and Molecular Structure* (Van Nostrand, Princeton, New Jersey, 1961), Vol. I.

[26] J. Margerie, J. Phys. Suppl. 28, C4-103 (1967); M. Thuau and J. Margerie, C. R. Acad. Sci. B 268, 1586 (1969).

[27] C. H. Henry and C. P. Slichter, in *Physics of Color Centers*, edited by W. Beal Fowler (Academic, New York, 1968), p. 351.

[28] U. M. Grassano, G. Margaritondo, and R. Rosei, Phys. Rev. B 2, 3319 (1970).

[29] L. D. Bogan and D. B. Fitchen, Phys. Rev. B 1, 4122 (1970).

[30] L. F. Stiles, M. D. Fontana, and D. B. Fitchen, Phys. Rev. B 2, 2077 (1971).

[31] S. Honda and M. Tamura, J. Phys. Soc. Jap. 33, 1003 (1972).

[32] K. Kojima and T. Kojima, Proceedings of the 1971 International Conference on Color Centers in Ionic Crystals (unpublished).

[33] F. Hamm, Phys. Rev. B 8, 2926 (1973).

[34] Kindly produced by Professor F. Lüty's group at the University of Utah, Salt Lake City, Utah.

[35] These measurements were carried out by C. Beetz in our laboratory.

[36] M. C. M. O'Brien, Phys. Rev. 187, 407 (1968); J. Phys. C 4, 2524 (1971).

[37] M. D. Sturge, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and E. Ehrenreich (Academic, New York, 1967), Vol. 20.

[38] A. M. Lemos and J. J. Markham, J. Phys. Chem. Solids 26, 1837 (1965).

[39] V. Grasso, P. Perillo, and G. Vermiglio, Solid State Commun. 11, 563 (1972).

[40] K. Cho, J. Phys. Soc. Jap. 27, 646 (1969); 25, 1372 (1968).

[41] S. Washimiya, Phys. Rev. Lett. 28, 556 (1972).

[42] M. Born and K. Huang, *Dynamic Theory of Crystal Lattices* (Oxford U. P., Oxford, 1966), p. 26.

[43] H. B. Huntington, in Ref. 37, Vol. 7.

[44] D. Bauerle and R. Hubner, Phys. Rev. B 2, 4252 (1970).

[45] F. Lüty, S. Mascarenhas, and C. Ribeiro, Phys. Rev. 168, 1080 (1968).

[46] R. R. Parsons, Can. J. Phys. 29, 1850 (1971).

[47] M. D. Habegger and H. Y. Fan, Phys. Rev. Lett. 12, 98 (1964).

[48] A. B. Kunz, Phys. Status Solidi 29, 115 (1968); Phys. Rev. 175, 1147 (1968).

[49] A. K. Ramdas, P. M. Lee, and P. Fisher, Phys. Lett. 7, 99 (1963).