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COLLEGE OF ENGINEERING
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Technical Report

GROUP THEORETICAL ANALYSIS OF LATTICE VIBRATIONS OF ZINC-BLENDE TYPE CRYSTALS

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ABSTRACT

In this report is presented a group theoretical analysis of the lattice dynamics of crystals possessing the zinc-blende structure.

The form of the dynamical matrix demanded by symmetry is derived for several symmetry points in the Brillouin zone. The construction of symmetry vectors and the block diagonalization of the dynamical matrix is shown in detail. Selection rules for two-phonon infrared absorption are presented for several critical points.

CHAPTER I

INTRODUCTION

We wish to present in this report a group theoretical analysis of the lattice vibrations of the zinc-blende lattice. The results described here were obtained in connection with the experimental study of phonon dispersion relations in cubic ZnS now in progress in this laboratory.[1] They are, however, equally applicable to all diatomic crystals having the zinc-blende (or sphalerite) structure; this includes several I-VII, II-VI, and III-V compounds.

The symmetry properties of the zinc-blende structure were first considered by Parmenter[2] in relation to electron band structure. Subsequently, Birman[3] classified the phonons in terms of the symmetry of the lattice for purposes of working out selection rules in optical spectra. No detailed discussion of the eigenvectors and the diagonalization of the dynamical matrix based on symmetry considerations has been presented so far for this lattice, and the purpose of this report is to fill in the vacuum.[4]

We begin in the following chapter with a brief resumé of the general principles involved in application of group theory to lattice dynamics. For a more detailed discussion of this topic, we refer the reader to two recently published reviews on this subject.[5,6] Chapter III is devoted to a description of the geometry of the zinc-blende lattice and its reciprocal lattice. Chapter IV forms the core of this report and contains a discussion of the eigenvectors and the dynamical matrix at several symmetry points in the Brillouin zone. The concluding chapter is devoted to selection rules for two phonon processes in optical spectra.

CHAPTER II

APPLICATION OF GROUP THEORY TO THE STUDY OF LATTICE DYNAMICS

In this chapter, we present a brief discussion concerning the application of group theory to the study of lattice dynamics. This is done more for the sake of completeness than as a detailed exposition of the subject, and follows closely the work of Maradudin and Vosko[5] referred to earlier.

The problem of finding the phonon frequencies and eigenvectors is essentially one of solving the eigenvalue problem

$$\underline{\underline{D}}(\underset{\sim}{q})\,\underline{\underline{e}}(\underset{\sim}{q},j) = \omega_j^2(\underset{\sim}{q})\,\underline{\underline{e}}(\underset{\sim}{q},j) \quad , \tag{1}$$

where $\omega_j(\underset{\sim}{q})$ is the normal mode frequency corresponding to the phonon wave vector $\underset{\sim}{q}$ and branch j, $\underset{\sim}{e}(\underset{\sim}{q},j)$ is the associated eigenvector, and $\underline{\underline{D}}(\underset{\sim}{q})$ is the dynamical matrix whose elements are given by

$$D_{\alpha\beta}\begin{pmatrix}0 & \ell'\\ \kappa & \kappa'\end{pmatrix} = (M_\kappa M_{\kappa'})^{-\frac{1}{2}} \sum_{\ell'} \phi_{\alpha\beta}\begin{pmatrix}0 & \ell'\\ \kappa & \kappa'\end{pmatrix} \exp\left[i\underset{\sim}{q}\cdot\underset{\sim}{x}(\ell')\right] \tag{2}$$

where $\underset{\sim}{x}(\ell')$ denotes the position of the ℓ'th primitive cell, M_κ and $M_{\kappa'}$ denote the masses of the κth and κ'th atoms, respectively, in the primitive cell, and $\phi_{\alpha\beta}\begin{pmatrix}0 & \ell'\\ \kappa & \kappa'\end{pmatrix}$ is the $\alpha\beta$th element of the three-dimensional force constant matrix connecting the κth atom in the cell at the origin and the κ'th atom in the cell ℓ'. If n is the number of atoms in the primitive cell, then $\underline{\underline{D}}(\underset{\sim}{q})$ is a 3n x 3n matrix, and correspondingly there are 3n eigenvalues $\omega_j^2(\underset{\sim}{q})$ ($j = 1,2,\ldots 3n$), and 3n associated eigenvectors each having 3n components. Arranging the eigenvectors into a 3n x 3n matrix $\underline{\underline{e}}(\underset{\sim}{q})$,

