Spectroscopic Study of the Symmetries and Deformation-Potential Constants of Singly Ionized Zinc in Germanium. Theory*

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This paper presents a theoretical study of the relative intensities and energy splittings of the excitation lines of a single-hole acceptor in a group-IV semiconductor. Group theoretical methods are used to obtain the selection rules for electric dipole transitions and to give the relative intensities of the stress-induced components of a given absorption line. This study became necessary in the course of our piezospectroscopic investigation of the excitation spectrum of singly ionized zinc in germanium because previous such studies lacked sufficient generality. The diagramatic representation of the results of our calculations are specifically suited to the above acceptor impurity. The theory reveals that the ratios of the intensities of the components of a $\Gamma_8 \rightarrow \Gamma_8$ transition depend upon two real parameters instead of one, as was previously believed. One of these parameters may be determined unambiguously from a measurement with uniaxial compression along a ⟨111⟩ direction. The magnitude of the other may be found from measurements with compression parallel to ⟨100⟩ and ⟨110⟩. At the same time symmetry assignments can be made to the stress-induced acceptor sublevels by comparison of the observed and theoretical relative intensities.

I. INTRODUCTION

Considerable effort has been devoted to the study of defects in crystals, and in the process of understanding such entities, the properties of both the defect and the host solid are elucidated. Some such defects which have been probed very thoroughly are chemical impurities introduced into semiconductors. Of these, group-III and group-V elements in silicon and germanium are classic examples. The model developed[1-15] to explain the effects of such impurities depicts these substitutional impurities as giant hydrogenlike atoms, their parameters being determined to a large extent by the anisotropic environment presented by the crystal. The spectroscopy of these and other impurities[16] has proved to be a powerful means for studying the nature of their energy states. The first observation of an excitation spectrum of an impurity in a semiconductor was that of Burstein *et al.*[17] Since then the effects of external perturbations such as magnetic field and uniaxial force have been used[16,18] to verify the quantum numbers, provided by theory, labelling the quantum states of the impurities. The present investigation represents such a spectroscopic study of singly ionized zinc in germanium. Preliminary work has been reported elsewhere.[19-21]

In the course of the present study, it was necessary to generalize the previous theories of the relative intensities of the stress-induced components of an excitation line belonging to a single-hole acceptor.[22-24] This generalization is discussed in detail in Sec. II. In it we establish that all the observed components have relative intensities that are determined at most by two independent real parameters. These parameters are related to the real and imaginary parts of two matrix elements of the electric-dipole moment. This holds for the most complex transition observed while for the simpler transitions no adjustable parameters are necessary. As will be seen, however, for a compression in directions other than ⟨100⟩ or ⟨111⟩, the relative intensities depend in addition on other parameters which are directly measurable. The detailed comparison of the experimental and theoretical studies has permitted us to establish the symmetry assignments of the ground state and several of the excited states. The deformation-potential constants of these states,[18,25] i.e., the splitting of the states per unit strain, have been determined. This paper contains the development of the theoretical machinery which we have employed in the analysis of our experiments. A second paper is being prepared in which the experimental results are described and analyzed.

II. THEORY

We consider the excitation spectrum of an acceptor in an elemental semiconductor such as silicon or germanium. The analysis of the excitation spectrum starts with the assumption that the states of a positive hole bound to a substitutional acceptor atom can be classified according to the irreducible representations of the point group T_d. Thus, we suppose that the distortion caused by the presence of the foreign atom does not alter the symmetry of the site. Our considerations will limit themselves at first to a single hole bound to a negatively charged acceptor ion. This model is applicable to the excitation spectrum of neutral group-III acceptors such as boron. However, we will devote particular interest to the excitation spectrum of singly

ionized group-II acceptors. Consider for example Zn in Ge. The neutral Zn acceptor can be regarded as Zn^{--} with two bound holes. If the material contains Sb as well as Zn the compensation can be such that not only will there be neutral zinc in the material but singly ionized Zn^- as well. The Zn^- acceptor can be regarded as a Zn^{--} ion with a single hole bound to it.

We are dealing with a system containing a particle of spin $\frac{1}{2}$ and characterized by a Hamiltonian which we designate by H_0. The states[16] of H_0 are classified according to the double-valued representations of the group $\bar{T}_d = \bar{E} \times T_d$, where $\bar{E}$ is the operation which describes a rotation by 2π. There are three representations of this sort, two of them two dimensional and one four dimensional. The character table and basis functions for the single-valued representations are given in Table I.[26] Here X, Y, Z behave as x, y, z, the components of a polar vector with respect to the cubic axes, and ξ, η, ζ behave as $yz(y^2-z^2)$, $zx(z^2-x^2)$, and $xy(x^2-y^2)$.

The double-valued representations of $\bar{T}_d$ are given in Table II. The basis functions of Γ_6 are α and β, the spin-$\frac{1}{2}$ states multiplied by a function φ_0 belonging to Γ_1, while the basis functions of Γ_7 are α and β multiplied by a function φ_0' belonging to Γ_2. We shall use two sets of functions that generate the representation Γ_8. They are the sets ψ_μ and $\varphi_\mu (\mu = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2})$ defined below

$$\psi_{3/2} = \frac{1}{\sqrt{2}}(X+iY)\alpha, \qquad \psi_{1/2} = \frac{i}{\sqrt{6}}[(X+iY)\beta - 2Z\alpha], \tag{1}$$

$$\psi_{-1/2} = \frac{1}{\sqrt{6}}[(X-iY)\alpha + 2Z\beta], \qquad \psi_{-3/2} = \frac{i}{\sqrt{2}}(X-iY)\beta,$$

and

$$\varphi_{3/2} = -\frac{1}{\sqrt{6}}[(\xi - i\eta)\alpha + 2\zeta\beta], \qquad \varphi_{1/2} = \frac{i}{\sqrt{2}}(\xi - i\eta)\beta, \tag{2}$$

$$\varphi_{-1/2} = \frac{1}{\sqrt{2}}(\xi + i\eta)\alpha, \qquad \varphi_{-3/2} = -\frac{i}{\sqrt{6}}[(\xi + i\eta)\beta - 2\zeta\alpha].$$

The reason why the sets (1) and (2) are needed will be explained later. We assume that the functions

TABLE I. Character table and basis functions for the point group T_d.

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	Basis functions
Γ_1	1	1	1	1	1	$X^2+Y^2+Z^2$
Γ_2	1	1	1	−1	−1	$X\xi + Y\eta + Z\zeta$
Γ_3	2	−1	2	0	0	$2Z^2-X^2-Y^2$ $\sqrt{3}(X^2-Y^2)$
Γ_4	3	0	−1	1	−1	ξ, η, ζ
Γ_5	3	0	−1	−1	1	X, Y, Z

TABLE II. Character table for the double-valued irreducible representations of $\bar{T}_d$.

$\bar{T}_d$	E	$\bar{E}$	$8C_3$	$8\bar{C}_3$	$3C_2$, $3\bar{C}_2$	$6S_4$	$6\bar{S}_4$	$6\sigma_d$, $6\bar{\sigma}_d$
Γ_6	2	−2	1	−1	0	$\sqrt{2}$	$-\sqrt{2}$	0
Γ_7	2	−2	1	−1	0	$-\sqrt{2}$	$\sqrt{2}$	0
Γ_8	4	−4	−1	1	0	0	0	0

X, Y, Z, ξ, η, ζ are real and normalized to unity. The two sets $\{\psi_\mu\}$ and $\{\varphi_\mu\}$ are orthonormal, and any ψ is orthogonal to any φ. The functions $\{\psi_\mu\}$ are eigenfunctions of the total angular-momentum operator J^2 with eigenvalue $\frac{15}{4}$ and of J_z with eigenvalue μ (where $\mu = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$) if X, Y, and Z are p functions. In general, however, this is not the case but the notation appropriate to $J=\frac{3}{2}$ states is kept for convenience. The notation for the φ functions has been selected with a considerable degree of arbitrariness purely with the object of simplifying the notation in the following developments; this will be pointed out in the pertinent places. The purpose of the study that follows is to analyze the relative intensities of the stress-induced components of the absorption lines.

A. Splitting of States under Stress

Within the linear approximation, the change in the potential energy of the hole, due to the stress is

$$V = \sum_{i,j} V_{ij}\epsilon_{ij}, \tag{3}$$

where

$$\epsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) \tag{4}$$

is the strain tensor, $\vec{u}(\vec{r})$ is the displacement, due to the stress, of the point originally at $\vec{r}$. In general, V_{ij} is an operator depending on both the position and the spin of the hole; we neglect the spin coordinate.

We now write V as follows:

$$V = V_{xx}\epsilon_{xx} + V_{yy}\epsilon_{yy} + V_{zz}\epsilon_{zz} + (V_{yz}+V_{zy})\epsilon_{yz} + (V_{zx}+V_{xz})\epsilon_{zx} + (V_{xy}+V_{yx})\epsilon_{xy}, \tag{5}$$

or

$$V = \tfrac{1}{3}(V_{xx}+V_{yy}+V_{zz})(\epsilon_{xx}+\epsilon_{yy}+\epsilon_{zz}) + \tfrac{1}{6}(2V_{zz}-V_{xx}-V_{yy})(2\epsilon_{zz}-\epsilon_{xx}-\epsilon_{yy}) + \tfrac{1}{2}(V_{xx}-V_{yy})(\epsilon_{xx}-\epsilon_{yy}) + (V_{yz}+V_{zy})\epsilon_{yz} + (V_{zx}+V_{xz})\epsilon_{zx} + (V_{xy}+V_{yx})\epsilon_{xy}. \tag{6}$$

In writing Eqs. (5) and (6), we have made use of the fact that ϵ_{ij} is a symmetric tensor. Needless to say, only the symmetric part of V_{ij} contributes

to V. It is sufficient to regard V_{ij} as a symmetric tensor; however, this conceals part of the symmetry properties of tensors of this form which we will make use of below. The advantage of Eq. (6) as compared to Eq. (5) is that $\frac{1}{3}(V_{xx}+V_{yy}+V_{zz})$ belongs to Γ_1, $2V_{zz}-V_{xx}-V_{yy}$ and $V_{xx}-V_{yy}$ to Γ_3, and $V_{zy}+V_{yz}$, $V_{zx}+V_{xz}$, and $V_{xy}+V_{yx}$ belong to Γ_5. This decomposition can be inferred from the reduction of the representation generated by the 6 components ϵ_{ij}, namely the symmetrized direct product[27] of Γ_5 by itself

$$[\Gamma_5\times\Gamma_5]=\Gamma_1+\Gamma_3+\Gamma_5 \quad . \tag{7}$$

The antisymmetric direct product[27] is

$$\{\Gamma_5\times\Gamma_5\}=\Gamma_4 \quad . \tag{8}$$

Under the influence of the field V induced by the strain, the levels of the acceptor can experience shifts and splittings. For a Γ_6 or a Γ_7 state only a shift occurs with no splitting as required by Kramers's theorem.[28] In considering the splitting of the Γ_8 states under stress, we require the matrix elements of V for states of the form

$$\Psi_\mu = a\psi_\mu + b\varphi_\mu \ , \tag{9}$$

where $|a|^2+|b|^2=1$ to ensure normalization. The matrix elements that we need are

$$\langle\Psi_{\mu'}|V|\Psi_\mu\rangle = |a|^2\langle\psi_{\mu'}|V|\psi_\mu\rangle + |b|^2\langle\varphi_{\mu'}|V|\varphi_\mu\rangle + a^*b\langle\psi_{\mu'}|V|\varphi_\mu\rangle + ab^*\langle\varphi_{\mu'}|V|\psi_\mu\rangle \ , \tag{10}$$

