5. CONCLUSIONS

(a) The accurate analysis of the first stage of the precipitation shows that the process is not simply represented by third-order kinetics, as found for Sr and Ba in KCl and Mn in NaCl.[7,12,13] The situation in $NaCl:SrCl_2$ suggests a step mechanism in which an aggregation of a couple of dipoles occurs as a first stage (dimer), followed by the addition of an isolated dipole to build up the final product (trimer). However, the results obtained from a simplified mathematical approach to the problem do not supply satisfactory agreement with the experimental data.

(b) The precipitation process has peculiar features depending on the impurity which precipitates: In fact Cook and Dryden[12] found an equilibrium stage between dipoles and trimers in $KCl:SrCl_2$, while we did not find this phenomenon in $NaCl:CdCl_2$ in the temperature range covered by our measurements.

(c) The fact that the activation energy of dipole orientation (measured in the temperature range from 190 to 240°K) is higher than that for aggregation into trimers (measured in the temperature range from 275 to 324°K) shows that the aggregation process is a complicated one and that it requires further analysis. Detailed study of the morphology of precipitates, such as may be given by means of Mössbauer-effect or EPR measurements, would help to clarify the problem.

ACKNOWLEDGMENTS

We are deeply indebted to the late Professor Elio Germagnoli and to Professor Roberto Fieschi for constant encouragement and helpful discussion, and to Mario Scalvini, who performed the chemical analysis.

PHYSICAL REVIEW VOLUME 165, NUMBER 3 15 JANUARY 1968

Magnetic Circular Dichroism of the R_2 Band in KCl and KF*

I. W. SHEPHERD
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York
(Received 10 August 1967)

Circular dichroism has been observed in both the zero-phonon line and sidebands of the R_2 transition in KCl and KF. The magnetic field was of magnitude 8 kG and the temperature range was $7°K>T>1.3°K$. The zero-phonon-line dichroism was analyzed by a method of moments. It is shown theoretically that the changes in zeroth moment depend on the strain in the sample, whereas the changes in first moment do not. Experimentally the strain dependence of the zeroth moment is measured by applying a variable external stress simultaneously with the magnetic field. Quite good agreement is found with theory in a non-parameter fit. An estimate of the ground-state splitting in the internal strain field of the crystal is made ($\delta_0=1.5$ cm^{-1}). The first-moment data yield values of the reduced angular momentum Λb (0.06 ± 0.01 for KCl and 0.11 ± 0.01 for KF) and of the reduced spin-orbit coupling $\Lambda\lambda b$ (-0.32 ± 0.03 cm^{-1} for KCl and -0.68 ± 0.07 cm^{-1} for KF). The strength of the Jahn-Teller interaction as defined by the parameter k^2 is deduced ($k^2=3.2$ for KCl and 2.3 for KF). A study of the well-resolved sideband peaks in KF enables a self-consistent assignment of phonon symmetries for the peaks in strain- and magnetic-field-induced dichroism to be made. The good agreement between theory and experiment in all measurements further confirms the Van Doorn F_3 model of the R center and Silsbee's analysis based on a dynamic Jahn-Teller effect in the ground state.

I. INTRODUCTION

THE Van Doorn model of the R center[1,2] is a triangle of three neighboring F centers (Fig. 1). The ground state has a twofold orbital degeneracy. In principle, it is possible to lift this electronic degeneracy by applying an external perturbation to the crystal such as a stress, a magnetic field, or an electric field. Silsbee[3] has carried out experiments on KCl with an applied uniaxial stress and he observed a marked optical dichroism in both the zero-phonon line and in the broad band associated with the R center. These experiments confirmed the Van Doorn model and also showed that the Jahn-Teller interaction, which results from the coupling of the degenerate electronic levels to the lattice modes, is strong and must be taken into account.

There have been attempts to observe a magnetic splitting of the levels directly by using very high pulsed magnetic fields,[4] but with no success. The reason for this is that the Jahn-Teller interaction effectively quenches the angular momentum and so reduces the interaction with the magnetic field. It is still possible to observe the effect of a magnetic field by looking for the small dichroism in the absorption of circularly polarized light which is induced by the field. Preliminary measurements, mainly on KCl, have been

* This work was supported in part by the Advanced Research Projects Agency, MSC Report No. 741 (unpublished).
[1] C. Z. Van Doorn, Phillips Res. Repts. 12, 309 (1957); Suppl. 4 (1962).
[2] H. Pick, Z. Physik 159, 69 (1960).
[3] R. H. Silsbee, Phys. Rev. 138, A180 (1965).
[4] A. E. Hughes, Proc. Phys. Soc. (London) 86, 615 (1965).

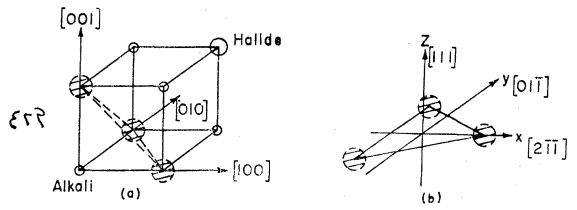

FIG. 1. (a) The Van Doorn model of the R center in an alkali halide is shown. It consists of three neighboring F centers which lie in a [111] plane. (b) The principal axes of the R center with respect to the crystal axes.

reported,[5,6] but discrepancies in the values of the parameters deduced from the measurements, the reduced angular momentum Λb, and reduced spin-orbit interaction $\Lambda\lambda b$, indicated that the strain in the sample may have an appreciable effect on the observed dichroism. The main purpose of this paper is to show that strains do indeed have a large effect.

The zero-phonon-line dichroism signal was analyzed by a method of moments, and it was found that the zeroth moment or area of the line was affected strongly by strains in the sample. The effect of strains was clarified by performing experiments where a uniaxial stress is applied in addition to the magnetic field. These experiments are interpreted by assuming that the magnetic interaction of the center is a perturbation on the stress interaction, and an estimate is made of the average internal strain in the crystal.

The change in first moment, or center of gravity, of the line caused by a magnetic field was found to be independent of strains as is expected theoretically (see Sec. II). The first-moment measurements as a function of temperature provide a direct way of measuring the strength of the Jahn-Teller interaction as they yield values of the reduced orbital moment and the reduced spin-orbit interaction. The magnitude of the reduction factor is a direct reflection of the Jahn-Teller strength. The results agree well with values obtained from spin-resonance data by Krupka and Silsbee.[7] Similar experiments were performed on KF which shows a better resolved structure than KCl. The dichroism is larger in this crystal indicating that the Jahn-Teller interaction is weaker.

