Selection Rules Connecting Different Points in the Brillouin Zone

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Selection rules for indirect radiative transitions and for intervalley scattering are investigated for Ge and Si. Comparison with experimental results of Haynes and of Benoit à la Guillaume supports (1) the present picture of the band structure of Ge with a conduction band minimum at the zone boundary, (2) the assignment of $L_{2'}$ as the symmetry of the LA phonon at the zone boundary in the [111] direction. The absence of the LA phonon in the Haynes radiative emission experiment still requires explanation. To obtain the required selection rules we take the product of two irreducible representations i and j that belong to *different* wave vectors $\mathbf{k}$ and $\mathbf{k}'$. The resulting character product is expressed in a form appropriate to a third group $G_{\mathbf{k}''}$ at $\mathbf{k}''=\mathbf{k}+\mathbf{k}'$. If the elements of $G_{\mathbf{k}''}$ are applied to $\mathbf{k}$ to generate a star and $N(C)$ is the number of points of the star invariant (or equivalent) under any element R in the class C (of $G_{\mathbf{k}''}$) then the character product is $N(C)\langle\chi^i(R)\chi^j(R)\rangle$ i.e., $N(C)$ times the product of the characters averaged over those R in C which belong to $G_{\mathbf{k}'}$ and $G_{\mathbf{k}''}$ (i.e., those whose characters can be found in the tables at $\mathbf{k}'$ and $\mathbf{k}''$).

THE PROBLEM

INTERVALLEY scattering of electrons and indirect transitions of electrons from the top of the valence band to the bottom of the conduction band, as seen in Ge and Si, are examples of processes in which different points of the Brillouin zone are connected by a perturbation—in this case due to phonons. Selection rules concern the vanishing or nonvanishing of an integral of the form

$$\int \psi_\lambda{}^i(\mathbf{k},\mathbf{r})\psi_\mu{}^j(\mathbf{k}',\mathbf{r})\psi_\nu{}^m(\mathbf{k}'',\mathbf{r})^* d\mathbf{r}, \tag{1}$$

where $\psi_\lambda{}^i(\mathbf{k},\mathbf{r})$ is a "Bloch wave" which belongs to the λth row of the ith irreducible representation of the group $G_{\mathbf{k}}$ of the wave vector $\mathbf{k}$, etc.

In Eq. (1) we can choose $\psi_\lambda{}^i(\mathbf{k},\mathbf{r})$ to represent an initial electron state, $\psi_\nu{}^m(\mathbf{k}'',\mathbf{r})$ a final electron state and $\psi_\mu{}^j(\mathbf{k}',\mathbf{r})$ as that portion of the perturbation Hamiltonian due to light, phonons, etc., which transforms according to the μth portion of irreducible representation j with propagation constant $\mathbf{k}'$.

In an experiment we are not concerned with an individual matrix element (1), but with transition probabilities which involve the absolute square of matrix element (1) summed over all final states of the same energy (i.e., over ν and over the star of $\mathbf{k}''$) and averaged with equal weight over the initial state (i.e., aside from a constant factor, one also sums over λ and the star of $\mathbf{k}$). This complete sum can be shown to be independent of μ and of which point of the star of $\mathbf{k}'$ is used. In other words, the experimentally observable results involve selection rules connecting *complete representations*, and not the more stringent rules which connect particular members of representations.

Character tables are available for the factor groups $G_{\mathbf{k}}/T_{\mathbf{k}}$, $G_{\mathbf{k}'}/T_{\mathbf{k}'}$, and $G_{\mathbf{k}''}/T_{\mathbf{k}''}$. [Here $T_{\mathbf{k}}$ is that invariant subgroup of the pure translations $(\boldsymbol{\varepsilon}|\mathbf{t})$ such that $\exp(i\mathbf{k}\cdot\mathbf{t})=1$.] Conventional methods for determining selection rules by taking products of characters depend on the three wave functions transforming according to irreducible representations of the same group. Since it is inconvenient to work with the complete space group, Elliott and Loudon[1] have suggested that one consider the group of elements G_s common to $G_{\mathbf{k}}$, $G_{\mathbf{k}'}$, and $G_{\mathbf{k}''}$. If T_s is the corresponding intersection of $T_{\mathbf{k}}$, $T_{\mathbf{k}'}$, $T_{\mathbf{k}''}$, Elliott and Loudon suggest that conventional group theory may then be applied using the irreducible representations of the (generally) new factor group G_s/T_s. This procedure, while correct, may require the construction of a new group and a new character table. Indeed, Elliott in constructing such character tables indicates that it is convenient for these computations to construct a complete character table including those in which the character of an element $(\boldsymbol{\varepsilon}|\mathbf{t}')$, say, of $G_{\mathbf{k}}$, is the dimension of the representation times $\exp(in\mathbf{k}\cdot\mathbf{t}')$ with integers n other than unity.

The purpose of this note is to show that the selection rules may be derived using *only existing* character tables, and only the representations *already found* in those tables.

THE NEW METHOD

We take for granted the selection rule

$$\mathbf{k}+\mathbf{k}'\doteq\mathbf{k}'', \tag{2}$$

which follows from the translations, where $\doteq$ implies that the two sides of the equation are equal, or equivalent (differ by a reciprocal lattice vector).

The conventional method of obtaining selection rules for (1) is to use any two factors say $\psi_\lambda{}^i(\mathbf{k},\mathbf{r})\psi_\mu{}^j(\mathbf{k}',\mathbf{r}')$ as a basis for constructing a product representation $\Gamma^{(i\times j)}$. One then decomposes the product representation to see if it contains Γ^m. This procedure is predicted on the assumption that i, j, and m constitute representations of the *same group*, whereas we prefer to regard them as belonging to three groups,

$$G_{\mathbf{k}}/T_{\mathbf{k}}, \quad G_{\mathbf{k}'}/T_{\mathbf{k}'} \quad \text{and} \quad G_{\mathbf{k}''}/T_{\mathbf{k}''}.$$

The inadequacy of the usual procedure, in our

[1] R. J. Elliott and R. Loudon, J. Phys. Chem. Solids **15**, 146 (1960).

present situation, may be summarized by the statement that the set of wave functions $\psi_\lambda{}^i(\mathbf{k},\mathbf{r})\psi_\mu{}^j(\mathbf{k}',\mathbf{r}')$ for all λ and μ may not span a complete representation of $G_{\mathbf{k}''}/T_{\mathbf{k}''}$ in the sense that an element S of the latter group may take one outside our starting set of wave functions. We must therefore augment our original product functions by using as a basis, the set

$$S\psi_\lambda{}^i(\mathbf{k},\mathbf{r})\psi_\mu{}^j(\mathbf{k}',\mathbf{r}'), \tag{3}$$

where λ and μ run over their usual values, and S runs over the factor group $G_{\mathbf{k}''}/T_{\mathbf{k}''}$.

[The above statement may seem mysterious if we happen to remember that the elements S of a factor group $G_{\mathbf{k}''}/T_{\mathbf{k}''}$ are cosets. However, these cosets have the form $(\alpha|\tau)T_{\mathbf{k}''}$ and for any elements of the translation group $T_{\mathbf{k}''}$ we have

$$T_{\mathbf{k}''}\psi(\mathbf{k}'',\mathbf{r})=\psi(\mathbf{k}'',\mathbf{r}),$$

as essentially the definition of the group $T_{\mathbf{k}''}$. Hence, all members of any one coset produce the same action in $\psi(\mathbf{k}'',\mathbf{r})$. For calculational purposes, we then do what we would have done without thinking, namely use for S not a coset, but any "representative element" of that coset. Since $\psi(\mathbf{k},\mathbf{r})\psi(\mathbf{k}',\mathbf{r}')$ has the same translational properties as $\psi(\mathbf{k}'',\mathbf{r})$, it is legitimate to regard S in Eq. (3) as such a representative element.]