which are thus decomposed into a sum of four which we now discuss one after another. Take first the calculation of $\langle\psi_{\mu'}|V|\psi_\mu\rangle$. This necessitates the evaluation of $\psi^\dagger_{\mu'}\psi_\mu$. These 16 quantities are displayed in Table III. The table is more general than is required for the calculation of the matrix elements of the potential. The reason for this added generality is that later on we shall need products of the same kind for calculating matrix elements for transitions between different levels. The added generality consists in the tabulation of $\psi'^\dagger_{\mu'}\psi_\mu$, where $\psi'_{\mu'}$ is formed in the same manner as the functions (1) except that we have X', Y', Z', instead of X, Y, Z. The functions X', Y', Z' behave in the same way as X, Y, Z but are not necessarily equal to them. The nine products $X'_iX_j(i,j=1,2,3)$ form the basis for the nine-dimensional representation $\Gamma_5\times\Gamma_5$ of T_d which we have decomposed into a symmetric part [Eq. (7)] and an antisymmetric part [Eq. (8)]. The basis vectors of $\Gamma_5\times\Gamma_5$ after its reduction has been carried out are

$$f_0 = X'X+Y'Y+Z'Z \ ; \qquad (\Gamma_1) \tag{11}$$

$$f_1 = 2Z'Z-X'X-Y'Y = 3Z'Z-f_0 \ , \qquad (\Gamma_3) \tag{12}$$
$$f_2 = \sqrt{3}(X'X-Y'Y) \ ;$$

$$f_X = \tfrac{1}{2}(Y'Z+Z'Y) \ , \qquad (\Gamma_5) \tag{13}$$
$$f_Y = \tfrac{1}{2}(Z'X+X'Z) \ ,$$
$$f_Z = \tfrac{1}{2}(X'Y+Y'X) \ ;$$

and

$$f_\xi = \tfrac{1}{2}(Y'Z-Z'Y) \ , \qquad (\Gamma_4) \tag{14}$$
$$f_\eta = \tfrac{1}{2}(Z'X-X'Z) \ ,$$
$$f_\zeta = \tfrac{1}{2}(X'Y-Y'X) \ ,$$

where the symbols in parentheses designate the irreducible representations to which the above basis vectors belong. Furthermore f_1 and f_2 belong to the first and second rows, respectively, of Γ_3 in the representation generated by the basis given in the last column of Table I. They, being orthonormal, generate a unitary irreducible representation of T_d. In a similar way, the functions f_X, f_Y, and f_Z belong to the first, second, and third rows, respectively, of the representation Γ_5 generated by X, Y, and Z. The functions f_ξ, f_η, and f_ζ bear the same relation to Γ_4. We notice that if $X'=X$, $Y'=Y$, and $Z'=Z$, all three functions in Eq. (14) vanish. A similar result holds for the products $\varphi'^\dagger_{\mu'}\varphi_\mu$. They are expressed in terms of the functions g_0, g_1, g_2, g_X, g_Y, g_Z, g_ξ, g_η, g_ζ defined by equations identical to those used to define f_0, f_1, f_2, f_X, f_Y, f_Z, f_ξ, f_η, f_ζ except that X, Y, Z, X', Y', Z' are replaced by ξ, η, ζ, ξ', η', ζ', respectively. In a similar manner to the case for the construc-

TABLE III. Products of the type $\psi'^\dagger_\mu\psi_\mu$.

$\psi'^\dagger_\mu\psi_\mu$	$\psi_{3/2}$	$\psi_{1/2}$	$\psi_{-1/2}$	$\psi_{-3/2}$
$\psi'_{3/2}$	$\frac{1}{3}f_0-\frac{1}{6}f_1+if_\zeta$	$-\frac{1}{\sqrt{3}}(f_X+if_Y)-\frac{1}{\sqrt{3}}(f_\xi-if_\eta)$	$\frac{1}{6}f_2-\frac{i}{\sqrt{3}}f_Z$	0
$\psi'_{1/2}$	$-\frac{1}{\sqrt{3}}(f_X-if_Y)+\frac{1}{\sqrt{3}}(f_\xi+if_\eta)$	$\frac{1}{3}f_0+\frac{1}{6}f_1+\frac{i}{3}f_\zeta$	$-\frac{2}{3}(f_\xi-if_\eta)$	$\frac{1}{6}f_2-\frac{i}{\sqrt{3}}f_Z$
$\psi'_{-1/2}$	$\frac{1}{6}f_2+\frac{i}{\sqrt{3}}f_Z$	$\frac{2}{3}(f_\xi+if_\eta)$	$\frac{1}{3}f_0+\frac{1}{6}f_1-\frac{i}{3}f_\zeta$	$\frac{1}{\sqrt{3}}(f_X+if_Y)-\frac{1}{\sqrt{3}}(f_\xi-if_\eta)$
$\psi'_{-3/2}$	0	$\frac{1}{6}f_2+\frac{i}{\sqrt{3}}f_Z$	$\frac{1}{\sqrt{3}}(f_X-if_Y)+\frac{1}{\sqrt{3}}(f_\xi+if_\eta)$	$\frac{1}{3}f_0-\frac{1}{6}f_1-if_\zeta$

tion of Eqs. (11)–(14), use has been made of the facts that $[\Gamma_4\times\Gamma_4]=\Gamma_1+\Gamma_3+\Gamma_5$ and $\{\Gamma_4\times\Gamma_4\}=\Gamma_4$. The results are given in Table IV. We now need tables for the cross terms $\psi_\mu^{\dagger}\varphi_\mu$ and $\varphi_\mu'^{\dagger}\psi_\mu$. Consider the products $\psi_\mu'^{\dagger}\varphi_\mu$ which are linear combinations of members of the set $X'\xi$, $X'\eta$, $X'\zeta$, $Y'\xi$, $Y'\eta$, $Y'\zeta$, $Z'\xi$, $Z'\eta$, $Z'\zeta$ that generates the representation

$$\Gamma_4\times\Gamma_5=\Gamma_2+\Gamma_3+\Gamma_4+\Gamma_5 \ . \tag{15}$$

The reduction of this representation is accomplished with the following functions:

$$h_0=X'\xi+Y'\eta+Z'\zeta \ ; \qquad (\Gamma_2) \tag{16}$$

$$h_1=Y'\eta-X'\xi \ , \qquad h_2=\sqrt{3}\,Z'\zeta \ ; \qquad (\Gamma_3) \tag{17}$$

$$h_X=\tfrac{1}{2}(Y'\zeta-Z'\eta) \ , \quad h_Y=\tfrac{1}{2}(Z'\xi-X'\zeta) \ , \quad h_Z=\tfrac{1}{2}(X'\eta-Y'\xi) \ ; \qquad (\Gamma_5) \tag{18}$$

and

$$h_\xi=\tfrac{1}{2}(Y'\zeta+Z'\eta) \ , \quad h_\eta=\tfrac{1}{2}(Z'\xi+X'\zeta) \ , \quad h_\zeta=\tfrac{1}{2}(X'\eta+Y'\xi) \ . \qquad (\Gamma_4) \tag{19}$$

The functions h_X, h_Y, h_Z behave as X, Y, Z while h_ξ, h_η, h_ζ behave as ξ, η, ζ. It is interesting to note that h_1 and h_2 behave as $xyz(2z^2-x^2-y^2)$ and $\sqrt{3}xyz(x^2-y^2)$, respectively. The above products are given in Table V.

In a similar way, we construct the functions $\bar{h}$ corresponding to the products $\varphi_\mu'^{\dagger}\psi_\mu$. They are identical to Eqs. (16)–(19) except that X', Y', Z' are replaced by X, Y, Z and ξ, η, ζ, by ξ', η', ζ'. The corresponding table for $\varphi_\mu'^{\dagger}\psi_\mu$ looks like the Hermitian conjugate of Table V except that the functions h are replaced by the functions $\bar{h}$. In the determination of the splitting of a Γ_8 state the two sets of functions h and $\bar{h}$ are identical.

The matrix elements of V on the left-hand side of Eq. (10) can now be evaluated using an orthogonality theorem[29] of the theory of group representations. From Eq. (6) and by inspection of Tables III–V, we obtain the following matrix expression of V:

$$\begin{aligned}[V]=&a'I\,(\epsilon_{xx}+\epsilon_{yy}+\epsilon_{zz})\\&+b'(\epsilon_{xx}(J_x^2-\tfrac{5}{4}I)+\epsilon_{yy}(J_y^2-\tfrac{5}{4}I)+\epsilon_{zz}(J_z^2-\tfrac{5}{4}I))\\&+(2d'/\sqrt{3})(\{J_yJ_z\}\epsilon_{yz}+\{J_zJ_x\}\epsilon_{zx}+\{J_xJ_y\}\epsilon_{xy}) \ ,\end{aligned} \tag{20}$$

where I is the unit 4×4 matrix, and J_x, J_y, and J_z are the matrix operators corresponding to the components of the angular-momentum operator $\vec{J}$ with $J=\frac{3}{2}$. We have used the form given by Luttinger.[30] Details of the derivation of Eq. (20), and other pertinent information including the definition of the symbols used, are given in the Appendix. The symbols used for the deformation-potential constants refer, in the literature,[25] explicitly to the ground state of an acceptor but the form of the expression is identical for all Γ_8 states. In referring to an excited Γ_8 state an appropriate symbol is chosen.[18] The conventional notation for the strain components is $e_{ij}=\epsilon_{ij}$ if $i=j$ and $e_{ij}=2\epsilon_{ij}$ if $i\neq j$.

In the experiments described in the present work, a uniaxial compression is applied along any one of the simple crystallographic directions $\langle111\rangle$, $\langle100\rangle$, and $\langle110\rangle$. Thus, we will be interested in determining the splitting of a Γ_8 state for compression along each of these directions.

1. *Applied Force along the* [111] *Axis*

Under a uniaxial compression $\vec{F}$ along a $\langle111\rangle$ axis the site symmetry of the substitutional impurity becomes that of the point group C_{3v}. The double-valued representations of C_{3v} are given in Table VI. A level characterized by $\Gamma_8(\bar{T}_d)$ reduces to $\Gamma_4+\Gamma_5+\Gamma_6$ of $\bar{C}_{3v}$. Except in such cases where no confusion can arise we will specify the point group to which a given irreducible representation belongs by including the Schoenflies symbol for this group in parentheses following the designation of

TABLE IV. Products of the type $\varphi_\mu'^{\dagger}\varphi_\mu$.

$\varphi_\mu'^{\dagger}\ \varphi_\mu$	$\varphi_{3/2}$	$\varphi_{1/2}$	$\varphi_{-1/2}$	$\varphi_{-3/2}$
$\varphi'^{\dagger}_{3/2}$	$\frac{1}{3}g_0+\frac{1}{6}g_1-\frac{i}{3}g_\zeta$	$-\frac{1}{\sqrt{3}}(g_X+ig_Y)+\frac{1}{\sqrt{3}}(g_\xi-ig_\eta)$	$-\frac{1}{6}g_2-\frac{i}{\sqrt{3}}g_Z$	$\frac{2}{3}(g_\xi+ig_\eta)$
$\varphi'^{\dagger}_{1/2}$	$-\frac{1}{\sqrt{3}}(g_X-ig_Y)-\frac{1}{\sqrt{3}}(g_\xi+ig_\eta)$	$\frac{1}{3}g_0-\frac{1}{6}g_1-ig_\zeta$	0	$-\frac{1}{6}g_2-\frac{i}{\sqrt{3}}g_Z$
$\varphi'^{\dagger}_{-1/2}$	$-\frac{1}{6}g_2+\frac{i}{\sqrt{3}}g_Z$	0	$\frac{1}{3}g_0-\frac{1}{6}g_1+ig_\zeta$	$\frac{1}{\sqrt{3}}(g_X+ig_Y)+\frac{1}{\sqrt{3}}(g_\xi-ig_\eta)$
$\varphi'^{\dagger}_{-3/2}$	$-\frac{2}{3}(g_\xi-ig_\eta)$	$-\frac{1}{6}g_2+\frac{i}{\sqrt{3}}g_Z$	$\frac{1}{\sqrt{3}}(g_X-ig_Y)-\frac{1}{\sqrt{3}}(g_\xi+ig_\eta)$	$\frac{1}{3}g_0+\frac{1}{6}g_1+\frac{i}{3}g_\zeta$

TABLE V. Products of the type $\psi'^{\dagger}_{\mu}\,\varphi_{\mu}$.