There is also a dichroism signal in the broad R_2 band. This was studied in KF where there are several distinct multiphonon peaks. These are not well enough resolved, however, to permit a moments analysis as was done for the zero-phonon line. It is seen that certain peaks which are observed in the absorption spectrum are accentuated in the dichroism spectrum, whereas others do not appear. A similar effect is also observed in stress-induced dichroism, and by comparing the results of the two experiments it is possible to assign phonons of definite symmetry to the sideband peaks.

[5] W. J. Burke, S. E. Schnatterly, and W. D. Compton, Bull. Am. Phys. Soc. **11**, 245 (1966).
[6] P. Duval, J. Gareyte, and Y. Merle d'Aubigne, Phys. Letters **22**, 67 (1966).
[7] D. C. Krupka and R. H. Silsbee, Phys. Rev. **152**, 816 (1966).

Section II contains a brief summary of the theoretical background of the Jahn-Teller interaction and a calculation of transition probabilities and moment changes. Section III is a description of the experimental technique and Sec. IV contains the experimental results.

II. THEORY

The theoretical formalism of the Jahn-Teller effect has been published in a series of papers[8–10] and only a brief sketch of the underlying theory is given here. Silsbee[3] has adopted a notation which is convenient to use for the R center and this will be used in the present work. The first step is to introduce this notation. Then, having obtained the relevant wave functions, the effect of a magnetic field on the transitions for circularly polarized light will be derived. The changes in first and zeroth moment of the absorption will then be calculated.

The Jahn-Teller distortion of the electronic ground state, which has E symmetry, is caused by lattice modes of E symmetry. It is assumed that the effect of all modes of E symmetry can be considered as resulting from a single pair of E modes, φ_1 and φ_2. In polar coordinates these can then be written $Q_1=r\cos\varphi$, $Q_2=r\sin\varphi$. The vibronic wave functions describing a state of E symmetry, as given by Longuet-Higgins *et al.*[9] (hereafter referred to as LHOPS), may then be written

$$\begin{aligned}\Psi_{xpl}{}^{(i)}=\epsilon_x{}^i\Big[&\frac{1}{(2\pi)^{1/2}}\mu_{pl}{}^i(-r)\cos l\varphi\cos\tfrac{1}{2}\varphi\\&+(-)^{l-1/2}\frac{1}{(2\pi)^{1/2}}\mu_{pl}{}^i(r)\sin l\varphi\sin\tfrac{1}{2}\varphi\Big]\\&+\epsilon_y{}^i\Big[\frac{1}{(2\pi)^{1/2}}\mu_{pl}(-r)\cos l\varphi\sin\tfrac{1}{2}\varphi\\&-(-1)^{l-1/2}\frac{1}{(2\pi)^{1/2}}\mu_{pl}{}^i(r)\sin l\varphi\cos\tfrac{1}{2}\varphi\Big],\\\Psi_{ypl}{}^{(i)}=\epsilon_x{}^i\Big[&\frac{1}{(2\pi)^{1/2}}\mu_{pl}{}^i(-r)\sin l\varphi\cos\tfrac{1}{2}\varphi\\&-(-)^{l-1/2}\frac{1}{(2\pi)^{1/2}}\mu_{pl}{}^i(r)\cos l\varphi\sin\tfrac{1}{2}\varphi\Big]\\&+\epsilon_y{}^i\Big[\frac{1}{(2\pi)^{1/2}}\mu_{pl}{}^i(-r)\sin l\varphi\sin\tfrac{1}{2}\varphi\\&+(-)^{l-1/2}\frac{1}{(2\pi)^{1/2}}\mu_{pl}{}^i(r)\cos l\varphi\cos\tfrac{1}{2}\varphi\Big].\end{aligned}\quad(1)$$

[8] U. Öpik and M. H. L. Price, Proc. Roy. Soc. (London) **A238**, 425 (1957), hereafter referred to as LHOPS.
[9] H. C. Longuet Higgins, U. Öpik, M. H. L. Price, and R. A. Sack, Proc. Roy. Soc. (London) **A244**, 1 (1958).
[10] M. S. Child and H. C. Longuet Higgins, Proc. Roy. Soc. (London) **A254**, 33 (1961).

$\epsilon_x{}^i$, $\epsilon_y{}^i$ are the pair of degenerate electronic wave functions. The x and y subscripts indicate that the functions are even and odd, respectively, under reflection in the xz plane of the center [Fig. 1(b)]. The superscript i refers to the electronic state and for the ground state is $i=0$. The $\mu_{pl}(r)$ are radial wave functions and the quantum numbers p and l can be thought of as describing the radial and rotational properties of the state. The value of p may be 1, 2, 3$\cdots$ and of l may be $\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}\cdots$. The ground state is given by $p=1$ and $l=\frac{1}{2}$. The transition of interest in the present work is the R_2 transition which occurs between the ground state and an excited state of A_2 symmetry. The vibrational E modes do not couple to this excited state and hence the wave functions can be written as the product of the vibrational and electronic parts. Thus,

$$\begin{aligned}\Phi_{xnm}&=a_2(2\pi)^{1/2}\rho_{nm}(r)\sin m\varphi\,,\\ \Phi_{ynm}&=a_2(2\pi)^{1/2}\rho_{nm}(r)\cos m\varphi\,,\end{aligned}\tag{2}$$

where a_2 is the electronic wave function and $\rho_{nm}(r)\sin m\varphi$ and $\rho_{nm}(r)\cos m\varphi$ are the vibrational functions. The normalization constant $(2\pi)^{1/2}$ is replaced by unity for $m=0$.