Of course, not all the elements S in Eq. (3) will produce new wave functions. Bearing in mind this possible redundancy, we may calculate the character of an element R in the class C of the factor group $G_{\mathbf{k}''}/T_{\mathbf{k}''}$ in the form

$$\chi^{i\times j}(C)=(1/r)\sum_{S,\lambda,\mu}\int\int[S\psi_\lambda{}^i(\mathbf{k},\mathbf{r})\psi_\mu{}^j(\mathbf{k}',\mathbf{r}')]^*\times RS\psi_\lambda{}^i(\mathbf{k},\mathbf{r})\psi_\mu{}^j(\mathbf{k}',\mathbf{r}')d\mathbf{r}d\mathbf{r}', \tag{4}$$

where r is an integer we divide by to eliminate the redundancy. However, a matrix element of the form

$$\int\psi_\lambda{}^i(\mathbf{k},\mathbf{r})^*S^{-1}RS\psi_\lambda{}^i(\mathbf{k},\mathbf{r})d\mathbf{r} \tag{5}$$

vanishes unless $S^{-1}RS$ leaves $\mathbf{k}$ invariant or changes it by a reciprocal lattice vector, i.e., unless $S^{-1}RS$ belongs to the group at $\mathbf{k}$. If the sums over λ and μ in (4) are performed we obtain

$$\chi^{i\times j}(C)=(1/r)\sum_S\chi^i(S^{-1}RS)\chi^j(S^{-1}RS)J(S^{-1}RS), \tag{6}$$

where $J(U)=1$, if U is common to the groups at $\mathbf{k}$, $\mathbf{k}'$, and $\mathbf{k}''$ (i.e., belongs to G_s/T_s) and zero otherwise. Note that $S^{-1}RS$ automatically belongs to $\mathbf{k}''$ since each factor does, i.e.,

$$S^{-1}RS\mathbf{k}''\doteq\mathbf{k}''. \tag{7}$$

If therefore,

$$S^{-1}RS\mathbf{k}\doteq\mathbf{k}, \tag{8}$$

then the same relation is obeyed for $\mathbf{k}'$ by subtraction. Thus in practice, we need only use $J(U)$ to "project" into the groups at $\mathbf{k}$ or $\mathbf{k}'$ but not both.

Since the sum over S takes $S^{-1}RS$ through the class C (an integral number of times), Eq. (6) automatically yields a result that is independent of which element R of C is chosen. We can rewrite (6) in the more useful form:

$$\chi^{i\times j}(C)=\langle\chi^i(C)\chi^j(C)\rangle K, \tag{9}$$

where

$$\langle\chi^i(C)\chi^j(C)\rangle=\sum_S\chi^i(S^{-1}RS)\chi^j(S^{-1}RS)J(S^{-1}RS)/\sum_S J(S^{-1}RS)$$

$$=\sum_{R\text{ in }C}\chi^i(R)\chi^j(R)J(R)/\sum_{R\text{ in }C}J(R) \tag{10}$$

is the character product averaged over the elements R in the class C of $\mathbf{k}''$ which belong to the common group and

$$K=(1/r)\textstyle\sum_S J(S^{-1}RS) \tag{11}$$

has a simple geometric interpretation. If we let $|\mathbf{k}\rangle$ denote the point $|\mathbf{k}\rangle$ in the Brillouin zone, then the set $S|\mathbf{k}\rangle$ constitutes a set of *nonequivalent* points $|\mathbf{k}_j\rangle$ repeated with a redundancy r. We may refer to the nonequivalent set of points $|\mathbf{k}_j\rangle$ as the $\mathbf{k}''$ star of $\mathbf{k}$ (or substar since it is generated from $|\mathbf{k}\rangle$ using the elements of the group at $\mathbf{k}''$ rather than the group at $\mathbf{k}''=0$). We can now write

$$J(S^{-1}RS)=\langle\mathbf{k}|S^{-1}RS|\mathbf{k}\rangle, \tag{12}$$

which is one or zero according as $S^{-1}RS$ belongs to $\mathbf{k}$ or not. Thus, we can rewrite Eq. (11):

$$K=(1/r)\textstyle\sum_S\langle S\mathbf{k}|R|S\mathbf{k}\rangle=\sum_j\langle\mathbf{k}_j|R|\mathbf{k}_j\rangle \tag{13}$$

in the form of the trace or character of R in this substar representation which is no longer redundant. Equation (9) can then be written more mnemonically as

$$\chi^{i\times j}(C)=\langle\chi^i(C)\chi^j(C)\rangle N_{\mathbf{k}''\text{ star }\mathbf{k}}(C), \tag{14}$$

where $K=N_{\mathbf{k}''\text{ star }\mathbf{k}}(C)$ is the number of points $|\mathbf{k}_j\rangle$ of the substar which are unchanged by (invariant or equivalent under) any element R of the class C. This substar simplifies in several cases. If $\mathbf{k}''=0$ the substar is identical to the usual star. If $\mathbf{k}$ or $\mathbf{k}'=0$, the substar has only one prong, and $K=1$ or 0, so that the last factor in (14) can be omitted providing the average over the nonvanishing contributions to the character product is taken to be zero when there are no such contributions.

DISCUSSION OF GROUP THEORETICAL RESULTS

If those elements R of the class C in the group at $\mathbf{k}''$ which contribute (i.e., belong to the groups at $\mathbf{k}$ and $\mathbf{k}'$) belong to a single class in $\mathbf{k}$, and to a single class in $\mathbf{k}'$, then a *typical character product agrees with*

the average character product and the averaging process indicated in (14) may be omitted. This may occur in a trivial way when only one element R in C contributes. It will often occur by accident. A nontrivial case, in which these conditions are automatically satisfied, occurs when $\mathbf{k}'=0$ since the group at $\mathbf{k}''=\mathbf{k}$ is then a subgroup of that at $\mathbf{k}'=0$ and the classes at $\mathbf{k}$ are contained within those at $\mathbf{k}'=0$. For the case $\mathbf{k}'=0$ then one merely takes $\chi^{i\times j}(C)=\chi^i(R)\chi^j(R)$ where R is any element in C.

The final formula (14), that we use in our applications, is independent of the redundancy r. However, this redundancy is known. If $S|\mathbf{k}\rangle=R|\mathbf{k}\rangle$, then $S^{-1}R=U$ is a member of the common group G_s/T_s of order h_s. Thus the h_s members of the coset SU (where U runs over the common group) produce the same point $S|\mathbf{k}\rangle$ of the star, and the redundancy factor is

$$r=h_s, \tag{15}$$

the order of the common group. In order to keep the number of translational elements the same, let us use the factor groups G_k/T_s, $G_{k'}/T_s$, $G_{k''}/T_s$, and G_s/T_s. The distinct elements of the $\mathbf{k}''$ star of $\mathbf{k}$ are then produced by the elements of the factor group

$$(G_{k''}/T_s)/(G_s/T_s)\equiv(G_{k''}/G_s), \tag{16}$$

if G_s is an invariant subgroup of $G_{k''}$. In any case, the use of the left cosets SU tells us that the number of elements in the star is:

$$N_{\mathbf{k}''\text{ star }\mathbf{k}}((\mathfrak{e}|0))=h_{\mathbf{k}''}/h_s, \tag{17}$$

where $h_{\mathbf{k}''}$ and $h_{\mathbf{k}}$ are the orders of the factor groups at $\mathbf{k}''$ and $\mathbf{k}$ with the same number of translational elements removed from each and $(\mathfrak{e}|0)$ is the identity element. Since $\mathbf{k}''=0$ yields the complete star of $\mathbf{k}$, we have the inequality

$$h_{\mathbf{k}''}/h_s\leq h_0/h_{\mathbf{k}},$$

or

$$h_s\geq h_{\mathbf{k}}h_{\mathbf{k}''}/h_0, \tag{18}$$

where h_0 is the order of the factor group at $\mathbf{k}''=0$. This inequality is useful in checking whether one has found all of the h_s elements of the "common group."

We have chosen to express our results (13) in terms of a geometric representation, the $\mathbf{k}''$ star of $\mathbf{k}$ whose properties are readily visualized, and whose characters can be calculated mentally. This is just a device, however, to avoid using the common group G_s/T_s. If we have this group available, then we could evaluate (11) in a different way using the class rearrangement theorem:

$$\sum_S J(S^{-1}RS)=\frac{h_{\mathbf{k}''}}{n_{\mathbf{k}''}(C)}\sum_{R\text{ in }C}J(R), \tag{19}$$

or

$$\textstyle\sum_S J(S^{-1}RS)=h_{\mathbf{k}''}n_s(C)/n_{\mathbf{k}''}(C), \tag{20}$$

where $n_{\mathbf{k}''}(C)$ is the number of elements in the class C of $(G_{\mathbf{k}''}/T_s)$ and $n_s(C)$ is the number of these elements which belong to the common group (G_s/T_s). They need not all fall in the same class in the latter group.