$\psi'^{\dagger}_{\mu}\,\varphi_{\mu}$	$\varphi_{3/2}$	$\varphi_{1/2}$	$\varphi_{-1/2}$	$\varphi_{-3/2}$
$\psi'_{3/2}$	$\frac{1}{2\sqrt{3}}h_1+\frac{i}{\sqrt{3}}h_\xi$	0	$\frac{1}{2}h_0-\frac{1}{2\sqrt{3}}h_2+ih_Z$	$\frac{1}{\sqrt{3}}(h_X-ih_Y)+\frac{1}{\sqrt{3}}(h_\xi+ih_\eta)$
$\psi'_{1/2}$	$\frac{2}{3}(h_X-ih_Y)$	$-\frac{1}{2\sqrt{3}}h_1-\frac{i}{\sqrt{3}}h_\xi$	$\frac{1}{\sqrt{3}}(h_X-ih_Y)-\frac{1}{\sqrt{3}}(h_\xi-ih_\eta)$	$-\frac{1}{6}h_0-\frac{1}{2\sqrt{3}}h_2-\frac{i}{3}h_Z$
$\psi'_{-1/2}$	$-\frac{1}{6}h_0-\frac{1}{2\sqrt{3}}h_2+\frac{i}{3}h_Z$	$-\frac{1}{\sqrt{3}}(h_X-ih_Y)+\frac{1}{\sqrt{3}}(h_\xi+ih_\eta)$	$-\frac{1}{2\sqrt{3}}h_1+\frac{i}{\sqrt{3}}h_\xi$	$-\frac{2}{3}(h_X+ih_Y)$
$\psi'_{-3/2}$	$-\frac{1}{\sqrt{3}}(h_X+ih_Y)-\frac{1}{\sqrt{3}}(h_\xi-ih_\eta)$	$\frac{1}{2}h_0-\frac{1}{2\sqrt{3}}h_2-ih_Z$	0	$\frac{1}{2\sqrt{3}}h_1-\frac{i}{\sqrt{3}}h_\xi$

the representation. Since the representations $\Gamma_5(\bar{C}_{3v})$ and $\Gamma_6(\bar{C}_{3v})$ are complex conjugates of one another, the levels to which they belong are degenerate under time-reversal symmetry.[31] The symmetry of the resultant level will be designated by Γ_{5+6}.

The components of strain in this case are $e_{xx}=e_{yy}=e_{zz}=(\frac{1}{3}T)(s_{11}+2s_{12})$ and $e_{xy}=e_{yz}=e_{zx}=(\frac{1}{3}T)s_{44}$, where T is the stress and is negative for compression, and the s_{ij}'s are the elastic compliance coefficients.[32,33] Equation (20) now becomes

$$[V]=[a'(s_{11}+2s_{12})-(5d'/8\sqrt{3})s_{44}]TI+(d'/2\sqrt{3})s_{44}TJ_n^2, \tag{21}$$

where J_n is the component of $\vec{J}$ along [111]. The orthonormal wave functions that diagonalize Eq. (21) are

$$\begin{aligned}
\Lambda_{3/2}&=\frac{i}{\sqrt{2}}\Psi_{3/2}+\frac{1+i}{\sqrt{6}}\Psi_{1/2}+\frac{1}{\sqrt{6}}\Psi_{-1/2}\ ,\\
\Lambda_{1/2}&=-\frac{i}{\sqrt{6}}\Psi_{1/2}+\frac{1+i}{\sqrt{6}}\Psi_{-1/2}+\frac{1}{\sqrt{2}}\Psi_{-3/2}\ ,\\
\Lambda_{-1/2}&=-\frac{i}{\sqrt{2}}\Psi_{3/2}+\frac{1+i}{\sqrt{6}}\Psi_{1/2}+\frac{1}{\sqrt{6}}\Psi_{-1/2}\ ,\\
\Lambda_{-3/2}&=\frac{i}{\sqrt{6}}\Psi_{1/2}-\frac{1+i}{\sqrt{6}}\Psi_{-1/2}+\frac{1}{\sqrt{2}}\Psi_{-3/2}\ .
\end{aligned} \tag{22}$$

The functions $\Lambda_{\pm 3/2}$ are degenerate, belong to Γ_{5+6} and correspond to the energy eigenvalue $a'(s_{11}+2s_{12})T+(d'/2\sqrt{3})s_{44}T$, while $\Lambda_{\pm 1/2}$ belong to $\Gamma_4(\bar{C}_{3v})$ and to the eigenvalue $a'(s_{11}+2s_{12})T-(d'/2\sqrt{3})s_{44}T$. The energy separation of these sublevels is, thus,

$$\Delta'_{111}=(d'/\sqrt{3})s_{44}T\ . \tag{23}$$

The subindices $-\frac{3}{2}$, $-\frac{1}{2}$, $\frac{1}{2}$, $\frac{3}{2}$ in Λ_μ should not be construed to have any more significance than that explicitly stated.

2. *Applied Force along the* [001] *Axis*

The new point group for $\vec{F}\parallel\langle 100\rangle$ is D_{2d}, and Γ_8 reduces to $\Gamma_6(\bar{D}_{2d})+\Gamma_7(\bar{D}_{2d})$. The double-valued irreducible representations of $\bar{D}_{2d}$ are given in Table VII. The components of the strain are $e_{xx}=e_{yy}=s_{12}T$, $e_{zz}=s_{11}T$ and $e_{xy}=e_{yz}=e_{zx}=0$. Equation (20) becomes

$$[V]=a'(s_{11}+2s_{12})TI+b'T(s_{11}-s_{12})(J_z^2-5I/4)\ . \tag{24}$$

The Γ_8 level splits into two sublevels with wave functions $\Psi_{\pm 3/2}$ which belong to $\Gamma_6(\bar{D}_{2d})$ with eigenvalue $a'(s_{11}+2s_{12})T+b'(s_{11}-s_{12})T$ and $\Psi_{\pm 1/2}$ which belongs to $\Gamma_7(\bar{D}_{2d})$ with eigenvalue $a'(s_{11}+2s_{12})T-b'(s_{11}-s_{12})T$. The difference in energy of these sublevels is

$$\Delta'_{100}=2b'(s_{11}-s_{12})T\ . \tag{25}$$

It should be noted that if the selection of the functions φ_μ [see Eqs. (2)] had been made in analogy to that of ψ_μ, then the association of the indices $\pm\frac{3}{2}$ with $\Gamma_6(\bar{D}_{2d})$ and of $\pm\frac{1}{2}$ with $\Gamma_7(\bar{D}_{2d})$ would have been misleading. Had we selected φ_μ in the same way as the ψ_μ, $\varphi_{\pm 3/2}$ would have generated the same representation as the $\psi_{\pm 1/2}$, and similarly for $\varphi_{\pm 1/2}$ and $\psi_{\pm 3/2}$.

3. *Applied Force along the* [110] *Axis*

For $\vec{F}\parallel\langle 110\rangle$, the site symmetry of the impurity becomes C_{2v}, and Γ_8 reduces to $2\Gamma_5(\bar{C}_{2v})$. The strain components are $e_{xx}=e_{yy}=(\frac{1}{2}T)(s_{11}+s_{12})$, $e_{zz}=s_{12}T$, $e_{yz}=e_{zx}=0$, and $e_{xy}=(\frac{1}{2}T)s_{44}$. Equation (20) now becomes

$$\begin{aligned}[V]=a'(s_{11}+2s_{12})TI-\tfrac{1}{2}b'(s_{11}-s_{12})T(J_z^2-5I/4)\\ +(d'/2\sqrt{3})s_{44}T\{J_xJ_y\}\ .\end{aligned} \tag{26}$$

The orthonormal wave functions that diagonalize $[V]$ are

TABLE VI. The double-valued representations of C_{3v}.

$\bar{C}_{3v}$	E	$\bar{E}$	$2C_3$	$2\bar{C}_3$	$3\sigma_v$	$3\bar{\sigma}_v$
Γ_4	2	−2	1	−1	0	0
Γ_5	1	−1	−1	1	i	$-i$
Γ_6	1	−1	−1	1	$-i$	i

TABLE VII. The double-valued representations of D_{2d}.

$\bar{D}_{2d}$	E	$\bar{E}$	$2S_4$	$2\bar{S}_4$	C_2, $\bar{C}_2$	$2C_2'$, $2\bar{C}_2'$	$2\sigma_d$, $2\bar{\sigma}_d$
Γ_6	2	−2	$\sqrt{2}$	$-\sqrt{2}$	0	0	0
Γ_7	2	−2	$-\sqrt{2}$	$\sqrt{2}$	0	0	0

$$\begin{aligned}
\Theta_{3/2} &= (1+\gamma^2)^{-1/2}(\Psi_{1/2} + i\gamma\Psi_{-3/2}) ,\\
\Theta_{1/2} &= (1+\gamma^2)^{-1/2}(i\Psi_{3/2} + \gamma\Psi_{-1/2}) ,\\
\Theta_{-1/2} &= (1+\gamma^2)^{-1/2}(\gamma\Psi_{1/2} - i\Psi_{-3/2}) ,\\
\Theta_{-3/2} &= (1+\gamma^2)^{-1/2}(-i\gamma\Psi_{3/2} + \Psi_{-1/2}) ,
\end{aligned} \tag{27}$$

where

$$\gamma = [\Delta'_{100} + (\Delta'^2_{100} + 3\Delta'^2_{111})^{1/2}]/\sqrt{3}\Delta'_{111} \quad . \tag{28}$$

$\Theta_{\pm 3/2}$ are degenerate with an eigenvalue of $a'(s_{11}+2s_{12})T + \frac{1}{4}(\Delta'^2_{100} + 3\Delta'^2_{111})^{1/2}\,\mathrm{sgn}\Delta'_{111}$ and $\Theta_{\pm 1/2}$ belong to the eigenvalue $a'(s_{11}+2s_{12})T - \frac{1}{4}(\Delta'^2_{100} + 3\Delta'^2_{111})^{1/2}\,\mathrm{sgn}\Delta'_{111}$. Here $\mathrm{sgn}\Delta'_{111}$ is +1 if Δ'_{111} is positive and −1 if it is negative. Hence the two $\Gamma_5(\bar{C}_{2v})$ sublevels are separated by

$$\Delta'_{110} = \tfrac{1}{2}(\Delta'^2_{100} + 3\Delta'^2_{111})^{1/2} \quad . \tag{29}$$

B. Relative Intensities of Optical Transitions

In order to extract the maximum information from the experiments described in this work it is necessary to compare the observed relative intensities of the stress-induced components of the excitation spectrum with those obtained from theory. Without an external perturbation, electric-dipole transitions are permitted between Γ_8 and Γ_6, Γ_7, and Γ_8 since the direct products $\Gamma_5\times\Gamma_l^*\times\Gamma_8$ all contain Γ_1, where $l=6$, 7, or 8. However, it should be noted that while Γ_1 appears only once for $l=6$ or 7, it appears twice for $l=8$. This means that for transitions from a Γ_8 state to either a Γ_6 or Γ_7 state, the matrix elements of the components of the dipole-moment operator can all be expressed in terms of only one of the complex matrix elements. Thus, since a given transition probability is proportional to the square of the magnitude of the appropriate matrix element, the relative intensities of all the stress-induced components of such a transition are completely determined by symmetry considerations alone. On the other hand, for a transition between two Γ_8 states, the matrix elements are expressed in terms of two independent complex matrix elements. Only the relative phase of these two parameters is significant and therefore the relative intensities of the stress-induced components depend upon two real constants.