If the two ground states $\Psi_{x1\frac{1}{2}}$ and $\Psi_{y1\frac{1}{2}}$ (referred to henceforth as Ψ_x,Ψ_y) are degenerate before external perturbation is applied, a magnetic field H in the z direction will lift the degeneracy and form the eigenfunctions $\Psi_x\pm i\Psi_y$. In the present case, however, the internal strains in the lattice lift the degeneracy and the effect of H must be regarded as a smaller perturbation. Figure 2(a) shows the situation before H is applied. The quantity δ is the splitting of the levels due to strain. The effect of H is to mix the levels by the amount ϵ as shown in Fig. 2(b). The quantity ϵ must be calculated from the spin-orbit Hamiltonian $\mathcal{H}_{SO}$ and the Hamiltonian describing the effect of the magnetic field $\mathcal{H}_H$. We have

$$\mathcal{H}_{SO}=\lambda b\mathbf{L}\cdot\mathbf{S}\,,\tag{3}$$

and

$$\mathcal{H}_H=\beta\mathbf{H}\cdot(b\mathbf{L}+2\mathbf{S})\,,\tag{4}$$

where $b=\int\mu_{1\frac{1}{2}}(r)\mu_{1\frac{1}{2}}(-r)rdr$ is the factor by which the Jahn-Teller interaction reduces the angular momentum. In this work it will be shown that $b\sim0.01$. (This factor has been calculated by Child and Longuet-Higgins.[10]) According to first-order perturbation theory, the small quantity ϵ is given by

$$\epsilon=\langle\Psi_x|\mathcal{H}_{SO}+\mathcal{H}_H|\Psi_y\rangle/\delta.\tag{5}$$

If H is applied along the z axis,

$$\epsilon=\langle\Psi_x|L_z|\Psi_y\rangle(\beta H_z+\lambda\langle S_z\rangle/\delta.\tag{6}$$

The first term is the orbital Zeeman interaction and may be written $\Lambda b\beta H_z$, where $\Lambda=\langle\epsilon_x{}^i|L_z|\epsilon_y{}^i\rangle$. The second term is a spin-polarization term and is temperature-dependent because

$$\langle S_z\rangle=-\tfrac{1}{2}\tanh(g\beta H/2kT)\sim-\tfrac{1}{2}(g\beta H/2kT)\,,\tag{7}$$

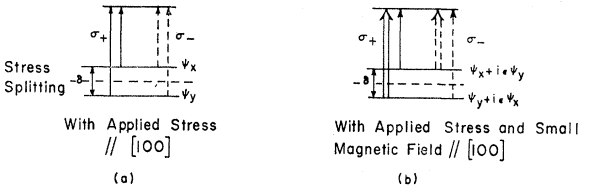

FIG. 2. The splitting of the vibronic ground state of the R center under applied stress is shown. The zero-phonon transitions for circular light to an excited state of A_2 symmetry are indicated by the arrows. In (a) there is no applied magnetic field and there is no circular dichroism. In (b) a small applied magnetic field has mixed the ground states by the small amount ϵ and a dichroism is induced. The double arrows indicate preferred transitions.

where $S=\frac{1}{2}$. The approximation is for $g\beta H\ll kT$. Thus we have

$$\epsilon=\left[\Lambda b\beta H_z-\tfrac{1}{2}\lambda b\Lambda\frac{g\beta H_z}{2kT}\right]\frac{1}{\delta}\,,\tag{8}$$

where Λ is assumed to be unity. The energies of the two states remain unchanged to first order in ϵ.

The effect of H is to increase slightly the transition probability for right circularly polarized light σ_+ from the lower level and to decrease it from the upper level. The transition probability is proportional to the square of the matrix element and the matrix elements for σ_+ in the R_2 zero phonon transition are

$$\langle\Phi_{y10}|x+iy|\Psi_x\rangle\quad\text{and}\quad\langle\Phi_{y10}|x+iy|\Psi_y\rangle.\tag{9}$$

For left circularly polarized light σ_-, the effect is the opposite. In this case the matrix elements are

$$\langle\Phi_{y10}|x-iy|\Psi_x\rangle\quad\text{and}\quad\langle\Phi_{y10}|x-iy|\Psi_y\rangle.\tag{10}$$

Here it is assumed that the light is polarized in the frame of reference of the center. In the experiment, we shine the light parallel to H which is parallel to a [100] crystal axis. The transformation from the crystal frame (primes) to the center frame is

$$x'\rightarrow(\sqrt{\tfrac{2}{3}})x,\quad y'\rightarrow\frac{1}{\sqrt{2}}y+\frac{1}{\sqrt{6}}x,\tag{11}$$

and the effect is to multiply the calculated changes in the line-shape moments by a constant factor. This is shown below. The matrix elements were calculated using the appropriate wave functions [Eqs. (1) and (2)] and the transition probabilities are given in Table I both for the light in the crystal and center frames. It can be seen from Table I that when there is no applied magnetic field the sum of the transition probabilities from Ψ_x and Ψ_y are the same for σ_+ and σ_-. There is then no dichroism signal. When a magnetic field is applied, the favored transition for σ_+ is from Ψ_y and the favored transition for σ_- is from Ψ_x.

The area or zeroth moment of the line is defined[11] as

$$A\eta=\int f\eta(E)dE\,,\tag{12}$$

[11] A complete discussion of moments is given in the paper by C. H. Henry, S. E. Schnatterly, and C. P. Slichter, Phys. Rev. 137, A583 (1965).

TABLE I. R_2 zero-phonon-transition probabilities for circularly polarized light. The light is considered to be polarized in either the crystal or the center frame. The cases with and without H are shown. ϵ is defined by Eq. (8). The notation is the same as that used by Silsbee (Ref. 3).

		Light σ_+ Initial state		Light σ_- Initial state	
		Ψ_x	Ψ_y	Ψ_x	Ψ_y
H=0	Light in center frame	$\frac{1}{2}\lvert G_{10}\rvert^2$	$\frac{1}{2}\lvert G_{10}\rvert^2$	$\frac{1}{2}\lvert G_{10}\rvert^2$	$\frac{1}{2}\lvert G_{10}\rvert^2$
	Light in crystal frame	$\frac{1}{4}\lvert G_{10}\rvert^2$	$(5/12)\lvert G_{10}\rvert^2$	$\frac{1}{4}\lvert G_{10}\rvert^2$	$(5/12)\lvert G_{10}\rvert^2$
H≠0	Light in center frame	$\frac{1}{2}\lvert G_{10}\rvert^2(1-2\epsilon)$	$\frac{1}{2}\lvert G_{10}\rvert^2(1+2\epsilon)$	$\frac{1}{2}\lvert G_{10}\rvert^2(1+2\epsilon)$	$\frac{1}{2}\lvert G_{10}\rvert^2(1-2\epsilon)$
	Light in crystal frame	$\frac{1}{2}\lvert G_{10}\rvert^2[\frac{1}{2}-(2/\sqrt{3})\epsilon]$	$\frac{1}{2}\lvert G_{10}\rvert^2(\frac{5}{6}+2\epsilon/\sqrt{3})$	$\frac{1}{2}\lvert G_{10}\rvert^2(\frac{1}{2}+2\epsilon/\sqrt{3})$	$\frac{1}{2}\lvert G_{10}\rvert^2(\frac{5}{6}-2\epsilon/\sqrt{3})$