$$\underline{\underline{e}}(\underset{\sim}{q}) = \left[\underline{\underline{e}}(\underset{\sim}{q},1),\ \underline{\underline{e}}(\underset{\sim}{q},2),\ \ldots\ \underline{\underline{e}}(\underset{\sim}{q},3n)\right] ,$$

where $\underset{\sim}{e}(\underset{\sim}{q},j)$ is a 3n element column vector, we see that

$$\underline{\underline{e}}^{\dagger}(\underset{\sim}{q})\,\underline{\underline{D}}(\underset{\sim}{q})\,\underline{\underline{e}}(\underset{\sim}{q}) = \underline{\underline{\Omega}} \tag{3a}$$

$$\underline{\underline{\Omega}} = \mathrm{diag}\left(\omega_1^2(\underset{\sim}{q}), \omega_2^2(\underset{\sim}{q}), \ldots \omega_{3n}^2(\underset{\sim}{q})\right) . \tag{3b}$$

Thus to bring the dynamical matrix into the diagonal form $\underline{\underline{\Omega}}$ what we need to find is the transformation matrix $\underline{\underline{e}}(\underset{\sim}{q})$. It turns out that if the crystal has some point group symmetry (as it generally does), then for $\underset{\sim}{q}$ corresponding to symmetry points or along directions of high symmetry it is possible using the techniques of group theory to find a transformation matrix $\underline{\underline{S}}(\underset{\sim}{q})$ which serves to bring $\underline{\underline{D}}(\underset{\sim}{q})$ into a block diagonal form. The matrix $\underline{\underline{S}}(q)$ depends on crystalline symmetry alone, unlike $\underline{\underline{e}}(\underset{\sim}{q})$ which depends on the force field between the atoms.

Let $\mathcal{S}_m = \{\underline{\underline{S}} | \underset{\sim}{v}(S) + \underset{\sim}{x}(m)\}$ be one of the elements of the space group of the crystal where $\underline{\underline{S}}$ denotes the rotational part, $\underset{\sim}{x}(m)$ a lattice translation, and $\underset{\sim}{v}(S)$ a fractional translation (which is zero for symmorphic groups). Then under this symmetry operation, the eigenvector $\underset{\sim}{e}(\underset{\sim}{q}, j)$ transforms as

$$\underline{\underline{e}}'(\underline{\underline{S}}\,\underset{\sim}{q}, j) = \underline{\underline{\Gamma}}(\underset{\sim}{q}, \mathcal{S}_m)\,\underline{\underline{e}}(\underset{\sim}{q}, j) \tag{4}$$

where the elements of the $3n \times 3n$ transformation matrix $\underline{\underline{\Gamma}}$ are given by

$$\Gamma_{\alpha\beta}(\kappa\kappa' | \underset{\sim}{q}; \mathcal{S}_m) = S_{\alpha\beta}\,\delta(\kappa, \mathcal{S}_m[\kappa'])$$

$$(\times)\ \exp\left[i\,\underline{\underline{S}}\,\underset{\sim}{q} \cdot (\underset{\sim}{x}(\kappa) - \mathcal{S}_m\,\underset{\sim}{x}(\kappa'))\right] . \tag{5}$$

Here $S_{\alpha\beta}$ is the $\alpha\beta$th element of the three-dimensional rotation matrix $\underline{\underline{S}}$, $\underset{\sim}{x}(\kappa)$ and $\underset{\sim}{x}(\kappa')$ denote the positions of the atoms κ and κ' in the primitive cell, and

$$\mathcal{S}_m\,\underset{\sim}{x}(\kappa') = \underline{\underline{S}}\,\underset{\sim}{x}(\kappa') + \underset{\sim}{v}(S) + \underset{\sim}{x}(m) . \tag{6}$$