The intensity of a given absorption line is proportional to $|\langle\chi_f|\hat{Q}_k|\chi_i\rangle|^2$, where χ_i and χ_f are the wave functions of the initial and final states, respectively, and $\hat{Q}_k$ is the component of the dipole moment along the direction of polarization of the light. An eigenstate of the perturbed system after a stress has been applied is expressed as a linear combination of the original degenerate eigenfunctions of that level. Thus for the initial state

$$\chi_m = \textstyle\sum_\mu S_{\mu m}\Psi_\mu$$

and a corresponding primed expression for the final state. For example, with stress in either a ⟨111⟩ or ⟨100⟩ direction, $S=S'$ for a transition which, in the absence of stress is described as a $\Gamma_8\to\Gamma_8$ transition. For a ⟨110⟩ direction we have just seen [see Eqs. (27)] that the matrix S depends upon the parameter γ and thus $S\neq S'$. We introduce the concept of a transition matrix defined by

$$\langle\chi'_{m'}|\hat{\underline{Q}}|\chi_m\rangle = (S'^{\dagger}\underline{Q}S)_{m'm} \quad , \tag{30}$$

where the vector $\underline{Q}$ without the circumflex accent stands for the vector matrix $[\langle\Psi'_\mu|\hat{\underline{Q}}|\Psi_\mu\rangle]$. Hence, we first address ourselves to the determination of the components of the matrix $\underline{Q}$.

For a $\Gamma_8\to\Gamma_6$ transition, the appropriate matrix elements are

$$\langle\Phi_{\pm1/2}|\hat{\underline{Q}}|\Psi_\mu\rangle = \langle\Phi_{\pm1/2}|\hat{\underline{Q}}|a\psi_\mu + b\varphi_\mu\rangle = a\langle\Phi_{\pm1/2}|\hat{\underline{Q}}|\psi_\mu\rangle . \tag{31}$$

Here $\Phi_{1/2}=\alpha\varphi_0$ and $\Phi_{-1/2}=\beta\varphi_0$, where φ_0 belongs to $\Gamma_1(T_d)$. The term in b vanishes since $\Gamma_1\times\Gamma_4$ does not contain Γ_5. The products $\Phi^\dagger_{\pm1/2}\psi_\mu$ are given in Table VIII. Using the orthogonality theorem mentioned before, we construct the components of the vector matrix in Eq. (31); these are given in Table IX.

For a $\Gamma_8\to\Gamma_7$ transition, the matrix elements are

$$\langle\Phi'_{\pm1/2}|\hat{\underline{Q}}|\Psi_\mu\rangle = \langle\Phi'_{\pm1/2}|\hat{\underline{Q}}|a\psi_\mu + b\varphi_\mu\rangle = b\langle\Phi'_{\pm1/2}|\hat{\underline{Q}}|\varphi_\mu\rangle ; \tag{32}$$

the functions $\Phi'_{\pm1/2}$ contain φ'_0 which belongs to $\Gamma_2(T_d)$. It is the term in a which now vanishes since $\Gamma_2\times\Gamma_5$ does not contain Γ_5. Tables X and XI contain the information appropriate to this case.

We see here the reason for the choice of the basis functions of Eqs. (9). If b were zero, the transition $\Gamma_8\to\Gamma_7$ would be forbidden whereas if a were zero, then the $\Gamma_8\to\Gamma_6$ transition would be forbidden. This is incompatible with the most general result permitted by symmetry.

For transitions between two Γ_8 states we need to evaluate the matrix

TABLE VIII. Products of the type $\Phi^\dagger_{\pm1/2}\,\psi_\mu$.

$\Phi^\dagger_{\pm1/2}\,\psi_\mu$	$\psi_{3/2}$	$\psi_{1/2}$	$\psi_{-1/2}$	$\psi_{-3/2}$
$\frac{1}{2}$	$\frac{1}{\sqrt{2}}(X+iY)\varphi_0$	$-i\sqrt{\frac{2}{3}}Z\varphi_0$	$\frac{1}{\sqrt{6}}(X-iY)\varphi_0$	0
$-\frac{1}{2}$	0	$\frac{i}{\sqrt{6}}(X+iY)\varphi_0$	$\sqrt{\frac{2}{3}}Z\varphi_0$	$\frac{i}{\sqrt{2}}(X-iY)\varphi_0$

TABLE IX. Matrix elements of the dipole moment for $\Gamma_8 \rightarrow \Gamma_6$ transitions.[a]

$\underline{Q}$	$\frac{3}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$
$\frac{1}{2}$	$\sqrt{3}D_0(\hat{x}+i\hat{y})$	$-2iD_0\hat{z}$	$D_0(\hat{x}-i\hat{y})$	0
$-\frac{1}{2}$	0	$iD_0(\hat{x}+i\hat{y})$	$2D_0\hat{z}$	$i\sqrt{3}D_0(\hat{x}-i\hat{y})$

[a] $D_0 = (a/\sqrt{6})\int X\varphi_0\,\hat{Q}_x\,d\vec{r}$ and $\hat{x}$, $\hat{y}$, $\hat{z}$ are unit vectors parallel to the cubic axes.

$$\underline{Q} = \langle \bar{a}\psi'_{\mu'} + \bar{b}\,\varphi'_{\mu'} | \underline{\hat{Q}} | a\psi_\mu + b\varphi_\mu \rangle \ , \tag{33}$$

which in turn requires the use of the matrix elements listed in Tables XII and XIII. These latter tables have been compiled from Tables III and V employing the previously quoted orthogonality theorem. The matrices $\langle \varphi'_{\mu'} | \underline{\hat{Q}} | \varphi_\mu \rangle$ and $\langle \varphi'_{\mu'} | \underline{\hat{Q}} | \psi_\mu \rangle$ can be obtained from those of Tables XII and XIII, respectively, by taking the Hermitian conjugates in each case and substituting $q_2 = (1/\sqrt{3})\int g_X \hat{Q}_x d\vec{r}$ for q_1 and $q'_2 = -\frac{1}{3}\int \bar{h}_X \hat{Q}_x d\vec{r}$ for q'_1.

We can now write Eq. (33) as follows:

$$\underline{Q} = -\frac{2}{\sqrt{3}}(D+D')\vec{U} - \frac{4i}{\sqrt{3}}D'\vec{V} \ , \tag{34}$$

where $\vec{U}$ and $\vec{V}$ are vectors whose components are the matrices $U_x = \{J_y J_z\}$, etc., and $V_x = \{(J_y^2 - J_z^2)J_x\}$, etc., while $D = \bar{a}^* a q_1 + \bar{b}^* b q_2 + 2\bar{a}^* b q'_1$ and $D' = \bar{b}^* a q'_2 - \bar{a}^* b q'_1$. Similar expressions have not been given for $\Gamma_8 \rightarrow \Gamma_6$ and $\Gamma_8 \rightarrow \Gamma_7$ transitions since they do not provide any further simplification. We are now in a position to calculate the relative intensities of the stress-induced components of all possible transitions from a Γ_8 state for any direction of $\vec{F}$.

1. *Applied Force along* [111]

The transition matrix $\underline{Q}$ appropriate to the basis vectors of Eq. (22) which diagonalize $[V]$ when $\vec{F} \parallel [111]$ will be designated by $\underline{Q}[111]$; a similar notation will be used for the other directions. The transformations S and S' of Eq. (30), for $\vec{F} \parallel [111]$, are

$$S = \frac{1}{\sqrt{6}}\begin{bmatrix} i\sqrt{3} & 0 & -i\sqrt{3} & 0 \\ 1+i & -i & 1+i & i \\ 1 & 1+i & 1 & -1-i \\ 0 & \sqrt{3} & 0 & \sqrt{3} \end{bmatrix} ,$$

and $S' = I$, the 2×2 identity matrix, for a Γ_6 or Γ_7 final state, and $S' = S$ for a Γ_8 final state. We will consider the two cases in which the electric vector of the radiation $\vec{E}$ is either parallel or perpendicular to $\vec{F}$. These two situations will be designated by $E_\parallel$ and $E_\perp$, respectively. Since we will require the components of $\underline{Q}$ along the directions of $\vec{F}$ and two perpendicular directions, we consider a Cartesian coordinate system x', y', z', where $\hat{z}' \parallel \vec{F}$ and $\hat{x}'$ and $\hat{y}'$ are any two orthogonal unit vectors perpendicular to $\hat{z}'$. We have selected $x' = (x+y-2z)/\sqrt{6}$, $y' = (y-x)/\sqrt{2}$, and $z' = (x+y+z)/\sqrt{3}$:

case (i) $\Gamma_8 \rightarrow \Gamma_6$:

$$Q_{x'}[111] = D_0\begin{bmatrix} -1+i & 1 & 0 & -1 \\ -1 & 0 & -1 & 1+i \end{bmatrix} ,$$

$$Q_{y'}[111] = \left(\frac{D_0}{\sqrt{3}}\right)\begin{bmatrix} -2-2i & -i & 1+i & i \\ -i & 1-i & -i & 2-2i \end{bmatrix} ,$$

$$Q_{z'}[111] = D_0\sqrt{2}\begin{bmatrix} 0 & 0 & 1-i & 0 \\ 0 & 1+i & 0 & 0 \end{bmatrix} ;$$

case (ii) $\Gamma_8 \rightarrow \Gamma_7$:

$$Q_{x'}[111] = \left(\frac{D'_0}{\sqrt{3}}\right)\begin{bmatrix} 0 & -i & 1+i & -3i \\ 3i & 1-i & -i & 0 \end{bmatrix} ,$$

$$Q_{y'}[111] = D'_0\begin{bmatrix} -1+i & -1 & 0 & 1 \\ 1 & 0 & 1 & 1+i \end{bmatrix} ,$$

$$Q_{z'}[111] = D'_0\left(\frac{2}{3}\right)^{1/2}\begin{bmatrix} 0 & 2i & 1+i & 0 \\ 0 & 1-i & 2i & 0 \end{bmatrix} ;$$

case (iii) $\Gamma_8 \rightarrow \Gamma_8$:

TABLE X. Products of the type $\Phi'_{\pm 1/2}\,\varphi_\mu$.

$\Phi'^{\uparrow}_{\pm 1/2}\,\varphi_\mu$	$\varphi_{3/2}$	$\varphi_{1/2}$	$\varphi_{-1/2}$	$\varphi_{-3/2}$
$\frac{1}{2}$	$-\frac{1}{\sqrt{6}}(\xi - i\eta)\varphi'_0$	0	$\frac{1}{\sqrt{2}}(\xi + i\eta)\varphi'_0$	$i(\frac{2}{3})^{1/2}\zeta\varphi'_0$
$-\frac{1}{2}$	$-(\frac{2}{3})^{1/2}\zeta\varphi'_0$	$\frac{i}{\sqrt{2}}(\xi - i\eta)\varphi'_0$	0	$-\frac{i}{\sqrt{6}}(\xi + i\eta)\varphi'_0$

TABLE XI. Matrix elements of the dipole moment for $\Gamma_8 \rightarrow \Gamma_7$ transitions.[a]

$\underline{Q}$	$\frac{3}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$
$\frac{1}{2}$	$-D'_0(\hat{x}-i\hat{y})$	0	$\sqrt{3}D'_0(\hat{x}+i\hat{y})$	$2iD'_0\hat{z}$
$-\frac{1}{2}$	$-2D'_0\hat{z}$	$i\sqrt{3}D'_0(\hat{x}-i\hat{y})$	0	$-iD'_0(\hat{x}+i\hat{y})$

[a] $D'_0 = (b/\sqrt{6})\int \xi\,\varphi'_0\,\hat{Q}_x\,d\vec{r}$.