$$G_{10}=g_i\int\rho_{10}(r)[\mu_{11/2}{}^{\circ}(-r)+\mu_{11/2}{}^{\circ}(r)]r\,dr$$
$$g_i=\langle a_2\lvert y\rvert\epsilon_x{}^{\circ}\rangle=\langle a_2\lvert x\rvert\epsilon_y{}^{\circ}\rangle$$

where $f_\eta(E)$ is the line-shape function and is connected with the absorption coefficient α by

$$\alpha_\eta(E)=CEf_\eta(E), \tag{13}$$

where $C=(4\pi^2N/\hbar cn_0)(\epsilon_{\text{eff}}/\epsilon_0)^2$, η is the polarization of the light, $\epsilon_{\text{eff}}/\epsilon_0$ is the ratio of the local electric field to the macroscopic field, and n_0 is the index of refraction. f_η can be expressed in terms of the matrix elements between initial and final states,

$$f\eta(E)=\mathrm{Av}_n\sum_n|\langle\Phi_{y10}|P\eta|\Psi_n\rangle|^2\delta(E_{y10}-E_n-E). \tag{14}$$

Here, E_{y10}, E_n, and E are the energies of the final state, initial state, and light, respectively. Av_n is a thermal average over the initial states Ψ_n where $n=x$ or y. The change in zeroth moment when a field is applied, $dA(H)$, can be written, using Table I, as

$$dA(H)=\frac{A_{\sigma+}(H)-A_{\sigma-}(H)}{A_{\sigma+}(0)+A_{\sigma-}(0)}=\frac{n_y-n_x}{n_y+n_x}\epsilon\sqrt{3}, \tag{15}$$

where $A_{\sigma+}(0)$ and $A_{\sigma-}(0)$ are measured at high temperature such that the populations n_y and n_x are equal. When no stress is applied this is approximately true at 10°K. This is for light parallel to a [100] direction in the crystal frame. n_y, n_x are the populations of Ψ_y, Ψ_x, respectively. {If the light is taken parallel to a [100] direction in the frame of the center, the same quantity is equal to $\{(n_y-n_x)/(n_y+n_x)\}2\epsilon$. The difference is just a geometrical factor $\frac{1}{2}\sqrt{3}=0.865$.} Calculating the populations assuming a Boltzmann distribution we have

$$dA(H)=\epsilon\sqrt{3}\tanh\delta/2kT, \tag{16}$$

and in the limit $\delta\ll kT$,

$$dA(H)\sim b\left(\beta\Lambda H_z-\tfrac{1}{2}\lambda\Lambda\frac{g\beta H_z}{2kT}\right)\frac{1}{2kT}\sqrt{3}. \tag{17}$$

In general the area change is a function of the stress splitting δ. In this high-temperature limit, however, there is no dependence on δ. This is because there are two competing effects:

(1) The dichroism depends on the difference in the populations of the levels (n_y-n_x). In the high-temperature limit this is proportional to δ.

(2) The dichroism depends on the angular momentum which is proportional to the mixing of the levels Ψ_x and Ψ_y by the magnetic field. This is proportional to $1/\delta$ as is seen in Eq. (6). Thus the dependence on δ cancels out.

The center of gravity or the first moment of the line is given by

$$\bar{E}_\eta=A_\eta{}^{-1}\int Ef_\eta(E)dE. \tag{18}$$

Before H is applied, $\bar{E}_{\sigma_+}$ is the same as $\bar{E}_{\sigma_-}$. When H is applied, there is a shift in first moment for both polarizations. This shift can be calculated from Table I.

$$(d\bar{E}_{\sigma_+}-d\bar{E}_{\sigma_-})=2d\bar{E}=\Delta\sqrt{3}$$
$$=b(\beta\Lambda H_z-\tfrac{1}{2}\lambda\Lambda g\beta H_z/2kT)\sqrt{3}. \tag{19}$$

The same quantity calculated with the light in the center frame is 2Δ, and the difference is again the factor $\frac{1}{2}\sqrt{3}$. It should be noted that the change in first moment is *independent* of the stress splitting δ. It is therefore possible to use the experimental data on the first moment to calculate the parameters Λb and $\Lambda\lambda b$. Then, using the zeroth moment data in addition to the calculated values of the parameters, the effect of the strain on the centers can be investigated.

Up to now only zero-phonon transitions have been considered, and Table I lists the transition probabilities for this case. Information can also be obtained from the dichroism signal in the sidebands, which, although less well resolved than the zero-phonon signal, still enables the symmetry of the phonons involved in each peak to be determined. Table II shows the transition probabilities for σ_+ and σ_- from the ground states Ψ_x and Ψ_y to the excited states Φ_{ynm} or Φ_{xnm} where either an odd or an even number of E symmetry phonons is involved. The light is assumed to be parallel to a [100] crystal direction and the cases for $H=0$ and $H\neq0$ are shown.

It is clear that when no magnetic field is applied there is again no dichroism signal. When H is applied

TABLE II. The R_2 transition probabilities for circularly polarized light. The cases considered are those where either an even or an odd number of E symmetry phonons are involved. The light is parallel to a crystal [100] axis. The notation employed is the same as that used by Silsbee (Ref. 3) and ϵ is defined in Eq. (8).

		Light polarization σ_+ Initial state		Light polarization σ_- Initial state	
		Ψ_x	Ψ_y	Ψ_x	Ψ_y
$H=0$	Even number of E phonons	$\frac{1}{4}\lvert G_{n0}\rvert^2$	$(5/12)\lvert G_{n0}\rvert^2$	$\frac{1}{4}\lvert G_{n0}\rvert^2$	$(5/12)\lvert G_{n0}\rvert^2$
	Odd number of E phonons	$\frac{2}{3}\lvert G_{n1}\rvert^2$	$\frac{2}{3}\lvert G_{n1}\rvert^2$	$\frac{2}{3}\lvert G_{n1}\rvert^2$	$\frac{2}{3}\lvert G_{n1}\rvert^2$
$H\neq 0$	Even number of E phonons	$\frac{1}{2}\lvert G_{n0}\rvert^2[\frac{1}{2}-(2/\sqrt{3})\epsilon]$	$\frac{1}{2}\lvert G_{n0}\rvert^2[\frac{5}{6}+(2/\sqrt{3})\epsilon]$	$\frac{1}{2}\lvert G_{n0}\rvert^2[\frac{1}{2}+(2/\sqrt{3})\epsilon]$	$\frac{1}{2}\lvert G_{n0}\rvert^2(\frac{5}{6}-2\epsilon/\sqrt{3})$
	Odd number of E phonons	$\lvert G_{n1}\rvert^2(\frac{2}{3}+2\epsilon/\sqrt{3})$	$\lvert G_{n1}\rvert^2(\frac{2}{3}-2\epsilon/\sqrt{3})$	$(-2\epsilon/\sqrt{3}+\frac{2}{3})\lvert G_{n1}\rvert^2$	$\lvert G_{n1}\rvert^2(\frac{2}{3}+2\epsilon/\sqrt{3})$
		$G_{n0}=g_i\int\rho_{n0}(r)[\mu_{11/2}{}^{\circ}(-r)+\mu_{11/2}{}^{\circ}(r)]rdr$			
		$G_{n1}=\pi 1/\sqrt{2}g_i\int\rho_{n1}(r)[\mu_{11/2}{}^{\circ}(-r)-\mu_{11/2}{}^{\circ}(r)]rdr$			