Combining (11), (14), and (20), we obtain

$$N_{\mathbf{k}''\text{ star }\mathbf{k}}(C)=(h_{\mathbf{k}''}/h_s)[n_s(C)/n_{\mathbf{k}''}(C)]. \tag{21}$$

$n_s(C)$ is most readily determined by taking the character table at $\mathbf{k}$ and counting the number of elements which are also in $\mathbf{k}''$. Equation (21), which provides a check on direct calculations in the star representation, requires a knowledge of the elements of the common group, but not their arrangement into classes or their character table.

REDUNDANCY AND RELATION TO ELLIOTT AND LOUDON

An assumption has been tacitly made in the analysis of this paper: The redundancy which enters the set of wave functions (3) is identical to the redundancy in producing the star representation (13). If this were not the case, our characters would be incorrect by a constant factor, which would not affect selection rules—but we might not know how many times c_{ijm}, the representation χ^m is repeated in the product representation:

$$\chi^{i\times j}(C)=\textstyle\sum_m c_{ijm}\chi^m(C). \tag{22}$$

This final result of our analysis:

$$c_{ijm}=(1/h_{k''})\textstyle\sum_C \chi^{i\times j}(C)n_{\mathbf{k}''}(C)\chi^m(C)^* \tag{23}$$

can also be computed using the nonredundant set of functions

$$\psi_\lambda{}^i(\mathbf{k},\mathbf{r})\psi_\mu{}^j(\mathbf{k}',\mathbf{r}')\psi_\nu{}^m(\mathbf{k}'',\mathbf{r}'')^* \tag{24}$$

as a basis for a representation of the common group G_s/T_s. No operators S need be applied since the elements U of the common group do not change $\mathbf{k}$, $\mathbf{k}'$, or $\mathbf{k}''$. We then need to know how many times this triple product representation contains the identity representation. Standard group theory takes the product of the characters and leads to the result

$$c_{ijm}=(1/h_s)\sum_{U\text{ in }h_s}\chi^i(U)\chi^j(U)\chi^m(U)^* \tag{25}$$

which is also a fairly convenient formula in practice. The equivalence of this procedure with our previous result (14) may be obtained by extending the sum over all the elements R of $\mathbf{k}''$ but inserting the projection $J(R)$ that selects the U among the R:

$$c_{ijm}=(1/h_s)\textstyle\sum_R \chi^i(R)\chi^j(R)J(R)\chi^m(R)^*. \tag{26}$$

Perform first sum over elements in a class, and then the sum over classes:

$$c_{ijm}=\frac{1}{h_{\mathbf{k}''}}\sum_C\left[\frac{h_{\mathbf{k}''}}{h_s}\frac{1}{n_{\mathbf{k}''}(C)}\sum_{R\text{ in }C}\chi^i(R)\chi^j(R)J(R)\right]\times n_{\mathbf{k}''}(C)\chi^m(C). \tag{27}$$

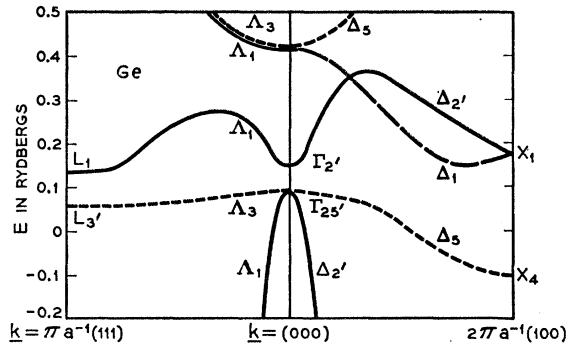

FIG. 1. The band structure of germanium near the energy gap, as computed by J. C. Phillips, Phys. Rev. 112, 685 (1958).

Comparison with (23) suggests that we interpret the quantity in brackets as the character in the $i\times j$ representation.

$$\chi^{i\times j}(C)=\frac{\sum\chi^i(R)\chi^j(R)J(R)}{\sum J(R)}\frac{h_{k''}}{h_s}\frac{\sum J(R)}{n_{k''}(C)}. \quad (28)$$

In view of (10) and

$$\sum_{R\text{ in }C} J(R)=n_s(C), \quad (29)$$

we see that (28) is identical with our previous result (14) combined with (21).

INDIRECT OPTICAL TRANSITIONS IN Ge

The band structure of Ge near the energy gap is shown in Fig. 1. The minimum in the conduction band occurs at the point $L=(\pi/a)(1,1,1)$ on the zone boundary with symmetry L_1^+ whereas the maximum in valence band occurs at $\Gamma=(0,0,0)$, with symmetry Γ_{25}^+. Thus, a direct optical transition which preserves $\mathbf{k}$ vector, (vertical on the diagram) does not connect the desired states. An electron could drop radiatively from L_1^+ to L_3^- and then be scattered by a phonon from L_3^- to Γ_{25}^+ or it could be scattered first from L_1^+ to Γ_2^- and thence drop radiatively to Γ_{25}^+.

In both cases, the radiative part of the transition is allowed. Light has the symmetry Γ_{15}^- [which transforms like an ordinary vector (x,y,z)]. Thus

$$\Gamma_{25}^+\times\Gamma_{15}^-=\Gamma_2^-+\Gamma_{12}^-+\Gamma_{25}^-+\Gamma_{15}^- \quad (30)$$

contains Γ_2^-, and

$$L_3^-\times\Gamma_{15}^-=L_1^++L_2^++2L_3^+ \quad (31)$$

contains L_1^+. These character products were computed directly from Tables II and III. The symmetry operations are given for reference in Table I.

We must, therefore, discuss the phonon part of the transition. In the conduction band, we have

$$L_1^+\times\Gamma_2^-=L_2^-\equiv LA, \quad (32)$$

TABLE I. Symmetry operations of factor group of space group O_h^7 (diamond).[a]