Further, $\mathcal{S}_m(\kappa')$ denotes the sublattice into which the sublattice κ' is transformed by the operation $\mathcal{S}_m$. The matrix $\underline{\underline{\Gamma}}$ is unitary.* Under $\mathcal{S}_m$, $\underline{\underline{D}}(\underset{\sim}{q})$ is transformed into

$$\underline{\underline{\Gamma}}(\underset{\sim}{q}; \mathcal{S}_m)\,\underline{\underline{D}}(\underset{\sim}{q})\,\underline{\underline{\Gamma}}^{\dagger}(\underset{\sim}{q}; \mathcal{S}_m) = \underline{\underline{D}}(\underline{\underline{S}}\,\underset{\sim}{q}) . \tag{7}$$

*Note that for symmorphic groups, the atoms always stay in the same sublattice and consequently $\underline{\underline{\Gamma}}$ has only diagonal boxes.

Consider now those particular space group elements $R_m = \{\underline{\underline{R}}|\underset{\sim}{v}(R) + \underset{\sim}{x}(m)\}$ for which

$$\underline{\underline{R}}\,\underline{q} = \underline{q} + \underline{G}(\underline{q}, \underline{\underline{R}}) \tag{8}$$

where $\underline{G}$ is a vector of the reciprocal lattice. We find that $\underline{\underline{\Gamma}}(\underset{\sim}{q};R_m)$ commutes with $\underline{\underline{D}}(\underset{\sim}{q})$ since $\underline{\underline{D}}(\underset{\sim}{q}) = \underline{\underline{D}}(\underset{\sim}{q} + \underline{G})$. The elements of the type R_m form a group $G(\underset{\sim}{q})$ called the group of the wave vector, and we note that corresponding to every element of this group there is a unitary matrix operator $\underline{\underline{\Gamma}}$ which commutes with $\underline{\underline{D}}(\underset{\sim}{q})$. It can be shown that the set of matrices $\underline{\underline{\Gamma}}$ furnish a 3n-dimensional unitary representation of $G(\underset{\sim}{q})$ which is reducible. We observe in passing that because of the commutation of $\underline{\underline{D}}(\underset{\sim}{q})$ with $\underline{\underline{\Gamma}}(q;R_m)$ there result interrelationships between the elements of $\underline{\underline{D}}(\underset{\sim}{q})$. Specifically,

$$D_{\mu\nu}\left(R_m(\kappa), R_m(\kappa')\right) = \sum_{\alpha\beta} S_{\mu\alpha}\, D_{\alpha\beta}\left(\underset{\kappa\kappa'}{q}\right) S_{\nu\beta}$$

$$(\kappa)\ \exp i\underline{q}\cdot\left[\underline{x}(R_m[\kappa]) - R_m\underline{x}(\kappa)\right] \exp -i\underline{q}\cdot\left[\underline{x}(R_m[\kappa']) - R_m\underline{x}(\kappa')\right]. \tag{9a}$$

In addition one has

$$\underline{\underline{D}}(\underline{q}) = \underline{\underline{D}}^{*}(-\underline{q}) \tag{9b}$$

which in some cases leads to additional interrelations.

Define now a matrix $\underline{\underline{T}}(\underset{\sim}{q};\underline{\underline{R}})$ by

$$\underline{\underline{T}}(\underline{q};\underline{\underline{R}}) = \exp i\underline{q}\cdot\left[\underline{v}(R) + \underline{x}(m)\right]\underline{\underline{\Gamma}}(\underline{q};R_m)\,. \tag{10}$$

Like the $\underline{\underline{\Gamma}}$ matrices, the $\underline{\underline{T}}$ matrices also commute with $\underline{\underline{D}}(\underset{\sim}{q})$. Further they obey the multiplication rule

$$\underline{\underline{T}}(\underline{q};\underline{\underline{R}}_i)\,\underline{\underline{T}}(\underline{q};\underline{\underline{R}}_j) = \phi(\underline{q};\underline{\underline{R}}_i\,\underline{\underline{R}}_j)\,\underline{\underline{T}}(\underline{q};\underline{\underline{R}}_i\,\underline{\underline{R}}_j) \tag{11}$$