we obtain for transitions involving an even number of E phonons

$$dA(H)=(n_y-n_x)/(n_y+n_x)\epsilon\sqrt{3}, \qquad (20)$$

which is just the same as the dichroism of the zero-phonon line [Eq. (15)]. When an odd number of E modes is involved the dichroism is

$$dA(H)=-(n_y-n_x)/(n_y+n_x)\epsilon\sqrt{3}, \qquad (21)$$

which is just the negative of Eq. (20). It should be noted that if the E symmetry phonons are combined with any number of A_2 symmetry phonons, Eqs. (20) and (21) remain unaltered. It should therefore be possible to use the sideband dichroism to decide which absorption peaks are due to an odd number of E phonons in addition to A phonons and which are due to A phonons plus an even number of E phonons.

The first-moment changes in sideband peaks caused by a magnetic field can be calculated in the same way as for the zero-phonon transition. However, the peaks observed experimentally are not well enough resolved to gain any quantitative information.

III. EXPERIMENTAL METHOD

The samples used were Harshaw single crystals of KCl and KF. They were typically cleaved to a thickness of approximately 3 mm. The R centers were formed in KCl by x irradiation at 125 kV and 10 mA and then by bleaching in the F band using a Corning 4–94 filter. Both steps were carried out at room temperature. The concentration of R centers could be varied by varying the irradiation time. The best results were obtained when the zero phonon line at 4°K had an optical density of approximately 1 which required about 2 h of x irradiation. The KCl could also be colored by γ rays or electron bombardment. Production of R centers in KF by x irradiation was inefficient. Instead optical density of 1 in the R_2 zero-phonon line was obtained by bombarding the sample with a 20-μA beam of 1.3-MeV electrons.

The first experiments were carried out using a small superconducting magnet.[12] However, the range of temperature over which measurements could be made was limited by the characteristics of the magnet. Furthermore, it was difficult to apply stress in this configuration. Therefore, in later experiments the sample was mounted in an optical immersion Dewar which was placed between the poles of a P.E.M. model 12A electromagnet. Holes were bored through the pole caps so that light could be shone parallel to the field.

The temperature of the bath in the range $4.2>T>1.3$°K was monitored by measuring the pressure above the helium. For experiments above 4.2°K a $\frac{1}{10}$-W carbon resistor with room temperature value of 100 Ω was mounted on the sample and the resistance was monitored as the helium fell below the sample. A heater in the helium allowed the temperature to be held to ±0.2°K up to 10°K. The stress was applied to the sample at right angles to the H field via an anvil and piston supported by two concentric thin-walled stainless-steel tubes which led out of the Dewar. The force was provided by a hydraulic pump.

The magnitude of the dichroism was only about 1% of the absorption, and it was necessary to use a phase-sensitive detection technique. Unpolarized light from a tungsten lamp was passed through a water filter and was focused on the sample. The emerging light passed through a quarter wave plate of appropriate wavelength (7420 Å for KCl and 5892 Å for KF) which was rotated at a frequency of 19 cps. Then the light passed through a linear polaroid and into a Jarrell Ash $\frac{1}{2}$-m Ebert scanning monochromator. The output of the photomultiplier (liquid nitrogen cooled 7102 for KCl and IP28 for KF) was fed into a Keithley 610B electrometer as a preamplifier and then into a PAR JB4 lock-in amplifier. The reference signal was provided by the rotating quarter wave plate and was double the rotation frequency. The output of the lock-in amplifier was then fed into a recorder. The final signal was then the difference between right and left circular light plotted versus wavelength.

IV. EXPERIMENTAL RESULTS

A typical experimental trace of the magnetic circular dichroism signal in KF is shown in Fig. 3. There is a pronounced zero-phonon line and two well-resolved

[12] This magnet was constructed by Dr. Harold Fetterman.

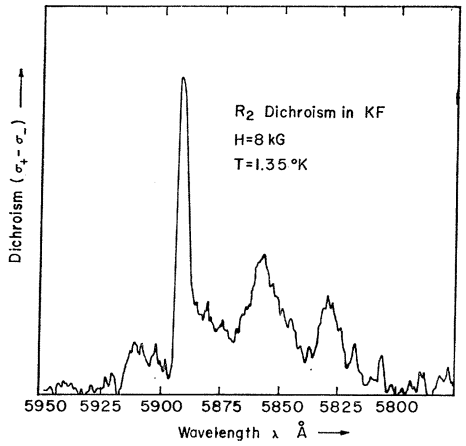

FIG. 3. The dichroism observed at 1.35°K in the R_2 band of KF with a magnetic field H parallel to [100] of magnitude 8 kG. The magnitude of the peak signal is of the order of 1% of the R_2 absorption.

sideband peaks. The dichroism in KCl is similar but the sidebands are not so well resolved. The discussion of the data is divided into three parts:

(1) Experiments with no applied stress: The change in first moment of the zero-phonon line is obtained and values of Λb and $\Lambda\lambda b$ are deduced.

(2) Experiments with applied stress: The stress dependence of the zeroth moment is analyzed.

(3) Experiments on the sidebands: The peaks are assigned to phonons of definite symmetry.