TABLE XII. Matrix elements of $\underline{\hat{Q}}$ for transitions $\Gamma_8 \rightarrow \Gamma_8$ between states of the form ψ_μ.[a]

$\langle \psi'_{\mu'} \vert \underline{\hat{Q}} \vert \psi_\mu \rangle$	$\frac{3}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$
$\frac{3}{2}$	0	$-q_1(\hat{x}+i\hat{y})$	$-iq_1\hat{z}$	0
$\frac{1}{2}$	$-q_1(\hat{x}-i\hat{y})$	0	0	$-iq_1\hat{z}$
$-\frac{1}{2}$	$iq_1\hat{z}$	0	0	$q_1(\hat{x}+i\hat{y})$
$-\frac{3}{2}$	0	$iq_1\hat{z}$	$q_1(\hat{x}-i\hat{y})$	0

[a] $q_1 = (1/\sqrt{3})\int f_X \hat{Q}_x\,d\vec{r}$.

$$Q_{x'}[111]=\frac{1}{\sqrt{2}}\begin{bmatrix} 0 & (1+i)(D+D') & -2D' & 0 \\ (1-i)(D+D') & 0 & -2(1-i)D' & -2D' \\ 2D' & 2(1+i)D' & 0 & (1+i)(D+D') \\ 0 & 2D' & (1-i)(D+D') & 0 \end{bmatrix},$$

$$Q_{y'}[111]=\frac{1}{\sqrt{6}}\begin{bmatrix} 0 & -(1-i)(D+3D') & -2iD & 0 \\ (1+i)(D'-D) & -4iD' & -2(1+i)D' & 2i(D+2D') \\ 2i(D+2D') & 2(1-i)D' & 4iD' & (1-i)(D'-D) \\ 0 & -2iD & -(1+i)(D+3D') & 0 \end{bmatrix},$$

$$Q_{z'}[111]=\begin{bmatrix} -(D+D') & 0 & 0 & -2(1+i)D' \\ 0 & D+D' & 0 & 0 \\ 0 & 0 & D+D' & 0 \\ 2(1-i)D' & 0 & 0 & -(D+D') \end{bmatrix}.$$

The relative intensities for the above three types of transitions are given in Table XIV, the selections rules are also shown in Fig. 1. Each intensity results from the superposition of four incoherent transitions since each level under stress is a doublet. Thus, each number appearing in the table in the columns labeled transition probability is a sum of four terms, for example, the entry for the $(\Gamma_{5+6}\rightarrow\Gamma_{5+6})_{\parallel}$ transition is given by the sum of the squares of the magnitudes of the four corner elements of the $Q_{z'}[111]$ matrix. It should be noted that these numbers are not the transition probabilities themselves but are proportional to them.

Notice that for each polarization, and for each zero-stress line, the sum of the relative intensities in Table XIV is the same. This quantity is $8|D_0|^2$, $8|D_0'|^2$, and $N=4|D+D'|^2+16|D'|^2$ for the transitions $\Gamma_8\rightarrow\Gamma_6$, $\Gamma_8\rightarrow\Gamma_7$, and $\Gamma_8\rightarrow\Gamma_8$, respectively. This assumes that the two doublets which are the initial sublevels are equally populated. This, of course, is not true for a finite splitting of the sublevels at low temperatures. It is interesting to note that had we not included the functions φ_μ in the basis for the Γ_8 states, $D'\equiv 0$, and therefore the line $(\Gamma_4\rightarrow\Gamma_4)_\perp$ would be strictly forbidden, and all the other allowed transitions would have equal intensities. The wave functions we have chosen are the most general possible consistent with the symmetry.

TABLE XIII. Matrix elements of $\hat{\underline{Q}}$ between states ψ'_μ, and φ_μ.[a]

$\langle\psi'_\mu\|\hat{\underline{Q}}\|\varphi_\mu\rangle$	$\frac{3}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$
$\frac{3}{2}$	0	0	$-3iq_1'\hat{z}$	$-\sqrt{3}q_1'(\hat{x}-i\hat{y})$
$\frac{1}{2}$	$-2q_1'(\hat{x}-i\hat{y})$	0	$-\sqrt{3}q_1'(\hat{x}+i\hat{y})$	$iq_1'\hat{z}$
$-\frac{1}{2}$	$-iq_1'\hat{z}$	$\sqrt{3}q_1'(\hat{x}-i\hat{y})$	0	$2q_1'(\hat{x}+i\hat{y})$
$-\frac{3}{2}$	$\sqrt{3}q_1'(\hat{x}+i\hat{y})$	$3iq_1'\hat{z}$	0	0

[a] $q_1'=-\frac{1}{3}\int h_X\hat{Q}_x\,d\vec{r}$.

It is a peculiarity of the $\langle 111\rangle$ direction that the relative intensities depend upon a single real parameter u (see Table XIV), which is defined as follows.

Take

$$|D+D'|^2+8|D'|^2=\tfrac{1}{2}N\cos^2\theta\ ,$$

and (35)

$$|D+D'|^2=\tfrac{1}{2}N\sin^2\theta\ ,$$

which define the angle θ. In Eqs. (35), we have exploited the fact that the total intensity for one direction of polarization is normalized to N. From the second of Eqs. (35) and the definition of N it follows that $\sin^2\theta\leq\frac{1}{2}$; thus it is enough to restrict θ to the range $0\leq\theta\leq\frac{1}{4}\pi$. It is more convenient for a graphical representation (see Fig. 2) to use the parameter $u=\cos 2\theta$ which is then restricted to the range $0\leq u\leq 1$.

2. *Applied Force along* [001]

This is the simplest case to determine since the initial representation also diagonalizes $[V]$. Hence S and S' are unit matrices:

case (i) $\Gamma_8\rightarrow\Gamma_6$:

$$Q_x[001]=D_0\begin{bmatrix}\sqrt{3} & 0 & 1 & 0\\ 0 & i & 0 & i\sqrt{3}\end{bmatrix},$$

$$Q_y[001]=D_0\begin{bmatrix}i\sqrt{3} & 0 & -i & 0\\ 0 & -1 & 0 & \sqrt{3}\end{bmatrix},$$

$$Q_z[001]=2D_0\begin{bmatrix}0 & -i & 0 & 0\\ 0 & 0 & 1 & 0\end{bmatrix};$$

case (ii) $\Gamma_8\rightarrow\Gamma_7$:

$$Q_x[001]=D_0'\begin{bmatrix}-1 & 0 & \sqrt{3} & 0\\ 0 & i\sqrt{3} & 0 & -i\end{bmatrix},$$

$$Q_y[001]=D_0'\begin{bmatrix}i & 0 & i\sqrt{3} & 0\\ 0 & \sqrt{3} & 0 & 1\end{bmatrix},$$

$$Q_z[001]=2D_0'\begin{bmatrix}0 & 0 & 0 & i\\ -1 & 0 & 0 & 0\end{bmatrix};$$

case (iii) $\Gamma_8\rightarrow\Gamma_8$:

TABLE XIV. Transition probabilities and relative intensities for stress-induced components with $\vec{F} \parallel \langle 111 \rangle$.

Zero-stress transition	Stress-induced component	Transition probability $E_\parallel$	Transition probability $E_\perp$	Relative intensity $E_\parallel$	Relative intensity $E_\perp$
$\Gamma_8 \rightarrow \Gamma_6$	$\Gamma_4 \rightarrow \Gamma_4$	$8\lvert D_0 \rvert^2$	$2\lvert D_0 \rvert^2$	4	1
	$\Gamma_{5+6} \rightarrow \Gamma_4$	0	$6\lvert D_0 \rvert^2$	0	3
$\Gamma_8 \rightarrow \Gamma_7$	$\Gamma_4 \rightarrow \Gamma_4$	$8\lvert D_0' \rvert^2$	$2\lvert D_0' \rvert^2$	4	1
	$\Gamma_{5+6} \rightarrow \Gamma_4$	0	$6\lvert D_0' \rvert^2$	0	3
$\Gamma_8 \rightarrow \Gamma_8$	$\Gamma_4 \rightarrow \Gamma_4$	$2\lvert D+D' \rvert^2$	$8\lvert D' \rvert^2$	$\frac{1}{2}(1-u)$	$\frac{1}{2}u$
	$\Gamma_4 \rightarrow \Gamma_{5+6}$	0	$2\lvert D+D' \rvert^2+4\lvert D' \rvert^2$	0	$\frac{1}{2}-\frac{1}{4}u$
	$\Gamma_{5+6} \rightarrow \Gamma_4$	0	$2\lvert D+D' \rvert^2+4\lvert D' \rvert^2$	0	$\frac{1}{2}-\frac{1}{4}u$
	$\Gamma_{5+6} \rightarrow \Gamma_{5+6}$	$2\lvert D+D' \rvert^2+16\lvert D' \rvert^2$	0	$\frac{1}{2}(1+u)$	0

$$Q_x[001] = \begin{bmatrix} 0 & -(D+2D') & 0 & \sqrt{3}D' \\ -D & 0 & \sqrt{3}D' & 0 \\ 0 & -\sqrt{3}D' & 0 & D \\ -\sqrt{3}D' & 0 & D+2D' & 0 \end{bmatrix},$$

$$Q_y[001] = i \begin{bmatrix} 0 & -(D+2D') & 0 & -\sqrt{3}D' \\ D & 0 & \sqrt{3}D' & 0 \\ 0 & \sqrt{3}D' & 0 & D \\ -\sqrt{3}D' & 0 & -(D+2D') & 0 \end{bmatrix},$$

$$Q_z[001] = i \begin{bmatrix} 0 & 0 & -(D-D') & 0 \\ 0 & 0 & 0 & -(D+3D') \\ D+3D' & 0 & 0 & 0 \\ 0 & D-D' & 0 & 0 \end{bmatrix}.$$

The intensities for the above three types of transitions are listed in Table XV, and the selection rules are shown in Fig. 1. The parameter v which appears in the last two columns of Table XV is defined by

$$\lvert D \rvert^2 = \tfrac{1}{4}N(1 - \tfrac{3}{4}u + v) . \tag{36}$$

An analysis similar to that given to restrict the range of u shows that it is enough to restrict v to the common range of the inequalities $-\frac{1}{2} \leq v \leq \frac{1}{2}$ and $-(1-\frac{3}{4}u) \leq v \leq 1-\frac{3}{4}u$.

In Fig. 3, we give a plot of the relative intensities of Table XV as a function of v for a specific value of the parameter u. The value chosen is the most probable value obtained from experiment with $\vec{F} \parallel \langle 111 \rangle$ for the D line of Zn^- in germanium.[19,20]

3. *Applied Force along* [110]

In this case $S \equiv S_\gamma$ depends upon the quantity γ already defined in Eq. (28). The matrix S_γ relates

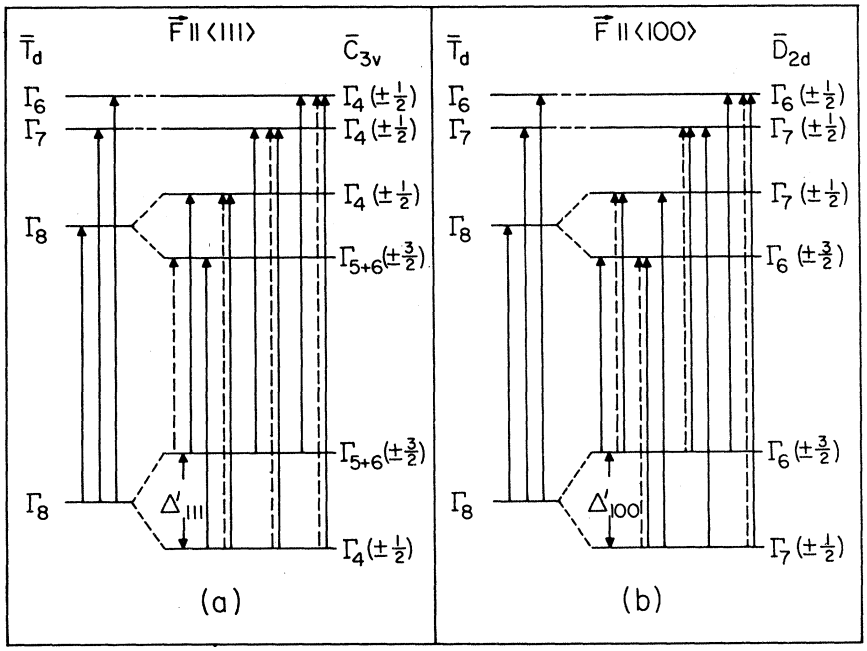

FIG. 1. Transitions from a Γ_8 ground state to Γ_6, Γ_7, and Γ_8 excited states of the double group $\bar{T}_d$ under (a) a uniaxial compression parallel to a $\langle 111 \rangle$ direction, (b) a uniaxial compression parallel to a $\langle 100 \rangle$ direction. The dashed arrows are for $\vec{E} \parallel \vec{F}$ while the full arrows are for $\vec{E} \perp \vec{F}$. The labels in parentheses are somewhat arbitrary and correspond to the wave functions defined in the text. The splitting of the ground state for the two cases is also shown.