Class	Simple operation		Class	Compound operation		Comments
E	$\mathfrak{e}$	XYZ	J	$\mathfrak{i}$	$\bar{X}\bar{Y}\bar{Z}$	$\mathfrak{i}$=inversion
C_2	$\mathfrak{d}_{2x}$	$X\bar{Y}\bar{Z}$	$3JC_4^2$	$\mathfrak{o}_x$	$\bar{X}YZ$	$\mathfrak{d}_{2x}$=180° rotation about x axis;
	$\mathfrak{d}_{2y}$	$\bar{X}Y\bar{Z}$		$\mathfrak{o}_y$	$X\bar{Y}Z$	$\mathfrak{o}_x=i\mathfrak{d}_{2x}$=(100) reflection plane.
	$\mathfrak{d}_{2z}$	$\bar{X}\bar{Y}Z$		$\mathfrak{o}_z$	$XY\bar{Z}$	
$6JC_4$	$\mathfrak{s}_{4x}$	$\bar{X}Z\bar{Y}$	$6C_4$	$\mathfrak{d}_{4x}$	$X\bar{Z}Y$	$\mathfrak{d}_{4x}$=90° counterclockwise rotation
	$(\mathfrak{s}_{4x})^{-1}$	$\bar{X}\bar{Z}Y$		$(\mathfrak{d}_{4x})^{-1}$	$XZ\bar{Y}$	about x axis. $\sigma_{4x}=i\delta_{4x}$
	$\mathfrak{s}_{4y}$	$Z\bar{Y}\bar{X}$		$\mathfrak{d}_{4y}$	$\bar{Z}YX$	
	$(\mathfrak{s}_{4y})^{-1}$	$\bar{Z}\bar{Y}X$		$(\mathfrak{d}_{4y})^{-1}$	$ZY\bar{X}$	
	$\mathfrak{s}_{4z}$	$Y\bar{X}\bar{Z}$		$\mathfrak{d}_{4z}$	$\bar{Y}XZ$	
	$(\mathfrak{s}_{4z})^{-1}$	$\bar{Y}X\bar{Z}$		$(\mathfrak{d}_{4z})^{-1}$	$Y\bar{X}Z$	
$6JC_2$	$\mathfrak{o}_{\bar{y}z}$	XZY	$6C_2$	$\mathfrak{d}_{2\bar{y}z}$	$\bar{X}\bar{Z}\bar{Y}$	$\mathfrak{d}_{2\bar{y}z}$=180° rotations about axis
	$\mathfrak{o}_{\bar{z}x}$	ZYX		$\mathfrak{d}_{2\bar{z}x}$	$\bar{Z}\bar{Y}\bar{X}$	which bisects $\bar{y}$ and z axes.
	$\mathfrak{o}_{\bar{x}y}$	YXZ		$\mathfrak{d}_{2\bar{x}y}$	$\bar{Y}\bar{X}\bar{Z}$	$\mathfrak{o}_{\bar{y}z}=i\mathfrak{d}_{2\bar{y}z}$=(011) reflection plane;
	$\mathfrak{o}_{yz}$	$X\bar{Z}\bar{Y}$		$\mathfrak{d}_{2yz}$	$\bar{X}ZY$	$\mathfrak{o}_{yz}=i\mathfrak{d}_{2yz}$=(01$\bar{1}$) reflection
	$\mathfrak{o}_{zx}$	$\bar{Z}Y\bar{X}$		$\mathfrak{d}_{2zx}$	$Z\bar{Y}X$	plane
	$\mathfrak{o}_{xy}$	$\bar{Y}\bar{X}Z$		$\mathfrak{d}_{2xy}$	$YX\bar{Z}$	
$8C_3$	$\mathfrak{d}_{3xyz}$	YZX	$8JC_3$	$\mathfrak{s}_{6xyz}$	$\bar{Y}\bar{Z}\bar{X}$	$\mathfrak{d}_{3x\bar{y}\bar{z}}$=120° counterclockwise rotation
	$\mathfrak{d}_{3x\bar{y}\bar{z}}$	$\bar{Y}Z\bar{X}$		$\mathfrak{s}_{6x\bar{y}\bar{z}}$	$Y\bar{Z}X$	about [1$\bar{1}\bar{1}$] direction
	$\mathfrak{d}_{3\bar{x}y\bar{z}}$	$\bar{Y}\bar{Z}X$		$\mathfrak{s}_{6\bar{x}y\bar{z}}$	$YZ\bar{X}$	$=\mathfrak{d}_{2x}\mathfrak{d}_{3xyz}\mathfrak{d}_{2x}$
	$\mathfrak{d}_{3\bar{x}\bar{y}z}$	$Y\bar{Z}\bar{X}$		$\mathfrak{s}_{6\bar{x}\bar{y}z}$	$\bar{Y}ZX$	
	$(\mathfrak{d}_{3xyz})^{-1}$	ZXY		$(\mathfrak{s}_{6xyz})^{-1}$	$\bar{Z}\bar{X}\bar{Y}$	$\mathfrak{s}_{6x\bar{y}\bar{z}}=i\mathfrak{d}_{3x\bar{y}\bar{z}}$
	$(\mathfrak{d}_{3x\bar{y}\bar{z}})^{-1}$	$\bar{Z}\bar{X}Y$		$(\mathfrak{s}_{6x\bar{y}\bar{z}})^{-1}$	$ZX\bar{Y}$	
	$(\mathfrak{d}_{3\bar{x}y\bar{z}})^{-1}$	$Z\bar{X}\bar{Y}$		$(\mathfrak{s}_{6\bar{x}y\bar{z}})^{-1}$	$\bar{Z}XY$	
	$(\mathfrak{d}_{3\bar{x}\bar{y}z})^{-1}$	$\bar{Z}X\bar{Y}$		$(\mathfrak{s}_{6\bar{x}\bar{y}z})^{-1}$	$Z\bar{X}Y$	

[a] Origin at an atom. Simple operation α is $(\alpha|0)$. Compound operation is $(\alpha|\tau)$, where $\tau=(a/4,a/4,a/4)$ connects the atom to its nearest neighbor in the first octant.

TABLE II. Group characters at $\Gamma\equiv(0,0,0)$.[a]

Class	Typical element	$\Gamma_1^{\pm}$	$\Gamma_2^{\pm}$	$\Gamma_{12}^{\pm}$	$\Gamma_{15}^{\pm}$	$\Gamma_{25}^{\pm}$	Star Δ	Star X	Star Λ	Star L
E	$(\mathfrak{e}\|0)$	1	1	2	3	3	6	3	8	4
$3C_4^2$	$(\mathfrak{d}_{2x}\|0)$	1	1	2	−1	−1	2	3	0	0
$6C_4$	$(\mathfrak{d}_{4x}\|\tau)$	1	−1	0	1	−1	2	1	0	0
$6C_2$	$(\mathfrak{d}_{2xy}\|\tau)$	1	−1	0	−1	1	0	1	0	2
$8C_3$	$(\mathfrak{d}_{3xyz}\|0)$	1	1	−1	0	0	0	0	2	1
J	$(\mathfrak{i}\|\tau)$	±1	±1	±2	±3	±3	0	1	0	4
$3JC_4^2$	$(\mathfrak{o}_x\|\tau)$	±1	±1	±2	∓1	∓1	4	3	0	0
$6JC_4$	$(\mathfrak{o}_{4x}\|0)$	±1	∓1	0	±1	∓1	0	1	0	0
$6JC_2$	$(\mathfrak{o}_{yz}\|0)$	±1	∓1	0	∓1	±1	2	1	4	2
$8JC_3$	$(\mathfrak{o}_{6xyz}\|\tau)$	±1	±1	∓1	0	0	0	0	0	1

[a] Note: $\Gamma_1^+=\Gamma_1$, $\Gamma_2^+=\Gamma_2$, $\Gamma_{12}^+=\Gamma_{12}$, $\Gamma_{15}^+=\Gamma_{15'}$, $\Gamma_{25}^+=\Gamma_{25'}$. Star Δ is the number of points in the star of Δ left invariant (or equivalent) by the group element.

whereas in the valence band

$$L_3^-\times\Gamma_{25}^+=L_1^-+L_2^-+2L_3^-=\text{none}+LA+2TO, \quad (33)$$

where LA=longitudinal acoustic phonon, and TO=transverse optical phonon. (See Fig. 2 for the phonon spectrum and its symmetry classification.) Thus only two phonons LA and TO are allowed. The Haynes[2] experimental data clearly show three peaks, which by comparison with the vibration spectrum determined by Brockhouse,[3] Fig. 2, can definitely be assigned to be TA, LA, and TO. Thus the forbidden TA is observed. Kane[4] has suggested that the reason for this is that the conduction-band minimum is not right at the zone boundary. The selection rule (33) using Tables II and IV is replaced by

$$\Lambda_3\times\Gamma_{25}^+=\Lambda_1+\Lambda_2+2\Lambda_3, \quad (34)$$

TABLE III. Group characters at $L=(\pi/a)(1,1,1)$.[a]

		$L_1^{\pm}$	$L_2^{\pm}$	$L_3^{\pm}$
E	$(\mathfrak{e}\|0)$	1	1	2
$2C_3$	$(\mathfrak{d}_{3xyz},\mathfrak{d}_{3xyz}^{-1}\|0)$	1	1	−1
$3C_2$	$(\mathfrak{d}_{2\bar{y}z},\mathfrak{d}_{2\bar{z}x},\mathfrak{d}_{2\bar{x}y}\|\tau)$	1	−1	0
6	$(\mathfrak{i}\|\tau)(\alpha\|\mathbf{t})$		$\pm\chi(\alpha\|\mathbf{t})$	

[a] Note: $L_1^+=L_1$, $L_2^+=L_2$, $L_3^+=L_3$, $L_1^-=L_{1'}$, $L_2^-=L_{2'}$, $L_3^-=L_{3'}$.

TABLE IV. Group characters at $\Lambda\equiv(k,k,k)$.