A. Change in First Moment of the Zero-Phonon Line

It is possible to write the results of Sec. II in a simpler form. The dichroism results from an excess absorption of σ_+ from level Ψ_y at energy $(E_0+\frac{1}{2}\delta_0)$ and an excess absorption of σ_- from level Ψ_x at energy $(E_0-\frac{1}{2}\delta_0)$. Here E_0 is the energy of the zero-phonon line with no internal stress or magnetic field and δ_0 is the splitting of Ψ_x and Ψ_y in the internal strain. Table I shows that the excess absorption is proportional to ϵ. If rigid shifts of the lines are assumed, the shape of the dichroism signal $f_0(E)$ can be written in the form

$$f_D(E)=f_{\sigma_+}(E)-f_{\sigma_-}(E)$$
$$=[n_y f(E_0-\tfrac{1}{2}\delta_0)-n_x f(E_0+\tfrac{1}{2}\delta_0)]\epsilon(2/\sqrt{3})\,|G_{10}|^2,$$

where $f(E_0)$ is the shape of the original zero-phonon lines. We shall see in the next section that the splitting of the levels Ψ_y, Ψ_x in the internal strain of the crystal δ_0 is approximately 1.5 cm^{-1}. The width of the line is 6 A or about 10 cm^{-1}. Making the assumption that $\delta_0 \ll$ linewidth we have to first order

$$f_D(E)=[(n_y-n_x)\epsilon f(E_0)$$
$$-(n_y+n_x)\tfrac{1}{2}\Delta f'(E_0)](2/\sqrt{3})\,|G_{10}|^2.$$

Thus the dichroism signal can be fitted to first order by the sum of the absorption shape function $f(E)$ and its derivative with respect to E, $f'(E)$. The first term, which involves $f(E)$, is just the area or zeroth moment. The second term which involves $f'(E)$ gives the first-moment change. It can be seen that the amount of $f'(E)$ required to fit the data yields a value of Δ.

An example of such a fit is shown in Fig. 4. A Gaussian line shape of half-width 6.0 A was assumed for $f(E_0)$ and was found to give the closest fit. The actual line shape is probably something between a Gaussian and a Lorentzian but the difference in the results is small. The largest error occurs in determining the precise experimental shape of the dichroism to be associated with the zero-phonon line as there is some overlap with the multiphonon structure. This is allowed for by extrapolating the first phonon peak under the zero-phonon line as accurately as possible. This procedure is likely to be inaccurate particularly at the short-wavelength side of the line (~7410 Å) and the fit is not good in this region. There is also some discrepancy at the long-wavelength side (~7428 Å) where the experimental curve has a small maximum. This shape cannot be reproduced theoretically without introducing higher moments. However, the base line is not flat at this side of the zero-phonon line but shows a slow change over several hundred angstroms that may indicate the presence of a broad underlying line. It is believed, then, that this subsidiary peak is not due to the R transition. The uncertainty in the base line makes it impossible to detect changes in the higher moments, and it is only attempted here to fit the main maximum and minimum by assuming that changes in moments higher than the first can be neglected. In Fig. 4, the fit is excellent between 7425 Å$>\lambda>$7415 Å and the

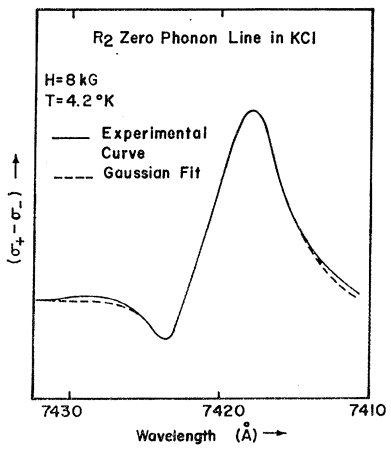

FIG. 4. The dichroism of the zero-phonon line in KCl plotted versus wavelength is shown as the full line. The effect of the first sideband has been subtracted. The broken line is a fit of the form $[f(\lambda)-5.1f'(\lambda)]$ where $f(\lambda)=A\exp(-\lambda^2/13)$ is a Gaussian of half-width 6 Å. The small peak in the experimental data at $\lambda=7428$ Å is believed to be due to an underlying line. The poor fit for $\lambda<7415$ Å is due to inaccuracy in estimating the contribution from the first sideband peak. A value of the first-moment change $2d\bar{E}=5.0\times10^{-6}$ eV is deduced from this data.

value of ΔE is obtained to an estimated accuracy of $\pm 10\%$.

Measurements were made on both KCl and KF in the range $4.2°K > T > 1.3°K$ and the calculated values of ΔE are plotted in Fig. 5 as a function of $1/T$. In both cases the points lie on a straight line. The gradients of the two lines give values of $\Lambda\lambda b$ and the intercepts at $1/T=0$ give values of Λb.

KF: $\Lambda b = 0.11 \pm 0.01$, $\Lambda\lambda b = -0.68 \pm 0.07$ cm^{-1};

KCl: $\Lambda b = 0.06 \pm 0.01$, $\Lambda\lambda b = -0.32 \pm 0.03$ cm^{-1}.

It is clear that in each crystal the angular momentum is quenched appreciably by the Jahn-Teller interaction, but that the coupling is less strong in KF. This is consistent with the fact that the sideband structure is better resolved in KF than in KCl. The values for KCl are close to those reported by Burke[13] who made similar measurements at higher fields and temperatures, and to those reported by Krupka and Silsbee[7] from spin-resonance data. The values of b, if Λ is assumed to be unity, correspond to values of the parameter k^2 (as defined by Child and Longuet-Higgins[10]) of $k^2=2.3$ for KF and $k^2=3.2$ for KCl. In each case λ is negative (as it is in the excited state of the F center) and we have

$\lambda = 6.18$ cm^{-1} for KF and $\lambda = 5.43$ cm^{-1} for KCl.

B. Effect of the Uniaxial Stress on the Zeroth Moment of the Dichroism Signal

The upper curve in Fig. 6 shows the zeroth moment of the dichroism in KCl plotted as a function of temperature. The broken line is a plot of the theoretical expression [Eq. (16)] assuming $\delta=0$ and using the values $\Lambda\lambda b = -0.32$ cm^{-1} and $\Lambda b = 0.06$ as obtained in the previous section. The fit of this curve to the experimental points is good except at the lowest temperature where the theory predicts too large a value. It was considered likely that the discrepancy could be explained by the effect of the internal strains in the lattice. When the temperature is of the same order as the splitting of the ground state by the strain, $kT \sim \delta_0$, the dichroism will be smaller than if δ_0 were negligible. In order to test this idea, the dichroism was measured with an applied stress Σ parallel to a [100] crystal direction and perpendicular to the magnetic field. The effect of the stress is shown in the lower curves of Fig. 6. The size of the dichroism signal decreases as the stress is increased. In particular, when $\delta \gg kT$, we have from Eq. (16) that

$$dA(H) = \epsilon\sqrt{3} = (\Delta/\delta)\sqrt{3},$$

which shows that the signal should be proportional to $1/\delta$ at fixed H and temperature. This condition holds for all values of applied stress at $T=1.4°K$, and it is seen that the magnitudes of the signals are inversely proportional to δ at this temperature. An estimate of δ_0 can be made by comparing the observed value of the dichroism at 1.4°K when there is no applied stress with