(where $\underline{\underline{R}}_i$ and $\underline{\underline{R}}_j$ are rotation matrices corresponding to the ith and jth elements of $G_o(\underset{\sim}{q})$)

and provide a unitary multiplier representation of the point group $G_o(\underset{\sim}{q})$ made up of only the rotational parts of R_m. The multiplier $\phi(\underset{\sim}{q};\underline{\underline{R}}_i\underline{\underline{R}}_j)$ is given by

$$\phi(\underset{\sim}{q};\underline{\underline{R}}_i\underline{\underline{R}}_j) = \exp -\left[i\,\underline{G}(\underset{\sim}{q};R_i^{-1})\cdot\underline{V}(R_j)\right] \tag{12}$$

$\underset{\sim}{G}(\underset{\sim}{q},\underline{\underline{R}}_i^{-1})$ being defined through the equation

$$\underline{\underline{R}}_i^{-1}\,\underline{q} = \underline{q} + \underline{\underline{G}}(\underline{q};R_i^{-1}) \tag{13}$$

Clearly $\phi = 1$ for symmorphic groups always. For nonsymmorphic groups, $\phi = 1$ for $\underset{\sim}{q}$ within the Brillouin zone, while on the surface of the zone it can be different from unity having the value given by Eq. (13). The representation (multiplier) provided by the $\underline{\underline{T}}$'s is a reducible representation, and the number n(s) of times the irreducible multiplier representation (IMR) occurs in the reducible representation can be found from the formula

$$n(s) = \frac{1}{h}\sum_{R\in G_o(\underline{q})} \chi^{(s)*}(\underline{q},\underline{\underline{R}})\,\mathrm{Tr}\left[\underline{\underline{T}}(\underline{q};\underline{\underline{R}})\right], \tag{14}$$

where h is the order of $G_o(\underset{\sim}{q})$ and

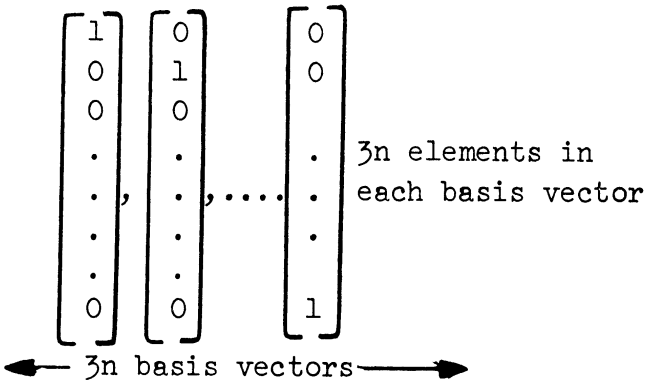
$$\chi^{(s)}(\underline{q};\underline{\underline{R}}) = \mathrm{Tr}\left[\underline{\underline{\tau}}^{(s)}(\underline{q};\underline{\underline{R}})\right] \tag{15}$$

is the character corresponding to the element $\underline{\underline{R}}$ of $G_o(\underset{\sim}{q})$ in the sth IMR, $\underline{\underline{\tau}}^{(s)}(\underset{\sim}{q};\underline{\underline{R}})$ being the matrix representative in the IMR s.

Except in the case of accidental degeneracy (which is rare), the eigenvectors belonging to the same eigenfrequency transform according to a unitary IMR of $G_o(\underset{\sim}{q})$, and consequently we can replace the branch index j by a triplet of symbols $\underset{\sim}{s}$, a, λ, where s denotes the IMR, a its occurrence, and λ the partner in that representation. λ takes the values $1,2,\ldots f_s$, where f_s is the dimensionality of the IMR. We thus have

$$\underline{\underline{T}}(\underline{q};\underline{\underline{R}})\,\underline{\underline{e}}(\underline{q};sa\lambda) = \sum_{\lambda'=1}^{f_s}\tau^{(s)}_{\lambda'\lambda}(\underline{q};\underline{\underline{R}})\,\underline{\underline{e}}(\underline{q};sa\lambda') \quad . \tag{16}$$