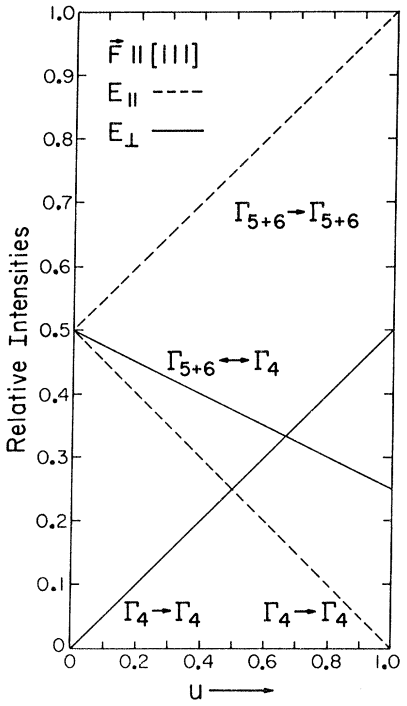

FIG. 2. Relative intensities for the stress-induced components of a $\Gamma_8 \rightarrow \Gamma_8$ transition for uniaxial compression along ⟨111⟩. The parameter u is defined in the text.

the bases Θ_μ to Ψ_μ. From Eqs. (27) we find

$$S_\gamma = (1+\gamma^2)^{-1/2} \begin{bmatrix} 0 & i & 0 & -i\gamma \\ 1 & 0 & \gamma & 0 \\ 0 & \gamma & 0 & 1 \\ i\gamma & 0 & -i & 0 \end{bmatrix} .$$

For transitions from Γ_8 to either Γ_6 or Γ_7, S' is again the 2×2 identity matrix whereas for a $\Gamma_8 \rightarrow \Gamma_8$ transition $S' \equiv S_\delta$, where δ is a quantity defined in the same way as γ but for the final state. For this direction of applied force, we construct the Cartesian coordinate system $x' = (x+y)/\sqrt{2}$, $y' = (y-x)/\sqrt{2}$, $z' = z$, where $\hat{x}' \parallel \vec{F}$:

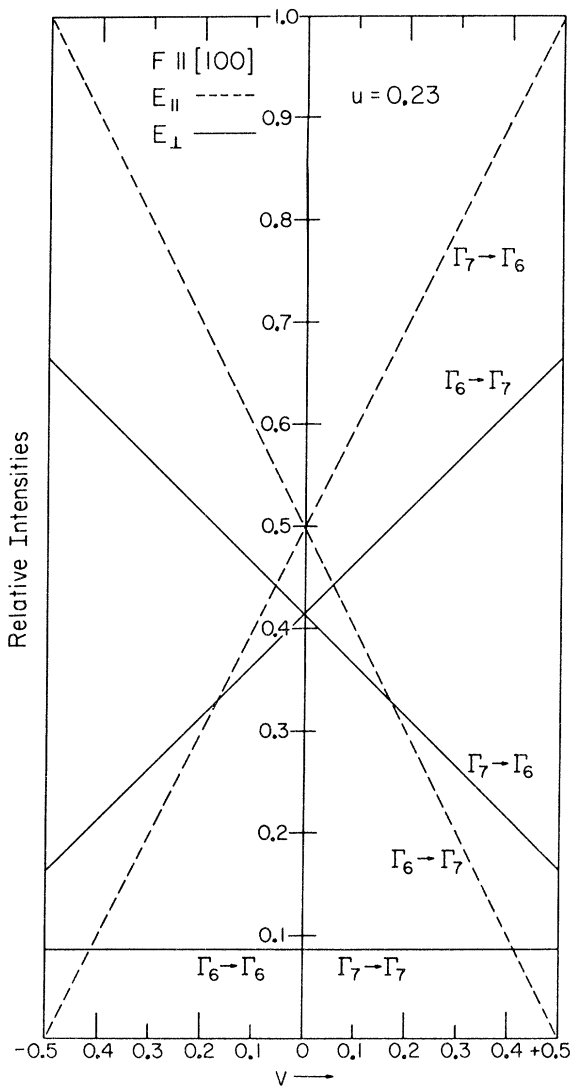

FIG. 3. Relative intensities for the stress-induced components of a $\Gamma_8 \rightarrow \Gamma_8$ transition for uniaxial compression along ⟨100⟩. The parameter v is defined in the text. This graph is drawn for the case $u = 0.23$ which is obtained from the experiments to be described in a later publication.

TABLE XV. Transition probabilities and relative intensities for $\vec{F} \parallel [001]$.

Zero-stress transition	Stress-induced components	Transition probability $E_\parallel$	Transition probability $E_\perp$	Relative intensity $E_\parallel$	Relative intensity $E_\perp$
$\Gamma_8 \rightarrow \Gamma_6$	$\Gamma_6 \rightarrow \Gamma_6$	0	$6\lvert D_0\rvert^2$	0	3
	$\Gamma_7 \rightarrow \Gamma_6$	$8\lvert D_0\rvert^2$	$2\lvert D_0\rvert^2$	4	1
$\Gamma_8 \rightarrow \Gamma_7$	$\Gamma_6 \rightarrow \Gamma_7$	$8\lvert D_0'\rvert^2$	$2\lvert D_0'\rvert^2$	4	1
	$\Gamma_7 \rightarrow \Gamma_7$	0	$6\lvert D_0'\rvert^2$	0	3
$\Gamma_8 \rightarrow \Gamma_8$	$\Gamma_6 \rightarrow \Gamma_6$	0	$6\lvert D'\rvert^2$	0	$\frac{3}{8}u$
	$\Gamma_6 \rightarrow \Gamma_7$	$2\lvert D+3D'\rvert^2$	$2\lvert D'\rvert^2$	$\frac{1}{2}-v$	$\frac{1}{2}(1-\frac{9}{4}u+v)$
	$\Gamma_7 \rightarrow \Gamma_6$	$2\lvert D-D'\rvert^2$	$2\lvert D+2D'\rvert^2$	$\frac{1}{2}+v$	$\frac{1}{2}(1-\frac{3}{4}u-v)$
	$\Gamma_7 \rightarrow \Gamma_7$	0	$6\lvert D'\rvert^2$	0	$\frac{3}{8}u$

case (i) $\Gamma_8 \rightarrow \Gamma_6$:

$$Q_{x'}[110] = \frac{(1-i)D_0}{[2(1+\gamma^2)]^{1/2}} \times \begin{bmatrix} 0 & \gamma-\sqrt{3} & 0 & 1+\gamma\sqrt{3} \\ -1-\gamma\sqrt{3} & 0 & \sqrt{3}-\gamma & 0 \end{bmatrix},$$

$$Q_{y'}[110] = \frac{(1+i)D_0}{[2(1+\gamma^2)]^{1/2}} \times \begin{bmatrix} 0 & -\gamma-\sqrt{3} & 0 & \gamma\sqrt{3}-1 \\ \gamma\sqrt{3}-1 & 0 & -\gamma-\sqrt{3} & 0 \end{bmatrix},$$

$$Q_{z'}[110] = \frac{2D_0}{[1+\gamma^2]^{1/2}} \begin{bmatrix} -i & 0 & -i\gamma & 0 \\ 0 & \gamma & 0 & 1 \end{bmatrix};$$

case (ii) $\Gamma_8 \rightarrow \Gamma_7$:

$$Q_{x'}[110] = \frac{(1+i)D_0'}{[2(1+\gamma^2)]^{1/2}} \times \begin{bmatrix} 0 & \gamma\sqrt{3}-1 & 0 & \gamma+\sqrt{3} \\ \gamma+\sqrt{3} & 0 & \gamma\sqrt{3}-1 & 0 \end{bmatrix},$$

$$Q_{y'}[110] = \frac{(1-i)D_0'}{[2(1+\gamma^2)]^{1/2}} \times \begin{bmatrix} 0 & -\gamma\sqrt{3}-1 & 0 & \gamma-\sqrt{3} \\ -\gamma+\sqrt{3} & 0 & \gamma\sqrt{3}+1 & 0 \end{bmatrix},$$

$$Q_{z'}[110] = \frac{2D_0'}{[1+\gamma^2]^{1/2}} \begin{bmatrix} -\gamma & 0 & 1 & 0 \\ 0 & -i & 0 & i\gamma \end{bmatrix};$$

see Table XVI for case (iii).

The relative intensities for the above three types of transitions are given in Tables XVII and XVIII. The reader should notice that in this case the direction of light propagation, $\vec{k}$, is important since the crystal becomes orthorhombic. In Table XVIII, the transitions are specified in an abbreviated manner, for example, the transition $\Gamma_5(\pm\frac{1}{2}) \rightarrow \Gamma_5(\pm\frac{1}{2})$ is designated by the symbol $\frac{1}{2} \rightarrow \frac{1}{2}$. The above intensities are shown graphically in Figs. 4–7. Figures 4 and 5 exhibit the results contained in Table XVI in which the relative intensities are plotted as functions of the splitting parameter γ, a quantity which is directly measurable, unlike u and v which are essentially ratios of matrix elements. In Table XVII and Figs. 4 and 5, the parameter ω is defined by the relation

$$\omega = \arctan\gamma = -\tfrac{1}{2}\,\mathrm{arccot}\left(\frac{\Delta'_{100}}{\sqrt{3}\Delta'_{111}}\right).$$

An experimental study of a $\Gamma_8 \rightarrow \Gamma_8$ transition under stress gives the magnitudes of the splittings of the two Γ_8 states and not their signs. To determine these a symmetry assignment must be made, which is part of the purpose of the present work. According to Eq. (28), there are two values of γ

TABLE XVI. Case (iii) $\Gamma_8 \rightarrow \Gamma_8$. Here $q_0 = [(1+\gamma^2)(1+\delta^2)]^{-1/2}$.

$$Q_{x'}[110] = -\frac{(1-i)q_0}{\sqrt{2}} \begin{bmatrix} 0 & i[D(1+\gamma\delta)+D'(2\gamma\delta-\gamma\sqrt{3}+\delta\sqrt{3})] & 0 & -i[D(\gamma-\delta)+D'(\sqrt{3}-2\delta+\gamma\delta\sqrt{3})] \\ D(1+\gamma\delta)+D'(2-\gamma\sqrt{3}+\delta\sqrt{3}) & 0 & D(\gamma-\delta)+D'(\sqrt{3}+2\gamma+\gamma\delta\sqrt{3}) & 0 \\ 0 & -i[D(\gamma-\delta)+D'(\sqrt{3}+2\gamma+\gamma\delta\sqrt{3})] & 0 & -i[D(1+\gamma\delta)+D'(2-\gamma\sqrt{3}+\delta\sqrt{3})] \\ D(\gamma-\delta)+D'(\sqrt{3}-2\delta+\gamma\delta\sqrt{3}) & 0 & -D(1+\gamma\delta)-D'(2\gamma\delta-\gamma\sqrt{3}+\delta\sqrt{3}) & 0 \end{bmatrix}$$

$$Q_{y'}[110] = \frac{(1-i)q_0}{\sqrt{2}} \begin{bmatrix} 0 & -D(1+\gamma\delta)-D'(2\gamma\delta+\gamma\sqrt{3}-\delta\sqrt{3}) & 0 & D(\gamma-\delta)-D'(\sqrt{3}+2\delta+\gamma\delta\sqrt{3}) \\ -i[D(1+\gamma\delta)+D'(2+\gamma\sqrt{3}-\delta\sqrt{3})] & 0 & -i[D(\gamma-\delta)-D'(\sqrt{3}-2\gamma+\gamma\delta\sqrt{3})] & 0 \\ 0 & D(\gamma-\delta)-D'(\sqrt{3}-2\gamma+\gamma\delta\sqrt{3}) & 0 & D(1+\gamma\delta)+D'(2+\gamma\sqrt{3}-\delta\sqrt{3}) \\ -i[D(\gamma-\delta)-D'(\sqrt{3}+2\delta+\gamma\delta\sqrt{3})] & 0 & i[D(1+\gamma\delta)+D'(2\gamma\delta+\gamma\sqrt{3}-\delta\sqrt{3})] & 0 \end{bmatrix}$$

$$Q_{z}[110] = q_0 \begin{bmatrix} D(\gamma+\delta)+D'(3\gamma-\delta) & 0 & -D(1-\gamma\delta)-D'(3+\gamma\delta) & 0 \\ 0 & -D(\gamma+\delta)+D'(\gamma-3\delta) & 0 & -D(1-\gamma\delta)+D'(1+3\gamma\delta) \\ -D(1-\gamma\delta)+D'(1+3\gamma\delta) & 0 & -D(\gamma+\delta)+D'(\gamma-3\delta) & 0 \\ 0 & -D(1-\gamma\delta)-D'(3+\gamma\delta) & 0 & D(\gamma+\delta)+D'(3\gamma-\delta) \end{bmatrix}$$

TABLE XVII. Transition probabilities and relative intensities with $\vec{F}\parallel[110]$, for $\Gamma_8\rightarrow\Gamma_6$, Γ_7 transitions.