		Λ_1	Λ_2	Λ_3
E	$(\mathfrak{e}\|0)$	1	1	2
$2C_3$	$(\mathfrak{d}_{3xyz},\mathfrak{d}_{3xyz}^{-1}\|0)$	1	1	−1
$3JC_2$	$(\mathfrak{o}_{\bar{y}z},\mathfrak{o}_{\bar{z}x},\mathfrak{o}_{\bar{x}y}\|0)$	1	−1	0

[2] J. R. Haynes, M. Lax, and W. F. Flood, J. Phys. Chem. Solids 8, 392 (1959).
[3] B. N. Brockhouse and P. K. Iyengar, Phys. Rev. 111, 747 (1958); 113, 1696 (1959).
[4] E. Kane (private communication).

which seems to have the identical structure. But as we can see from Fig. 2 both TA and TO phonons have symmetry Λ_3. (In other words, they are coupled together for finite $\mathbf{k}$ but decoupled at the zone boundary.) Thus both TA and TO would be allowed.

A more likely explanation of the data is that the minimum is *at* the zone boundary, but if electrons and holes have some kinetic energy they occupy a region *near* the zone boundary of width Δk determined by $(\hbar^2/2m^*)(\Delta\mathbf{k})^2\simeq\kappa T$. The selection rules would then be governed by Eq. (34) but we would be looking at a

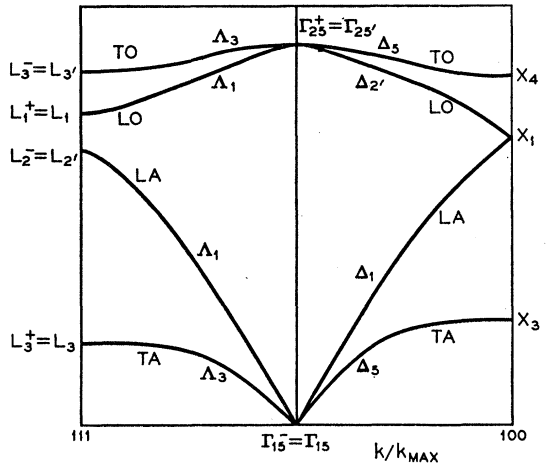

FIG. 2. The vibration spectrum of germanium determined by B. N. Brockhouse and P. K. Iyengar, Phys. Rev. 111, 747 (1958). The symmetry assignment is slightly ambiguous and is to be made as follows: $LO>LA$, therefore L_1 or $L_{2'}$ is LO whichever is higher. Similarly $TO>TA$, therefore the higher of $L_{3'}$ and L_3 (and of X_4 and X_1) is to be assigned to TO. On a nearest neighbor model, with central and noncentral forces α and β, the frequency (or rather $M\omega^2$) for each symmetry type is given by: $X_4=4\alpha+4\beta$, $X_1=4\alpha$, $X_3=4\alpha-4\beta$; $L_{3'}=6\alpha+2\beta$, $L_1=2\alpha+4\beta$, $L_{2'}=6\alpha-4\beta$, $L_3=2\alpha-2\beta$. The above assignment is consistent with $\beta>\frac{1}{2}\alpha$. The Haynes observation of LA phonons when $L_{2'}$ are allowed by Eqs. (32) and (33), clinches the assignment $L_{2'}=LA$. The remaining assignments merely require $\beta>0$ which is required to obtain a sensible fit to the vibration spectrum even when longer range forces are present. See F. Herman, J. Phys. Chem. Solids 8. 405 (1959).

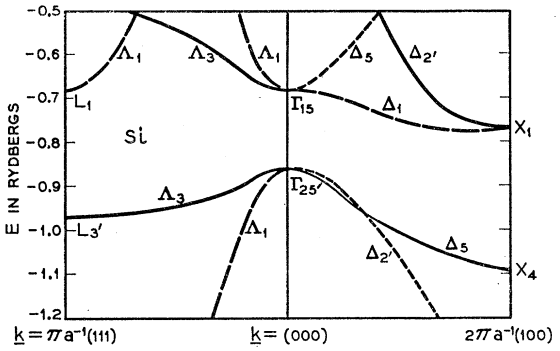

FIG. 3. The band structure of silicon near the energy gap as computed by J. C. Phillips, Phys. Rev. 112, 685 (1958).

first-forbidden transition whose matrix element is proportional to $\Delta\mathbf{k}$. The ratio of the integrated intensities of the TA line to either of the allowed lines should then be proportional to $\langle(\Delta k)^2\rangle$ or T. Recent experiments at the Ecole Normale[5] below 20°K show just this behavior. These experiments provide a *qualitative* proof that the minimum in Ge is at the zone boundary. Previous experimental results[6,7] attempted *quantitative* measurements of the density of states to better than a factor of two to distinguish between the four minimum picture at the zone boundary and the eight minimum picture in the interior.

The results of Macfarlane *et al.*[7] that the indirect optical absorption with TA was $\propto(\Delta E)^{\frac{3}{2}}$ had *previously established* that TA was *forbidden*. However, the *above conclusions could only be drawn with the help of the group theoretical results that TA is forbidden at L* (and allowed at Λ) whereas at the time a parity argument[8,9] seemed to indicate that TA is *allowed*. (The error in the parity argument seems to be the assumption that the parity at L is identical to that at Γ.)

INDIRECT OPTICAL TRANSITIONS IN Si

The band structure of Si is shown in Fig. 3. The minimum in the conduction band occurs in the [100] direction about 85% of the way to the zone boundary. The symmetry is Δ_1. The corresponding point in the valence band is Δ_5. Using Tables II and V and Eq. (14) we find,

$$\Delta_1\times\Delta_5=\Gamma_{15}^+ +\Gamma_{25}^+ +\Gamma_{15}^- +\Gamma_{25}^-. \tag{35}$$

The presence of Γ_{15}^- means the radiative transition is allowed.

[5] C. Benoit à la Guillaume and O. Parodi, *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Publishing House of the Czechoslovak Academy of Sciences, Prague, 1961), p. 426.
[6] D. K. Stevens, J. W. Cleland, J. H. Crawford, Jr., and H. C. Schweinler, Phys. Rev. **100**, 1084 (1955). E. M. Conwell, *ibid.* **99**, 1195 (1955). M. Pollak, *ibid.* **111**, 798 (1958).
[7] G. G. Macfarlane, T. P. McLean, J. E. Quarrington, and V. Roberts, Phys. Rev. **108**, 1377 (1957).
[8] R. J. Elliott, Phys. Rev. **108**, 1384 (1957).
[9] J. R. Haynes, M. Lax, and W. F. Flood, Proceedings of the Prague Conference on Semiconductors (op. cit.), pp. 423–425.

TABLE V. Group characters at $\Delta=(k,0,0)$.[a]

		Δ_1	Δ_2	$\Delta_{2'}$	$\Delta_{1'}$	Δ_5	Δ star Δ
1	$(\varepsilon\|0)$	1	1	1	1	2	4
1	$(\delta_{2x}\|0)$	1	1	1	1	−2	0
2	$(\delta_{4x},\delta_{4x}^{-1}\|\tau)$	λ	$-\lambda$	$-\lambda$	λ	0	0
2	$(\varrho_y,\varrho_z\|\tau)$	λ	λ	$-\lambda$	$-\lambda$	0	0
2	$(\varrho_{yz},\varrho_{\bar{y}z}\|0)$	1	−1	1	−1	0	2
	$(\varepsilon\|t_{xy})(\alpha\|\mathbf{t})$			$\lambda^2\chi(\alpha\|\mathbf{t})$			

[a] Notes: $\mathbf{t}_{xy}=(a/2,a/2,0)$, where $\lambda=\exp(-ik_xa/4)$. At X, $\lambda=-i$. Δ star Λ = number of points of the star of Λ formed using elements of Δ that are invariant under the group element.

The maximum in the valence band occurs at $k=0$ with symmetry Γ_{25}^+. Equation (30) shows that the transition to the conduction band state Γ_{15}^- via a Γ_{15}^- photon is allowed.

The silicon phonon spectrum is shown in Fig. 4.

The phonon transition in the valence band from Γ_{25}^+ to Δ_5

$$\begin{aligned}\Gamma_{25}^+\times\Delta_5&=(\Delta_5)+(\Delta_1+\Delta_{2'})+\Delta_{1'}+\Delta_2\\&=(TO+TA)+(LA+LO),\end{aligned} \tag{36}$$

i.e., all phonons are permitted. These transitions may be weak, however, since the energy denominator in the intermediate state is fairly large in this case, where the radiative transition occurs first.