The eigenvector $\underset{\sim}{e}(\underset{\sim}{q};sa\lambda)$ is a unit vector in 3n-dimensional space in which the basis vectors are



Using the results of group theory we can construct vectors, the so-called symmetry adapted vectors, which have the same transformation properties with respect to $G_0(\underset{\sim}{q})$ as do the eigenvectors. The prescription for doing this is as follows: Form first the projection operator

$$\mathcal{P}^{(s)}_{\lambda\lambda}(\underset{\sim}{0}) = \frac{f_s}{h} \sum_{R \in G_0(\underset{\sim}{q})} \left[\tau^{(s)}_{\lambda\lambda}(\underset{\sim}{q};\underset{=}{R})\right]^{*} \underset{=}{T}(\underset{\sim}{q};\underset{=}{R}) \quad . \tag{17}$$

When this operator is applied successively to the 3n basis vectors mentioned above, it will project out only n(s) linearly independent vectors. Label them after normalization as $\underset{\sim}{\psi}(\underset{\sim}{q};s1\lambda)$, $\psi(\underset{\sim}{q};s2\lambda),\ldots\underset{\sim}{\psi}(\underset{\sim}{q};sn(s)\lambda)$. All these symmetry adapted vectors transform according to the λth row of the IMR's. The partners associated with each of these $\underset{\sim}{\psi}$'s may be found using the result

$$\mathcal{P}^{(s)}_{\lambda'\lambda}(\underset{\sim}{q})\,\underset{\sim}{\Psi}(\underset{\sim}{q},s\lambda) = \underset{\sim}{\Psi}(\underset{\sim}{q};s\lambda') \quad , \tag{18}$$

where $\mathcal{P}^{(s)}_{\lambda'\lambda}(\underset{\sim}{q})$ is obtained from (17) by replacing $\tau^{(s)}_{\lambda\lambda}$ by $\tau^{(s)}_{\lambda'\lambda}$. This gives the required symmetry vectors. Next as with the $\underset{\sim}{e}(\underset{\sim}{q},j)$'s, form a 3n x 3n matrix $\underset{=}{S}(\underset{\sim}{q})$ in which the columns are made up of the symmetry adapted vectors $\underset{\sim}{\psi}$. Arrange the symmetry vectors so that all those which transform according to the same row λ of the same IMR are grouped together. Then

$$\underset{=}{S}^{\dagger}(\underset{\sim}{q})\,\underset{=}{D}(\underset{\sim}{q})\,\underset{=}{S}(\underset{\sim}{q}) = \underset{=}{D}'(\underset{\sim}{q}) \tag{19}$$

will be block diagonal. In particular,

(1) if an IMR occurs only once in the reducible representation $\underset{=}{T}$, the block of $\underset{=}{D}'$ associated with this species will be completely diagonal no matter what the dimension of the IMR. The symmetry vectors are the required eigenvectors in this case;

(2) if the IMR occurs more than once, n(s) times say, then there will be f_s boxes each of dimension n(s) associated with this species. The n(s) different frequencies must be obtained by diagonalizing one of the n(s)-dimensional blocks of $\underline{\underline{D}}'(\underset{\sim}{q})$.

The eigenvectors in the case n(s) > 1 are obtained as follows: The n(s) eigenvectors $\underset{\sim}{e}(\underset{\sim}{q};sa\lambda)(\lambda = 1,\ldots n(s))$ all transform according to the λth row of the IMR s. They may therefore be expressed as linear combinations of the n(s) symmetry vectors which also transform according to the same row of the same IMR, i.e.,

$$\underline{e}(\underline{q};sa\lambda) = \sum_{i=1}^{n(s)} C_i(\underline{q};sa\lambda)\underline{\psi}(\underline{q};si\lambda) \quad . \tag{20}$$

Since the eigenvectors are orthonormal, it is evident that the complex coefficients c_i must satisfy the condition

$$\sum_i C_i^*(\underline{q};sa\lambda)C_i(sa\lambda) = 1 \tag{21}$$

The coefficients are obtained by feeding (20) and the eigenvalue appropriate to the mode (determined previously by diagonalizing the n(s)-dimensional block of $\underline{\underline{D}}'(\underset{\sim}{q})$) into Eq. (1). This yields n(s) complex homogeneous equations in the c_i's which are then solved for subject to the restraint in (21).