Zero-stress transition	Stress-induced components	Transition probability[a] $E_\parallel$	$E_\perp$ $\vec{k}\parallel[001]$	$E_\perp$ $\vec{k}\parallel[1\bar{1}0]$	Relative intensity $E_\parallel$	$E_\perp$ $\vec{k}\parallel[001]$	$E_\perp$ $\vec{k}\parallel[1\bar{1}0]$
$\Gamma_8\rightarrow\Gamma_6$	$\Gamma_5(\pm\frac{1}{2})\rightarrow\Gamma_5$	$(\gamma-\sqrt{3})^2\lvert D_0\rvert^2$	$(\gamma+\sqrt{3})^2\lvert D_0\rvert^2$	$4\gamma^2\lvert D_0\rvert^2$	$\sin^2(\omega-\frac{1}{3}\pi)$	$\sin^2(\omega+\frac{1}{3}\pi)$	$\sin^2\omega$
	$\Gamma_5(\pm\frac{3}{2})\rightarrow\Gamma_5$	$(\gamma\sqrt{3}+1)^2\lvert D_0\rvert^2$	$(\gamma\sqrt{3}-1)^2\lvert D_0\rvert^2$	$4\lvert D_0\rvert^2$	$\cos^2(\omega-\frac{1}{3}\pi)$	$\cos^2(\omega+\frac{1}{3}\pi)$	$\cos^2\omega$
$\Gamma_8\rightarrow\Gamma_7$	$\Gamma_5(\pm\frac{1}{2})\rightarrow\Gamma_5$	$(\gamma\sqrt{3}-1)^2\lvert D_0'\rvert^2$	$(\gamma\sqrt{3}+1)^2\lvert D_0'\rvert^2$	$4\lvert D_0'\rvert^2$	$\cos^2(\omega+\frac{1}{3}\pi)$	$\cos^2(\omega-\frac{1}{3}\pi)$	$\cos^2\omega$
	$\Gamma_5(\pm\frac{3}{2})\rightarrow\Gamma_5$	$(\gamma+\sqrt{3})^2\lvert D_0'\rvert^2$	$(\gamma-\sqrt{3})^2\lvert D_0'\rvert^2$	$4\gamma^2\lvert D_0'\rvert^2$	$\sin^2(\omega+\frac{1}{3}\pi)$	$\sin^2(\omega-\frac{1}{3}\pi)$	$\sin^2\omega$

[a]All entries in this part of the table are to be multiplied by the factor $2(1+\gamma^2)^{-1}$.

consistent with a given magnitude of the ratio $\Delta'_{100}/\Delta'_{111}$, one being the reciprocal of the other. If this ratio is positive (negative) $\gamma>1(\gamma<1)$. Similarly for δ, as this is defined by an equation analogous to Eq. (28). If in Table XVIII, γ and δ are replaced by their reciprocals, the expressions for the relative intensities are the same as those for the original values of γ and δ except for a change in sign of the term in v. Figures 6 and 7 are constructed for the case where $\Delta'_{100}/\Delta'_{111}$ is positive, i.e., $\gamma>1$, and similarly for the excited state. In order to construct figures corresponding to the case where the signs of the ratios of the deformation-potential constants are opposite, we simply reflect the figures about the vertical axes $v=0$. If in Table XVII, γ is replaced by its reciprocal, all the expressions for $\Gamma_8\rightarrow\Gamma_6$ interchange with those for $\Gamma_8\rightarrow\Gamma_7$. For the special situation where $\Delta'_{100}=\Delta'_{111}$, the so-called isotropic case $\gamma=\sqrt{3}$.

In the interpretation of the experiments discussed in this work, the relative sign of Δ'_{100} and Δ'_{111} cannot be determined from a $\Gamma_8\rightarrow\Gamma_8$ transition alone. It can be determined, however, if the final state of a transition originating from a Γ_8 state is

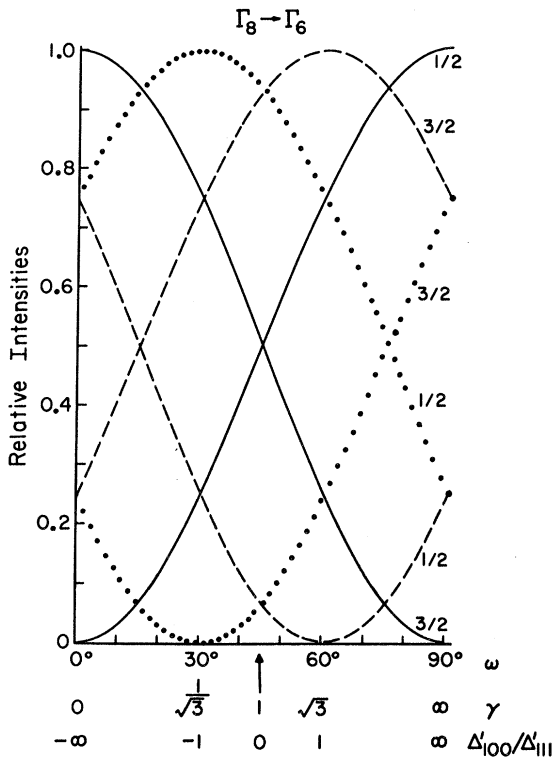

FIG. 4. Relative intensities for the stress-induced components of a $\Gamma_8\rightarrow\Gamma_6$ transition for $\vec{F}\parallel[110]$ as functions of the parameter γ defined in the text. The dashed curve is for $\vec{E}\parallel\vec{F}$, the full curve is for $\vec{E}\perp\vec{F}$, $\vec{k}\parallel[1\bar{1}0]$, where $\vec{k}$ is the propagation vector of the light. The dotted curve is for $\vec{E}\perp\vec{F}$ with $\vec{k}\parallel[001]$. The labels $\frac{1}{2}$ and $\frac{3}{2}$ designate the Γ_5 sublevels into which the Γ_8 initial state splits under strain (see Table XVI).

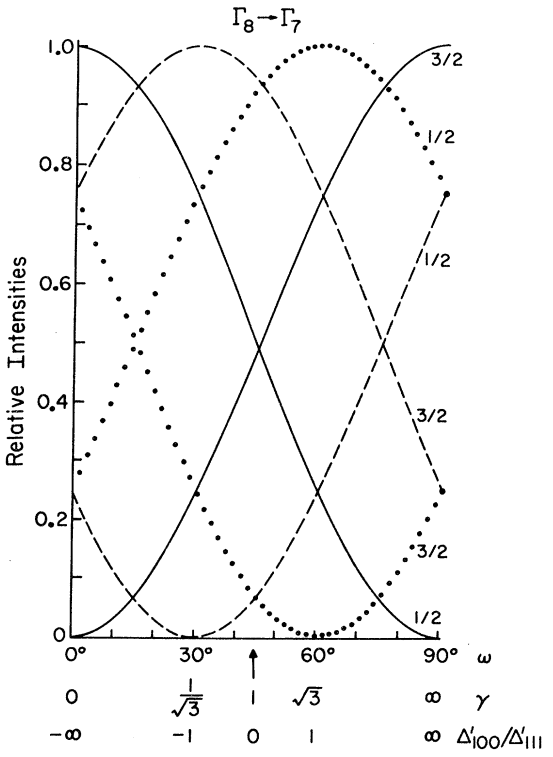

FIG. 5. Same as Fig. 4 but for $\Gamma_8\rightarrow\Gamma_7$ transitions.

TABLE XVIII. Transition probabilities and relative intensities with $\vec{F} \parallel [110]$ for $\Gamma_8 \rightarrow \Gamma_8$ transitions.[a]

	$E_{\parallel}$	$E_{\perp}$	
	$\vec{k} \parallel [001]$		$\vec{k} \parallel [1\bar{1}0]$
	Transition Probability		
$\frac{1}{2} \rightarrow \frac{1}{2}$	$\lvert D(\gamma-\delta)+D'(\sqrt{3}+2\gamma+\gamma\delta\sqrt{3})\rvert^2$	$\lvert D(6-\gamma)+D'(\sqrt{3}-2\gamma+\gamma\delta\sqrt{3})\rvert^2$	$\lvert D(\gamma+\delta)+D'(3\delta-\gamma)\rvert^2$
$\frac{1}{2} \rightarrow \frac{3}{2}$	$\lvert D(1+\gamma\delta)+D'(2\gamma\delta-\gamma\sqrt{3}+\delta\sqrt{3})\rvert^2$	$\lvert D(1+\gamma\delta)+D'(2\gamma\delta+\gamma\sqrt{3}-\delta\sqrt{3})\rvert^2$	$\lvert D(\gamma\delta-1)-D'(\gamma\delta+3)\rvert^2$
$\frac{3}{2} \rightarrow \frac{1}{2}$	$\lvert D(1+\gamma\delta)+D'(2-\gamma\sqrt{3}+\delta\sqrt{3})\rvert^2$	$\lvert D(1+\gamma\delta)+D'(2+\gamma\sqrt{3}-\delta\sqrt{3})\rvert^2$	$\lvert D(\gamma\delta-1)+D'(3\gamma\delta+1)\rvert^2$
$\frac{3}{2} \rightarrow \frac{3}{2}$	$\lvert D(\gamma-\delta)+D'(\sqrt{3}-2\delta+\gamma\delta\sqrt{3})\rvert^2$	$\lvert D(6-\gamma)+D'(\sqrt{3}+2\delta+\gamma\delta\sqrt{3})\rvert^2$	$\lvert D(\gamma+\delta)+D'(3\gamma-\delta)\rvert^2$
	Relative intensity[b]		
$\frac{1}{2} \rightarrow \frac{1}{2}$	$(\gamma-\delta)^2+\frac{1}{4}u[\rho+2\sqrt{3}(\gamma+\delta)(1+\gamma\delta)]-v[\sqrt{3}(1+\gamma\delta)+\gamma+\delta](\gamma-\delta)$	$(\gamma-\delta)^2+\frac{1}{4}u[\rho-2\sqrt{3}(\gamma+\delta)(1+\gamma\delta)]+v[\sqrt{3}(1+\gamma\delta)-\gamma-\delta](\gamma-\delta)$	$(\gamma+\delta)^2-4u\gamma\delta+2v(\gamma^2-\delta^2)$
$\frac{1}{2} \rightarrow \frac{3}{2}$	$(1+\gamma\delta)^2+\frac{1}{4}u[-\rho+2\sqrt{3}(\gamma-\delta)(1-\gamma\delta)]+v[1-\gamma\delta+\sqrt{3}(\gamma-\delta)](1+\gamma\delta)$	$(1+\gamma\delta)^2+\frac{1}{4}u[\rho+2\sqrt{3}(\gamma-\delta)(1-\gamma\delta)]+v[1-\gamma\delta-\sqrt{3}(\gamma-\delta)](1+\gamma\delta)$	$(1-\gamma\delta)^2+4u\gamma\delta+2v(\gamma^2\delta^2-1)$
$\frac{3}{2} \rightarrow \frac{1}{2}$	$(1+\gamma\delta)^2-\frac{1}{4}u[\rho+2\sqrt{3}(\gamma-\delta)(1-\gamma\delta)]+v[\sqrt{3}(\gamma-\delta)-1+\gamma\delta](1+\gamma\delta)$	$(1+\gamma\delta)^2-\frac{1}{4}u[\rho-2\sqrt{3}(\gamma-\delta)(1-\gamma\delta)]-v[\sqrt{3}(\gamma-\delta)+1-\gamma\delta](1+\gamma\delta)$	$(1-\gamma\delta)^2+4u\gamma\delta-2v(\gamma^2\delta^2-1)$
$\frac{3}{2} \rightarrow \frac{3}{2}$	$(\gamma-\delta)^2+\frac{1}{4}u[\rho-2\sqrt{3}(\gamma+\delta)(1+\gamma\delta)]-v[\sqrt{3}(1+\gamma\delta)-\gamma-\delta](\gamma-\delta)$	$(\gamma-\delta)^2+\frac{1}{4}u[\rho+2\sqrt{3}(\gamma+\delta)(1+\gamma\delta)]+v[\sqrt{3}(1+\gamma\delta)+\gamma+\delta](\gamma-\delta)$	$(\gamma+\delta)^2-4u\gamma\delta-2v(\gamma^2-\delta^2)$