The more important phonon transition in the conduction band from Δ_1 to Γ_{15}^-

$$\Gamma_{15}^-\times\Delta_1=\Delta_1+\Delta_5=LA+(TO+TA), \tag{37}$$

so that via the conduction band, only LO is forbidden by group theory. On the other hand, the Haynes experimental results exhibit peaks associated only with the two transverse phonons. The LA phonon contribution is weak for reasons that do not seem to be group theoretical. The possible influence of time reversal will be discussed in a subsequent paper.

POSSIBLE PITFALLS: INTERVALLEY SCATTERING IN Ge

In order to illustrate the possible pitfalls which can occur in both intuitive and formal arguments, we shall discuss intervalley scattering in Ge. Here the minimum in the conduction band $\mathbf{k}_0$ occurs at the zone boundary in the [111] direction and at three other nonequivalent points: $\mathbf{k}_0=(1,1,1)$; $(1,-1,-1)$; $(-1,1,-1)$ and $(-1,-1,1)$. The points $-\mathbf{k}_0$ are equivalent to $\mathbf{k}_0$.

The conduction band state at k_0 is $L_1=L_1^+$, i.e., the state is even under inversion, and belongs to the nondegenerate identity representation whose characters are all plus one.

We now make the following intuitive argument: To scatter an electron from an even L_1 state at (1,1,1) to an even L_1 state at $(1,-1,-1)$, we need an even (2,0,0) phonon. However, an examination of the character table at X shows four irreducible represen-

tations, X_1, X_2, X_3, and X_4 all of which are two-dimensional, and all of which have character zero for inversion. Thus these representations can be taken to be half-even and half-odd. This might be interpreted to mean that one of the two $X_3(TA)$ phonons is allowed, one of the two $X_4(TO)$ phonons is allowed, and one of the two $X_1(LO+LA)$ phonons is allowed and the other is forbidden. This conclusion, however, contradicts our statement following Eq. (1), that selection rules must involve entire representations. Perhaps, then, X_1, X_3, and X_4 are all allowed—or all forbidden.

Elliott and Loudon, using Eq. (25), have found that X_1 and X_4 are allowed, whereas our calculation leads to

$$L_1 \times L_{1t} = X_1 + X_3, \tag{38}$$

where L_{1t} is the L_1 representation transformed from the (1,1,1) point to the (1, −1, −1) point. Since we have established that our group theoretical procedure is equivalent to the Elliott-Loudon one,[1] the discrepancy must lie in how they were applied. A conversation with Elliott has revealed the source of the discrepancy. He has taken L_{1t} to be the identity representation at (1, −1, −1) with characters all plus one, whereas we have used the characters shown in Table VI. These characters have been obtained using the relation

$$\Psi_{Lt}(\mathbf{r}) = \mathfrak{d}_{2x}\Psi_L(\mathbf{r}) \tag{39}$$

between corresponding wave functions at the two symmetry points. Thus the character at Lt may be expressed in terms of characters at L by

$$\begin{aligned} L_t[(\boldsymbol{\alpha}|\mathbf{t})] &= L[(\mathfrak{d}_{2x}|0)(\boldsymbol{\alpha}|\mathbf{t})(\mathfrak{d}_{2x}|0)] \\ &= L[(\mathfrak{d}_{2x}\boldsymbol{\alpha}\mathfrak{d}_{2x}|\mathfrak{d}_{2x}\mathbf{t})] \end{aligned} \tag{40}$$

when we abbreviate $\chi_{Lt}[(\boldsymbol{\alpha}|\mathbf{t})]$ by $L_t[(\boldsymbol{\alpha}|\mathbf{t})]$.

The relations

$$\mathfrak{d}_{2x}\mathbf{t}_{xy} = 0; \quad \mathfrak{d}_{2x}\boldsymbol{\tau} = \mathfrak{d}_{2x}(\boldsymbol{\tau}+\mathbf{t}_{xy}) = \boldsymbol{\tau}+\mathbf{t}_{xy} \tag{41}$$

facilitate evaluating the desired characters, and lead to the relationship

$$L_t(\boldsymbol{\alpha}|\mathbf{t}+\mathbf{t}_{xy}) = L_t(\boldsymbol{\alpha}|\mathbf{t}), \tag{42}$$

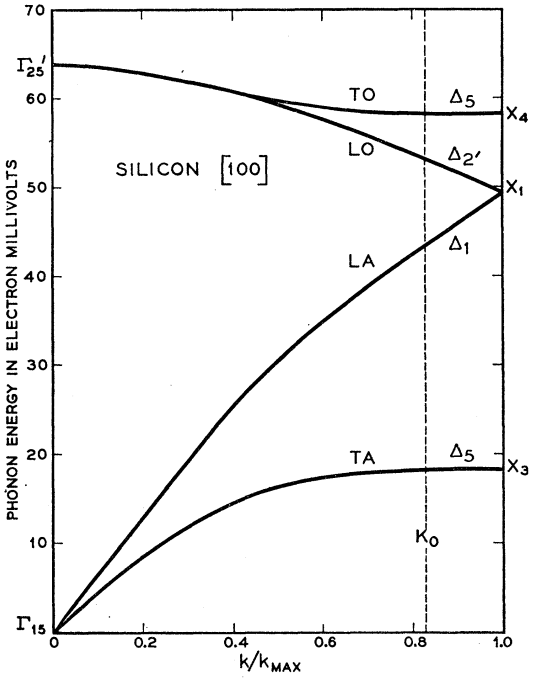

FIG. 4. The vibration spectrum of silicon, is determined by B. N. Brockhouse, Phys. Rev. Letters 2, 256 (1959). See legend for Fig. 2.

whereas the corresponding relations at L and X are

$$L(\boldsymbol{\alpha}|\mathbf{t}+\mathbf{t}_{xy}) = -L(\boldsymbol{\alpha}|\mathbf{t}), \tag{43}$$

$$X(\boldsymbol{\alpha}|\mathbf{t}+\mathbf{t}_{xy}) = -X(\boldsymbol{\alpha}|\mathbf{t}). \tag{44}$$

The fact that L_t is even under $(\boldsymbol{\varepsilon}|\mathbf{t}_{xy})$ ensures that $L \times L_t$ is odd, so that only the odd representations at X are used. These are the four physically allowed representations, X_1, X_2, X_3, and X_4, since their translational properties are determined by $\exp(i\mathbf{k}\cdot\mathbf{r})$ for $\mathbf{k} = (2\pi/a)(1,0,0)$, whereas the remaining 10 representations (discussed by Elliott) which are even under $(\boldsymbol{\varepsilon}|\mathbf{t}_{xy})$ are forbidden.

TABLE VI. Characters for intervalley scattering in Ge.

	X star L	L_1^+	L_{1t}^+	$L_1^+ \times L_{1t}^+$	X_1	X_2	X_3	X_4
$(\boldsymbol{\varepsilon}\|0)$	4	1	1	4	2	2	2	2
$(\mathfrak{d}_{2x}\|0)$	0	...	...	0	2	2	−2	−2
$(\mathfrak{d}_{2\tilde{y}z}\|\boldsymbol{\tau})$	2	1	−1	−2	0	0	−2	2
$(\varrho_{\tilde{y}z}\|0)$	2	1	1	2	2	−2	0	0
$(\mathbf{i}\|\boldsymbol{\tau})$	4	1	−1	0	0	0	0	0
$(\mathbf{i}\|\boldsymbol{\tau}+\mathbf{t}_{xy})$		−1	−1					

$X(\boldsymbol{\alpha}|\mathbf{t}+\mathbf{t}_{xy}) = -X(\boldsymbol{\alpha}|\mathbf{t})$
$L(\boldsymbol{\alpha}|\mathbf{t}+\mathbf{t}_{xy}) = -L(\boldsymbol{\alpha}|\mathbf{t})$
$L_t(\boldsymbol{\alpha}|\mathbf{t}+\mathbf{t}_{xy}) = L_t(\boldsymbol{\alpha}|\mathbf{t})$
$\mathfrak{d}_{2x}\mathbf{t}_{xy} = 0$