It should be noted that the block diagonalization of $\underline{\underline{D}}(\underset{\sim}{q})$ and the determination of the eigenvectors could be achieved equally well through the use of the matrices $\underline{\underline{\Gamma}}(\underset{\sim}{q};R_m)$ and the irreducible or small representations $\underline{\underline{\gamma}}^s(\underset{\sim}{q};R_m)$ of $G(\underset{\sim}{q})$ rather than $\underline{\underline{T}}(\underset{\sim}{q};\underline{\underline{R}})$ and $\underline{\underline{\tau}}^{(s)}(\underset{\sim}{q};\underline{\underline{R}})$ of $G_o(\underset{\sim}{q})$. In the former case, we have instead of (14),

$$n(s) = \frac{1}{h\mathcal{T}} \sum_{R_m \in G(\underline{q})} [\chi^{(s)}(\underline{q};R_m)]^* \mathrm{Tr}[\underline{\underline{\Gamma}}(\underline{q};R_m)] \tag{22}$$

where $\mathcal{T}$ is the order of the translational group, and

$$\chi^{(s)}(\underline{q};R_m) = \mathrm{Tr}[\underline{\underline{\gamma}}^{(s)}(\underline{q};R_m)]$$

$$= \mathrm{Tr}[\exp(-i\underline{q}\cdot\underline{X}(m))\underline{\underline{\gamma}}^s(\underline{q};R_o)] \quad . \tag{23}$$

Equation (22) can be easily seen to reduce to

$$n(s) = \frac{1}{h} \sum_{R_0} \left[\chi^{(s)}(\underset{\sim}{q}; R_0) \right]^* \mathrm{Tr} \left[\underline{\underline{\Gamma}}(\underset{\sim}{q}; R_0) \right]$$

$$R_0 = \{ \underline{\underline{R}} \mid \underline{\nu}(R) \} \quad .$$

The projection operators are formed using the formula

$$\mathcal{P}^{(s)}_{\lambda'\lambda}(\underset{\sim}{q}) = \frac{f_s}{h} \sum_{R_0} \left[\gamma^{(s)}_{\lambda'\lambda}(\underset{\sim}{q}; R_0) \right]^* \underline{\underline{\Gamma}}(\underset{\sim}{q}; R_0) \quad .$$

Techniques for obtaining both the irreducible multiplier[7] and the small representations[8] are available. For symmorphic groups the representations are identical and in fact are nothing but the representations of the crystallographic point group to which $G_0(\underset{\sim}{q})$ belongs.

There exists besides the space group symmetry one other symmetry, viz., time reversal (i.e., the invariance of the equations of matrices under the transformation $t \to -t$) which also sometimes leads to degeneracies. By this we mean a degeneracy of two frequencies not required by space group symmetry considerations, i.e.,

$$\omega_{sa}(\underset{\sim}{q}) = \omega_{sa'}(\underset{\sim}{q}) \quad , \qquad a' \neq a$$

$$\omega_{sa}(\underset{\sim}{q}) = \omega_{s'a'}(\underset{\sim}{q}) \quad , \qquad s' \neq s \quad .$$

Without going into details, we shall note that the criterion for additional degeneracy may be stated as follows.[5]

(i) $\underset{\sim}{q}$ inside the Brillouin zone:

Compute $Q = 1/h \sum x^{(s)}(\underset{\sim}{q}; \underline{\underline{A}}^2)$ where $\underline{\underline{A}}$ is an element such that $\underline{\underline{A}}\underset{\sim}{q} = -\underset{\sim}{q}$, and the summation is over all such elements. If $Q = 1$, there is no additional degeneracy. If $Q = -1$ there is an additional degeneracy of the form,

$$\omega_{sa}(\underset{\sim}{q}) = \omega_{sa'}(\underset{\sim}{q}) \quad , \quad a' \neq a \quad . \qquad (24)$$

If $Q = 0$, then also there is an additional degeneracy with $\omega_{sa}(\underset{\sim}{q}) = \omega_{s'a'}(\underset{\sim}{q})$, $s' \neq s$. The extra degeneracy introduced in the last two cases is referred to as time reversal degeneracy.