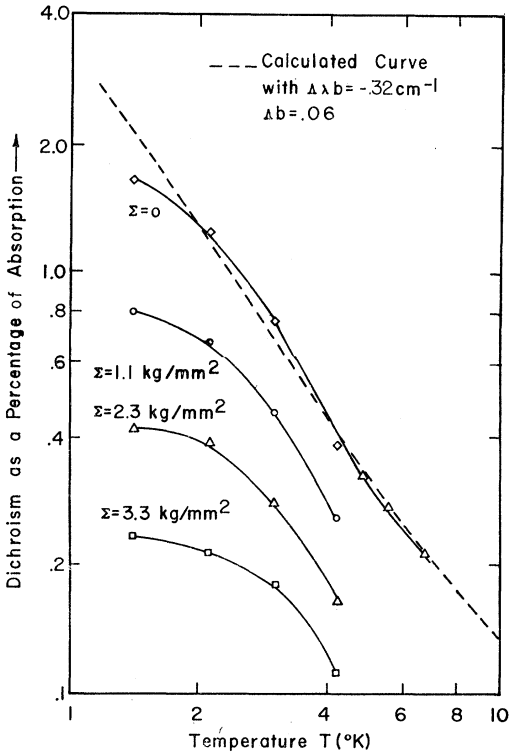

FIG. 6. The values of the zeroth moment of the R_2 dichroism in KCl as a percentage of the absorption plotted versus T. The upper curve shows the case where no stress is applied. The three points at the highest temperature were measured on a different sample than the other four points and the internal strains may be different. The broken line is a plot of the theoretical expression given in Eq. (17) using the values of the parameters deduced in the previous section. The lower curves demonstrate than an applied uniaxial stress Σ decreases the dichroism. In all cases $H=6$ kG.

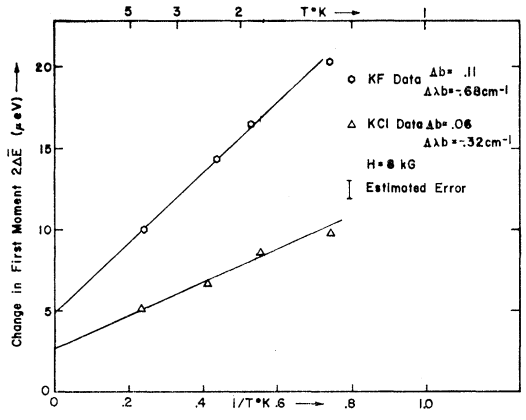

FIG. 5. The values of the first moment shift in the R_2 zero phonon line dichroism when a magnetic field of 8 kG is applied to KF and KCl are plotted versus $1/T$. In both cases the points fall on a straight line. The gradient yields values of $\Lambda\lambda b$ and the intercept yields values of Λb [see Eq. (19)].

[13] W. J. Burke, private communication (to be published).

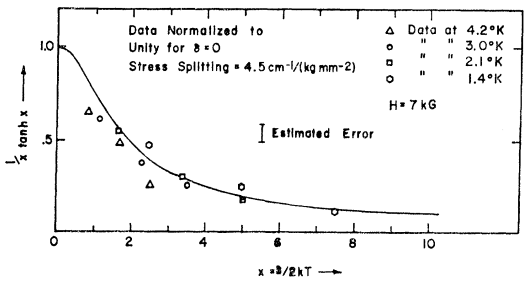

FIG. 7. The zeroth moment of the R_2 dichroism in KCl is plotted versus the splitting caused by an applied uniaxial stress δ. The measurements were made at four different temperatures, and in order to compare the data with the theoretical line they were normalized to unity for $\delta=0$ at each temperature. The line is a plot of the theoretical expression given in Eq. (16). The constant factor connecting δ with the stress Σ, 4.5 cm^{-1}/kg/mm^2, was obtained from Silsbee (Ref. 3).

the value predicted if $\delta_0=0$. From Eqs. (16) and (17) and Fig. 6,

$$\frac{2kT}{\delta_0}\tanh\frac{\delta_0}{2kT}=\frac{1.65}{2.10}=0.79,$$

where $T=1.4$°K. Thus $\delta_0=1.5$ cm^{-1}. Of course, the internal strain is different at different centers and δ_0 is really some average value. It is within a factor of two of the estimates in Refs. 3 and 6 of internal strain.

The validity of the expression giving the stress dependence of the dichroism [Eq. (16)] can be tested by plotting the data obtained at different stresses and temperatures and comparing it with an expression of the form given in Eq. (16). In order to do this the factor connecting an applied stress with the level splitting δ must be known. Fortunately, a value is known from Silsbee's[3] work which is 4.5 cm^{-1}/kg/mm^2. If this value is used, the comparison between experiment and theory has all the parameters fixed. This is shown in Fig. 7 where an expression of the form $(1/x)\tanh x$ is plotted versus the dimensionless quantity $x=\delta/2kT$. The data at each temperature are scaled so that for $\delta=0$ the dichroism signal is unity. The parameter x must be regarded as a measure of δ with T constant. This enables the data at all four temperatures to be compared with a single curve. The percentage error is large when the dichroism is small, i.e., at large x, and no allowance has been made for δ_0. The agreement between theory and experiment is good, within the limits of the errors.

C. Dichroism in the Sidebands

The dichroism in the sidebands, as shown in Fig. 3, is not well enough resolved to permit a moments analysis. However, the selection rules summarized in Table II show that when an absorption sideband peak is caused by an odd number of E phonons the dichroism signal will have the opposite sign than for a peak associated with an even number of E phonons [Eqs. (20) and (21)]. The dichroism signal does not have "negative" peaks, but some absorption peaks correlate with minima in the dichroism signal. The upper two curves

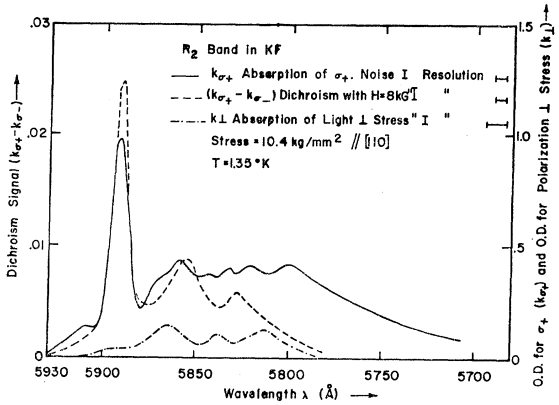

FIG. 8. Three curves of absorption in KF are shown plotted versus wavelength. The full line is the absorption of σ_+, with no applied perturbations. The sideband peaks may be due to symmetric of unsymmetric phonons. The broken line is the dichroism with $H=8$ kG. The peaks are due to even numbers of E symmetry phonons. The lower curve is the absorption of light polarized perpendicular to an applied stress. The stress is parallel to a [110] direction. The peaks in this case are due to odd number of E phonons and correlate with the minima of the dichroism signal.

in Fig. 8 are plots of the absorption of σ_+ light, $k_{\sigma+}$, and of the dichroism $(k_{\sigma+}-k_{\sigma-})$.