$\Psi_{Lt}(\mathbf{r}) = \mathfrak{d}_{2x}\Psi_L(\mathbf{r})$
$L_t(\boldsymbol{\alpha}|\mathbf{t}) = L((\mathfrak{d}_{2x}|0)(\boldsymbol{\alpha}|\mathbf{t})(\mathfrak{d}_{2x}|0))$
$= L(\mathfrak{d}_{2x}\boldsymbol{\alpha}\mathfrak{d}_{2x}|\mathfrak{d}_{2x}\mathbf{t})$
$\mathfrak{d}_{2x}\boldsymbol{\tau} = \mathfrak{d}_{2x}(\boldsymbol{\tau}+\mathbf{t}_{xy}) = \boldsymbol{\tau}+\mathbf{t}_{xy}$

$L_1^+ \times L_{1t}^+ = X_1 + X_3$. X_3 forbidden by time reversal

TABLE VII. Characters at $X=(2\pi/a)(1,0,0)$.[a]

32	Classes	X_1	X_2	X_3	X_4
1	$(\varepsilon\|0)$	2	2	2	2
1	$(\delta_{2x}\|0)$	2	2	−2	−2
2	$(\delta_{2yz}\|\tau+t_{xy}),(\delta_{2\bar{y}z}\|\tau)$	0	0	−2	2
2	$(\varrho_{yz},\varrho_{\bar{y}z}\|0)$	2	−2	0	0
1	$(\varepsilon\|t_{xy})$	−2	−2	−2	−2
1	$(\delta_{2x}\|t_{xy})$	−2	−2	2	2
2	$(\delta_{2yz}\|\tau),(\delta_{2\bar{y}z}\|\tau+t_{xy})$	0	0	2	−2
2	$(\varrho_{yz},\varrho_{\bar{y}z}\|t_{xy})$	−2	2	0	0
2	$(i\|\tau,\ \tau+t_{xy})$	0	0	0	0
4	$(\delta_{2y},\delta_{2z}\|0,t_{xy})$	0	0	0	0
4	$(\delta_{4x},\delta_{4x}^{-1}\|\tau,\ \tau+t_{xy})$	0	0	0	0
4	$(\varrho_y,\varrho_z\|\tau,\ \tau+t_{xy})$	0	0	0	0
2	$(\varrho_x\|\tau,\ \tau+t_{xy})$	0	0	0	0
4	$(\sigma_{4x},\sigma_{4x}^{-1}\|0,t_{xy})$	0	0	0	0

[a] $\tau=\frac{1}{2}(t_{xy}+t_{yz}+t_{zx})$ is the vector from the origin atom to its nearest neighbor in the first octant.

The above Eqs. (42)–(44) in fact exhaust the information provided by the translational element $(\varepsilon|t_{xy})$. All additional information on selection rules can be obtained from elements without translation. We have therefore in Table VI rearranged Herring's[10] character Table VII at X, so that the first four classes will provide all of the remaining symmetry information. If a typical element in one of these classes contains $(\alpha|t)$ then *another* class contains $(\alpha|t+t_{xy})$ and has the opposite character, and so adds no new information. We have so far accounted for eight classes. The remaining six classes contain element pairs $(\alpha|t)$ and $(\alpha|t+t_{xy})$ which have the same character, yet by Eq. (44) must have opposite character. Hence all such characters vanish for the physically allowed representations X_1, X_2, X_3, X_4.

We shall show that these classes provide no new symmetry information by discussing in detail the class

TABLE VIII. Characters at $W=(2\pi/a)(1,0,\frac{1}{2})$.

32	Classes	W_1	W_2
1	$(\varepsilon\|0)$	2	2
2	$(\sigma_{4z}\|0),(\sigma_{4z}^{-1}\|t_{zx})$	$1+i$	$-1-i$
1	$(\varepsilon\|t_{yz})$	$-2i$	$-2i$
1	$(\varepsilon\|t_{xy})$	−2	−2
1	$(\varepsilon\|t_{zx})$	$2i$	$2i$
2	$(\sigma_{4z}\|t_{yz}),(\sigma_{4z}^{-1}\|0)$	$1-i$	$-1+i$
2	$(\sigma_{4z}\|t_{xy}),(\sigma_{4z}^{-1}\|t_{yz})$	$-1-i$	$1+i$
2	$(\sigma_{4z}\|t_{zx}),(\sigma_{4z}^{-1}\|t_{xy})$	$-1+i$	$1-i$
2	$(\delta_{2z}\|0,t_{xy})$	0	0
2	$(\delta_{2z}\|t_{yz},t_{zx})$	0	0
4	$(\delta_{2xy}\|\tau+t_{yz},\ \tau+t_{zx}),(\delta_{2\bar{x}y}\|\tau,\ \tau+t_{xy})$	0	0
4	$(\delta_{2xy}\|\tau,\ \tau+t_{xy}),(\delta_{2\bar{x}y}\|\tau+t_{yz},\ \tau+t_{zx})$	0	0
4	$(\varrho_x\|\tau,\ \tau+t_{xy}),(\varrho_y\|\tau+t_{yz},\ \tau+t_{zx})$	0	0
4	$(\varrho_x\|\tau+t_{yz},\ \tau+t_{zx}),(\varrho_y\|\tau,\ \tau+t_{xy})$	0	0

[10] C. Herring, J. Franklin Institute **233**, 525 (1942).

TABLE IX. Characters at $Z=(2\pi/a)(1,0,q)$.

8	Classes	Z_1
1	$(\varepsilon\|0)$	2
1	$(\varepsilon\|t_{xy})$	−2
2	$(\delta_{2z}\|0,t_{xy})$	0
2	$(\varrho_x\|\tau,\ \tau+t_{xy})$	0
2	$(\varrho_y\|\tau,\ \tau+t_{xy})$	0

$(i|\tau)$, $(i|\tau+t_{xy})$. Equations (42) and (43) guarantee that the character product $L\times L_t$ have opposite sign for these elements. Hence the character product averaged as in Eq. (10) over the elements of the class vanishes. This agrees with the character of all four translationally allowed states X_1, X_2, X_3, and X_4. *Hence inversion provides no selection rules.* And neither will any of the other five classes that contain such paired elements.

It is no accident then, that the *four physically admissible representations* have properties determined by the *four relevant classes*. Our abbreviated Table VI then provides all the necessary information to yield the selection rule:

$$L_1^+\times L_{1t}^+=X_1+X_3. \tag{45}$$

One of us (M.L.) will show later that X_3 is in fact forbidden by time reversal.

For completeness, Tables VIII and IX show the characters at $W=(2\pi/a)(1,0,\frac{1}{2})$ and $Z=(2\pi/a)(1,0,q)$. In the former, only the top two lines contain information other than translational. In the latter, only the top line, the identity element is significant. Hence there are two permissible representations at W and one at Z. The table at W is based on Herring's correction[11] of an error in his earlier work.[10] The table at Z is taken from Herring. The existence of a two-dimensional representation at Z was known to Hund.[12]

INTERVALLEY SCATTERING IN SILICON

There are two types of intervalley scattering in silicon. The first carries an electron from momentum $\mathbf{k}$ to $-\mathbf{k}$ using a phonon of momentum $-2\mathbf{k}$. This involves the matrix element

$$\int\psi_{-\mathbf{k}}^*V(-2\mathbf{k})\psi_{\mathbf{k}}d\tau=\int\psi_{\mathbf{k}}\psi_{\mathbf{k}}V^*(2\mathbf{k})d\tau. \tag{46}$$

Thus we can take $\mathbf{k}\equiv(k,0,0)$, $\mathbf{k}'=\mathbf{k}$ and $\mathbf{k}''=2\mathbf{k}$. Since $\mathbf{k}$ and $\mathbf{k}''$ are in the same direction, $\mathbf{k}''$ star $\mathbf{k}$ is simply the one vector $\mathbf{k}$. Thus no factor is added by the star, and we may simply use the group $G_{\mathbf{k}}$ taking character products in the usual way! The important selection rule is

$$\Delta_1\times\Delta_1=\Delta_1, \tag{47}$$

[11] C. Herring (private communication).
[12] F. Hund, Z. Physik **99**, 119 (1936).