(ii) $\underset{\sim}{q}$ on surface of the Brillouin zone:

Compute $Q = 1/h \sum_{A} \{\exp -i[\underset{\sim}{q} + A^{-1}\underset{\sim}{q}]\cdot\underset{\sim}{v}(A)\}\, x^{(s)}(\underset{\sim}{q};\underline{\underline{A}}^2)$ where once again $\underline{\underline{A}}$ is a rotational element which sends $\underset{\sim}{q}$ into $-\underset{\sim}{q}$. The occurrence or nonoccurrence of extra degeneracies due to time reversal symmetry follows the same pattern as in case (i) depending on whether $Q = 1$, -1, or 0.

(iii) $\underset{\sim}{q}$ on the surface of the zone and equal to $\underset{\sim}{G}/2$:

If $\underset{\sim}{q} = (\underset{\sim}{G}/2)$, then Q must be computed according to the formula

$$Q = \frac{1}{h}\sum_{R}\left\{\exp -i\left[\frac{\underset{\sim}{G}}{2} + \underline{\underline{R}}^{-1}\frac{\underset{\sim}{G}}{2}\right]\cdot\underline{v}(R)\right\}\chi^{(s)}(\underline{q};\underline{\underline{R}}^2)$$

and the test applied as before.

CHAPTER III

SYMMETRY OF THE ZINC-BLENDE LATTICE

The zinc-blende lattice can be looked upon as two interpenetrating face centered cubic lattices displaced relative to each other along the cube diagonal by an amount (a/4, a/4, a/4) where a is the cube edge, each lattice containing the same species of atoms. Figure 1 shows the arrangement of atoms in the cubic unit cell. Here the positive ions are indicated by filled circles and the negative ions by open circles. The face centered lattice formed by the positive ions is clearly evident. With a little effort, it can be seen that the negative ions also form a F-C-C lattice and that the latter is displaced along the cube diagonal with respect to the lattice of positive ions. Note that our choice of locating a positive ion at the origin is arbitrary. We might just as well have constructed the unit cell with the negative ion at the origin. Figure 2 shows the basis vectors $\underset{\sim}{a}_1$, $\underset{\sim}{a}_2$, $\underset{\sim}{a}_3$ of the direct lattice, where

$$\begin{aligned} \underline{a}_1 &= \frac{a}{2}(\underline{i} + \underline{j}) \quad , \\ \underline{a}_2 &= \frac{a}{2}(\underline{j} + \underline{k}) \quad , \\ \underline{a}_3 &= \frac{a}{2}(\underline{i} + \underline{k}) \quad , \end{aligned} \tag{25}$$

$\underset{\sim}{i}$, $\underset{\sim}{j}$, $\underset{\sim}{k}$ being unit vectors along the cartesian axes. Also shown in the figure is the trigonal primitive cell, which we note contains two atoms in contrast to the cubic unit cell which contains eight atoms. The coordinates of the two atoms in the primitive cell are:

$$\begin{aligned} \underline{x}(1) &= (0, 0, 0) \\ \underline{x}(2) &= (a/4, a/4, a/4) \quad . \end{aligned}$$

The reciprocal lattice, as is well known, has the body centered cubic structure; a portion of this is shown in Figure 3 along with the basis vectors $\underset{\sim}{b}_1$, $\underset{\sim}{b}_2$, $\underset{\sim}{b}_3$, where

$$\begin{aligned} \underline{b}_1 &= \frac{2\pi}{a}(\underline{i} + \underline{j} - \underline{k}) \quad , \\ \underline{b}_2 &= \frac{2\pi}{a}(-\underline{i} + \underline{j} + \underline{k}) \quad , \\ \underline{b}_3 &= \frac{2\pi}{a}(\underline{i} - \underline{j} + \underline{k}) \quad . \end{aligned} \tag{26}$$