The zero-phonon line is pronounced in both curves which is consistent with the fact that this peak involves an even number (i.e., zero) of E modes. The absorption peaks at 5861 and 5832 Å can be correlated with the two dichroism peaks and are therefore presumed to be due to symmetric (i.e., A) phonons. (The dichroism peaks are at a slightly lower value of λ and this is believed to be due to the first-moment shift.) There are several peaks in the absorption curve that are absent in the dichroism. These are at $\lambda\sim5870$, 5841, 5820, and 5803 Å, and they correlate well with minima in the dichroism. It is believed that these peaks result from an odd number of E-symmetry phonons plus any number of symmetric phonons. This hypothesis was tested in a positive fashion by making absorption measurements in a sample subjected to a uniaxial stress. The light was polarized perpendicular to the stress which was applied parallel to a [110] crystal axis. In this configuration, when the stress splitting is much greater than kT, the only absorption occurs at sideband peaks caused by E symmetry phonons (this is discussed fully by Silsbee[3]). The lowest curve in Fig. 8 shows the experimental results at $T=1.35$°K when the stress splitting was approximately equivalent to 20°K. The zero-phonon line has almost entirely disappeared, as expected, and only three peaks are visible at 5867, 5839, and 5817 Å. These are close to the positions of the peaks in the absorption of σ_+ which do not appear in the dichroism. This demonstrates effectively that they are due to odd numbers of E modes. The observed peaks and their E-phonon assignments are summarized in Table III.

The dichroism signal falls to zero below the second peak at 5832 Å, whereas the σ_+ absorption continues

TABLE III. The observed sideband peaks in the R_2 transition in KF are listed according to wavelength and also according to the distance in energy from the zero-phonon line. The number of E modes involved in each peak are also shown. The energies are in approximate agreement with the calculations of Karo and Hardy.[a]

Wavelength (Å)	Distance from zero-phonon line (eV)	Number of E modes
5870	0.007	odd
5861	0.011	even
5841	0.020	odd
5832	0.022	even
5820	0.026	odd

[a] A. M. Karo and J. R. Hardy, Phys. Rev. **129**, 2024 (1963).

to below 5700 Å. There is thus no true broad-band dichroism. The decrease is due to the competition between the signals derived from peaks having even and odd numbers of E-symmetry phonons. In the higher-energy part of the band there are many phonons involved and the signals cancel.

V. SUMMARY

Magnetic circular dichroism has been observed with relatively low magnetic fields of about 8 kG in the zero-phonon line and sidebands of the R_2 transition in KCl and KF. The zero-phonon-line data were analyzed by a method of moments. The transition probabilities for circularly polarized light were calculated using vibronic ground-state wave functions appropriate to an E state that is distorted by the Jahn-Teller effect. The first-moment data provided a measure of the reduced orbital angular momentum and hence a measure of the Jahn-Teller coupling strength. The reduced spin-orbit interaction is also determined and is found to be negative in both crystals. The zeroth moment of the zero-phonon line was found to be sensitive to applied stress. The data, taken as a function of applied stress, are interpreted assuming that the interaction of the center with the magnetic field can be treated as a perturbation on the stress interaction. The splitting of the ground state in the internal crystal strain field is estimated. The sideband dichroism yields information about the symmetry of the phonons involved in the sideband peaks. All the experimental results agree well with the theoretical predictions which are based on the Van Doorn model with an E ground state distorted by a dynamic Jahn-Teller interaction.

ACKNOWLEDGMENTS

The author wishes to acknowledge many helpful discussions with Professor D. B. Fitchen and Professor R. H. Silsbee. He also wishes to thank Professor Silsbee for the use of his electromagnet. Special thanks are due to Dr. H. Fetterman for constructing the magnet used in the preliminary measurements and for helping in those measurements. Thanks are also due to Dr. W. Burke who made available his high-field data.

PHYSICAL REVIEW VOLUME 165, NUMBER 3 15 JANUARY 1968

Motion of the Piezoelectric Polaron at Zero Temperature

GEORGE WHITFIELD AND J. GERSTNER
Department of Physics, The Pennsylvania State University, University Park, Pennsylvania
AND
K. THARMALINGAM*
School of Engineering and Applied Science, Princeton University, Princeton, New Jersey
(Received 12 May 1967)

We analyze a series of theories which are used to obtain the energy-momentum relation for the piezoelectric polaron. Perturbation theory cannot be trusted, because there is a degeneracy in the unperturbed energy levels. The Tamm-Dancoff one-quantum cutoff in this case diagonalizes the degenerate states exactly, but has other shortcomings. The intermediate coupling theory gives what we believe is a reasonable energy-momentum relation, which starts out quadratically and becomes approximately linear as the velocity approaches the speed of sound.

I. INTRODUCTION

INTEREST in the polaron problem has been maintained for many years because it is a simple example of a particle interacting with a field, as well as an integral part of the understanding of electronic motion in ionic crystals.[1] It has recently become clear that the problem of electrons interacting with acoustic phonons in a piezoelectric crystal can be approximated by a Hamiltonian[2] which has the same form as the original polaron problem, and hence it serves as another interesting example of a particle-field interaction.

Whereas the original polaron problem (which we will refer to as the optical polaron) was analogous to a proton interacting with chargeless, spinless mesons, the piezoelectric polaron problem is analogous to quantum electrodynamics.

* Present address: Department of Mathematics, Westfield College, London, England.

[1] A recent review of work on the polaron is contained in *Polarons and Excitons*, edited by C. G. Kuper and G. D. Whitfield (Plenum Press, Inc., New York, 1963).

[2] A. R. Hutson, J. Appl. Phys. **32**, 2287 (1961).