TABLE X. Characters at $\Sigma=(k,k,0)$.[a]

	Σ_1	Σ_2	Σ_3	Σ_4	Σ star Δ	$\Delta_1\times\Delta_1$
$(\varepsilon\|0)$	1	1	1	1	2	2
$(\varrho_{\bar{x}y}\|0)$	1	−1	+1	−1	0	0
$(\varrho_z\|\tau)$	λ^2	$-\lambda^2$	$-\lambda^2$	λ^2	2	$2\lambda^2$
$(\delta_{2xy}\|\tau)$	λ^2	λ^2	$-\lambda^2$	$-\lambda^2$	0	0

[a] $\lambda^2=\exp(-i\mathbf{k}\cdot\tau)=\exp(-ika/2)$, where $\mathbf{k}=(k,k,0)$.

i.e., the longitudinal acoustic phonon is the only one which carries a Si band edge electron from one valley to an opposite valley. (The same statement would be true if the electronic wave function at the band edge were Δ_2, $\Delta_{1'}$, or $\Delta_{2'}$, i.e., any nondegenerate state.)

The second type of intervalley scattering carries an electron to a nearby valley. Let us take $\mathbf{k}=(k,0,0)$; $\mathbf{k}'=(0,k,0)$; $\mathbf{k}''=(k,k,0)$. The point $(k,k,0)$ is the point Σ whose character table is given in Table X.

The wave functions at the transformed Δ point $\Delta t=(0,\mathbf{k},0)$ are obtained from those at the original point by means of

$$\psi^{\Delta t}=\varrho_{\bar{x}y}\psi^{\Delta}. \tag{48}$$

Thus the character at Δt of an arbitrary operator $(\alpha|\mathbf{t})$ can be written:

$$\begin{aligned}\Delta t[(\alpha|\mathbf{t})]&=\textstyle\sum_\mu(\varrho_{\bar{x}y}\psi_\mu{}^{\Delta},(\alpha|\mathbf{t})\varrho_{\bar{x}y}\psi_\mu{}^{\Delta})\\&=\Delta[\varrho_{\bar{x}y}(\alpha|\mathbf{t})\varrho_{\bar{x}y}]\\&=\Delta[(\varrho_{\bar{x}y}\alpha\varrho_{\bar{x}y}|\varrho_{\bar{x}y}\mathbf{t})].\end{aligned} \tag{49}$$

Only the operations $(\varepsilon|0)$ and $(\varrho_z|\tau)$, however, leave points of the Σ star of Δ invariant, and for these particular operators, we find that the character at Δt is identical to its value at Δ. The decomposition of the character product, according to Table X yields

$$\Delta_1\times\Delta_{1t}=\Sigma_1+\Sigma_4, \tag{50}$$

where Σ_4 is a transverse acoustic (TA) mode polarized perpendicular to the z axis, i.e., $TA_{\perp z}$, and Σ_1 is a phonon which is a mixture $LA+TO_{\parallel z}$, i.e., longitudinal acoustic plus a transverse optical part polarized in the z direction. The forbidden phonons are $\Sigma_2=TO_{\perp z}$ and $\Sigma_3=$ a mixture of LO and $TA_{z\parallel}$. In a succeeding paper we shall find that Σ_4 is destroyed by time reversal.

TABLE XI. Summary of results: (Representations not appearing on the right-hand side are forbidden. Some which do appear may be forbidden by time reversal.)

$\Delta_1\times\Delta_1{}^*=\Delta_2\times\Delta_2{}^*=\Delta_{1'}\times\Delta_{1'}{}^*=\Delta_{2'}\times\Delta_{2'}{}^*=\Gamma_1+\Gamma_{12}+\Gamma_{15}$

$\Delta_1\times(\Delta_{2'})^*=\Delta_2\times(\Delta_{1'})^*=\Gamma_{2'}+\Gamma_{12'}+\Gamma_{25'}$

$\Delta_1\times\Delta_2{}^*=\Delta_{1'}\times(\Delta_{2'})^*=\Gamma_2+\Gamma_{12}+\Gamma_{25}$

$\Delta_1\times(\Delta_{1'})^*=\Delta_2\times(\Delta_{2'})^*=\Gamma_{1'}+\Gamma_{12'}+\Gamma_{15'}$

$\Delta_1\times\Delta_5{}^*=\Delta_2\times\Delta_5{}^*=\Delta_{2'}\times\Delta_5{}^*=\Delta_{1'}\times\Delta_5{}^*=\Gamma_{15}+\Gamma_{25}+\Gamma_{15'}+\Gamma_{25'}$

$\Delta_5\times\Delta_5{}^*=\Gamma_{15}+\Gamma_{25}+\Gamma_{15'}+\Gamma_{25'}+\Gamma_1+\Gamma_{1'}+\Gamma_2+\Gamma_{2'}+2\Gamma_{12}+2\Gamma_{12'}$

$\Delta_1\times\Delta_{1t}=\Sigma_1+\Sigma_4=\Delta_2\times\Delta_{2t}=\Delta_{1'}\times\Delta_{1t'}=\Delta_{2'}\times\Delta_{2t'}$

$\Delta_5\times\Delta_{5t}=\Sigma_1+\Sigma_3+\Sigma_2+\Sigma_4$

$L_1\times\Gamma_{2'}=L_{2'}$

$L_{3'}\times\Gamma_{25'}=L_{1'}+L_{2'}+2L_{3'}$

$\Lambda_1\times\Gamma_{2'}=\Lambda_1$

$\Lambda_3\times\Gamma_{25'}=\Lambda_1+\Lambda_2+2\Lambda_3$

$L_1\times L_{1t}=X_1+X_3$

$\Lambda_1\times\Lambda_{1t}=\Delta_1+\Delta_{2'}+\Delta_5$

$X_1\times X_1=X_2\times X_2=\Gamma_1+\Gamma_{12}+\Gamma_{25'}+\Gamma_{2'}+\Gamma_{12'}+\Gamma_{15}$

$X_1\times X_3=X_1\times X_4=X_2\times X_3=X_2\times X_4=\Gamma_{15'}+\Gamma_{25'}+\Gamma_{15}+\Gamma_{25}$

$X_3\times X_3=X_4\times X_4=\Gamma_1+\Gamma_{12}+\Gamma_{25'}+\Gamma_{1'}+\Gamma_{12'}+\Gamma_{25}$

$X_1\times X_2=\Gamma_2+\Gamma_{12}+\Gamma_{15'}+\Gamma_{1'}+\Gamma_{12'}+\Gamma_{25}$

$X_3\times X_4=\Gamma_2+\Gamma_{2'}+\Gamma_{12}+\Gamma_{12'}+\Gamma_{15}+\Gamma_{15'}$

Cross checks:

$\Gamma_{25'}\times\Delta_1=\Delta_5+\Delta_{2'}=\Gamma_{15}\times\Delta_{2'}=\Gamma_{15'}\times\Delta_2=\Gamma_{25}\times\Delta_{1'}$

$\Gamma_{25'}\times\Delta_{2'}=\Delta_5+\Delta_1=\Gamma_{25}\times\Delta_2=\Gamma_{15}\times\Delta_1=\Gamma_{15'}\times\Delta_{1'}$

$\Gamma_{25'}\times\Delta_5=\Delta_5+\Delta_1+\Delta_2+\Delta_{2'}+\Delta_{1'}=\Gamma_{25}\times\Delta_5=\Gamma_{15}\times\Delta_5=\Gamma_{15'}\times\Delta_5$

$\Gamma_{25'}\times\Delta_{1'}=\Delta_5+\Delta_2=\Gamma_{25}\times\Delta_1+\Gamma_{15'}\times\Delta_{2'}=\Gamma_{15}\times\Delta_2$

$\Gamma_{25'}\times\Delta_2=\Delta_5+\Delta_{1'}=\Gamma_{25}\times\Delta_{2'}=\Gamma_{15'}\times\Delta_1=\Gamma_{15}\times\Delta_{1'}$

ADDITIONAL RESULTS

A summary of some of the more important selection rules for the diamond structure, obtained with the help of Eq. (14), are given in Table XI.

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