[a] All entries are to be multiplied by the factor $2[(1+\gamma^2)(1+\delta^2)]^{-1}$.

[b] $\rho \equiv 3(\gamma^2-1)(\delta^2-1)+16\gamma\delta$.

known to be either a Γ_6 or Γ_7 state.

If D and D' were complex numbers having the same phase, then all the foregoing expressions depend upon the single parameter u, and then v becomes[34] $\pm[u(1-u)]^{1/2}$. This was the special case considered by Onton *et al.*[24] and appears to be that treated by Kaplyanskii.[22]

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APPENDIX

We wish to write Eq. (10) in matrix form; to accomplish this we make use of the 4×4 matrices J_x, J_y, and J_z, the components of the angular-momentum matrices for angular momentum $J=\frac{3}{2}$. It is noticed that J_x, J_y, and J_z belong to $\Gamma_4(T_d)$.

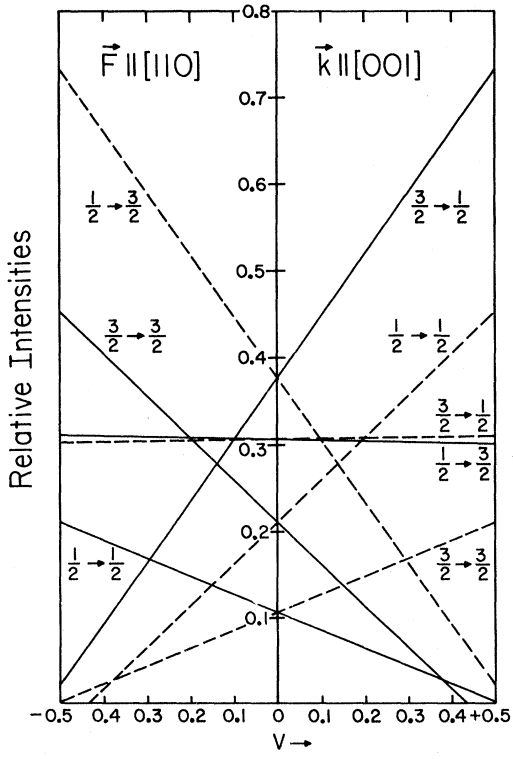

FIG. 6. Relative intensities for the stress-induced components of a $\Gamma_8 \rightarrow \Gamma_8$ transition for $\vec{F} \parallel [110]$ and $\vec{k} \parallel [001]$. The parameters used in this graph are: $u=0.23$, $\gamma=1.63$, and $\delta=13$. The dashed lines are for $\vec{E} \parallel \vec{F}$, while the full lines correspond to $\vec{E} \perp \vec{F}$.

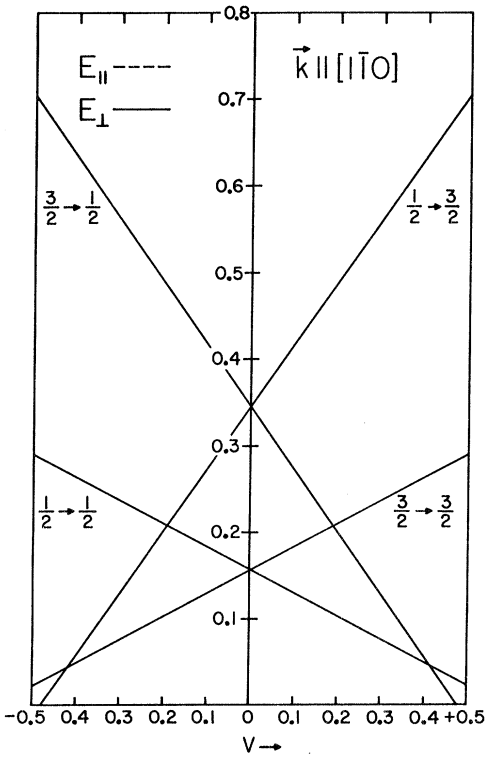

FIG. 7. Same as Fig. 6 except $\vec{k} \parallel [1\bar{1}0]$. In this figure we show the case for $\vec{E} \perp \vec{F}$ only, since the relative intensities for $\vec{E} \parallel \vec{F}$ are identical to those given in Fig. 6.

Since $[\Gamma_4 \times \Gamma_4] = \Gamma_1 + \Gamma_3 + \Gamma_5$, we conclude that $J^2 = J_x^2 + J_y^2 + J_z^2 = \frac{15}{4} I$ belongs to Γ_1, $2J_z^2 - J_x^2 - J_y^2 = 3J_z^2 - \frac{15}{4} I$ and $\sqrt{3}(J_x^2 - J_y^2)$ belong to Γ_3, and $\{J_y J_z\} = \frac{1}{2}(J_y J_z + J_z J_y)$, $\{J_z J_x\} = \frac{1}{2}(J_z J_x + J_x J_z)$, and $\{J_x J_y\} = \frac{1}{2}(J_x J_y + J_y J_x)$ belong to Γ_5. We can write, then, $[V]$, which is a scalar quantity, as a linear combination of $(\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}) J^2$, $(2\epsilon_{zz} - \epsilon_{xx} - \epsilon_{yy}) \times (3J_z^2 - J^2) + 3(\epsilon_{xx} - \epsilon_{yy})(J_x^2 - J_y^2)$, and $\{J_y J_z\}\epsilon_{yz} + \{J_z J_x\}\epsilon_{zx} + \{J_x J_y\}\epsilon_{xy}$. Hence Eq. (20) is established, where we have chosen the coefficients to conform with the conventional ones.

We can, of course, proceed directly with the evaluation of the matrix elements from Tables III–V. For example, $[V_{yz}]$ is the sum of four contributions as seen in Eq. (10), thus the coefficient of a^*b is $(2/3\sqrt{3})(\int h_X V_{yz} d\vec{r})[\{J_y J_z\} - 2iV_x]$. In writing these expressions, we have used[30]

$$J_x = \frac{i}{2}\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ -\sqrt{3} & 0 & 2 & 0 \\ 0 & -2 & 0 & \sqrt{3} \\ 0 & 0 & -\sqrt{3} & 0 \end{bmatrix},$$

$$J_y = \frac{1}{2}\begin{bmatrix} 0 & \sqrt{3} & 0 & 0 \\ \sqrt{3} & 0 & 2 & 0 \\ 0 & 2 & 0 & \sqrt{3} \\ 0 & 0 & \sqrt{3} & 0 \end{bmatrix},$$

$$J_z = \frac{1}{2}\begin{bmatrix} 3 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -3 \end{bmatrix}.$$

After determining the matrix elements for the different contributions to V and collecting terms, we obtain Eq. (20) with

$$a' = \tfrac{1}{9} \int d\vec{r}\,(V_{xx} + V_{yy} + V_{zz})(|a|^2 f_0 + |b|^2 g_0),$$

$$b' = -\tfrac{1}{18} \int d\vec{r}\,(2V_{zz} - V_{xx} - V_{yy})(|a|^2 f_1 - |b|^2 g_1 - (a^*b + ab^*)\sqrt{3} h_1),$$

and

$$d' = -(2/\sqrt{3}) \int d\vec{r}\, V_{yz}(|a|^2 f_X + |b|^2 g_X - (a^*b + ab^*) h_X/\sqrt{3}).$$

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[31]See, for example, Refs. 26 and 28.
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[34]This can be shown as follows. If D and D' have the same phase, in the expressions for the relative intensities, they can be chosen to be real without loss of generality, then

$$u=(2D')^2/[(D+D')^2+(2D')^2]\,,$$

$$v=-2D'(D+D')/[(D+D')^2+(2D')^2],$$

and thus $u^2+v^2=u$.

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Cycle-Free Approximations to Amorphous Semiconductors*

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The Hall-Weaire tight-binding semiconductor Hamiltonian is solved when the geometric structure has no closed cycles and is homogeneous, using a method developed by Onsager for ionic energies in ice. The solution yields two bands and two δ functions in the density of states in agreement with the general theorem of Weaire. This solution is proposed to be a reasonable first approximation for the band structures of amorphous semiconductors. The Hamiltonian is also solved when the underlying structure is the inhomogeneous Cayley tree for which surface states predominate. In this case the bands have the property of being nowhere continuous. Instead of just two δ functions outside the bands, there are sequences of bound-state δ functions which bridge the energy gap between bands when the model parameters fall in a finite interval.

I. INTRODUCTION

Recently Weaire[1,2] has proved that the Hamiltonian of tight-binding type

$$H=-V_1\sum_{\substack{ij\\nn}}|\Psi_i\rangle\langle\Psi_j|-V_2\sum_{\substack{km\\nn}}|\Psi_k\rangle\langle\Psi_m| \qquad (1.1)$$

has a band gap for all positive values of V_1 and V_2 except $V_2/V_1=2$. The basis states Ψ_i in (1.1) represent localized directed orbitals of sp^3 type. V_1 is the overlap integral on the four-coordinated atoms ($q=4$) and V_2 is the overlap integral on the bonds. The sums are restricted to nearest-neighbor (nn) pairs.

Also, recently[3] the problem of obtaining the band structure for ionic hopping energies in ice has been reduced to the Hamiltonian

$$H=-V\sum_{\substack{ij\\nn}}|\Psi_i\rangle\langle\Psi_j|\,, \qquad (1.2)$$

where $2V$ is the difference in energy between bonding and antibonding ionic orbitals and the underlying "lattice" is three-coordinated ($q=3$), infinite dimensional, and the shortest closed cycle has 18 steps. Therefore, a calculation was developed which assumed homogeneity and which ignored all closed cycles.[3] This approximation, which we call the bulk solution for cycleless structures, is analogous to the Bethe or quasichemical approximations in statistical mechanics.[4]

The first objective of this paper is to find the bulk solution for cycleless structures for the Hamiltonian in (1.1). We feel that the bulk solution provides the standard first approximation to both periodic structures, such as the diamond lattice, and