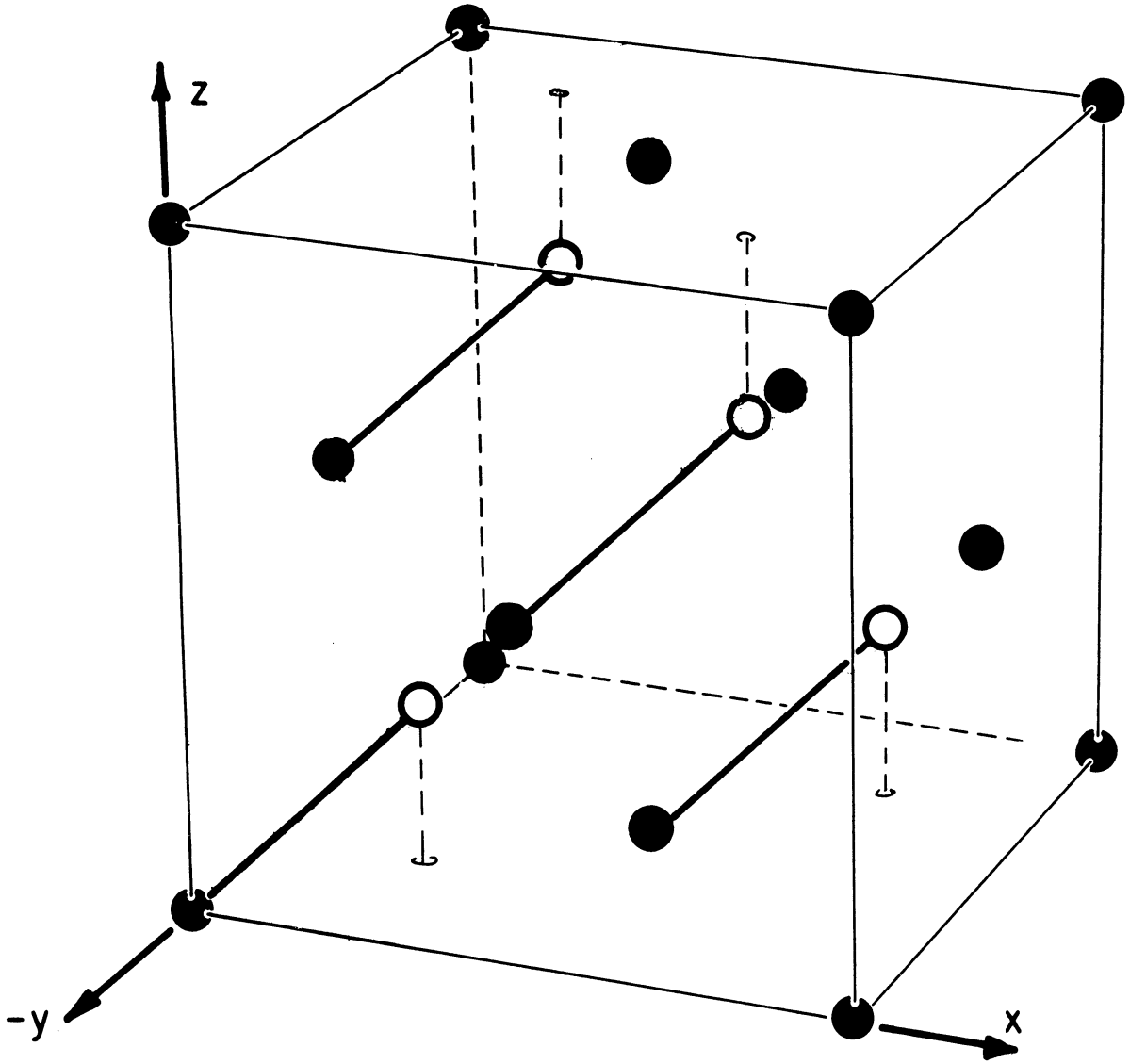


Figure 1. Cubic unit cell of the zinc-blende lattice.

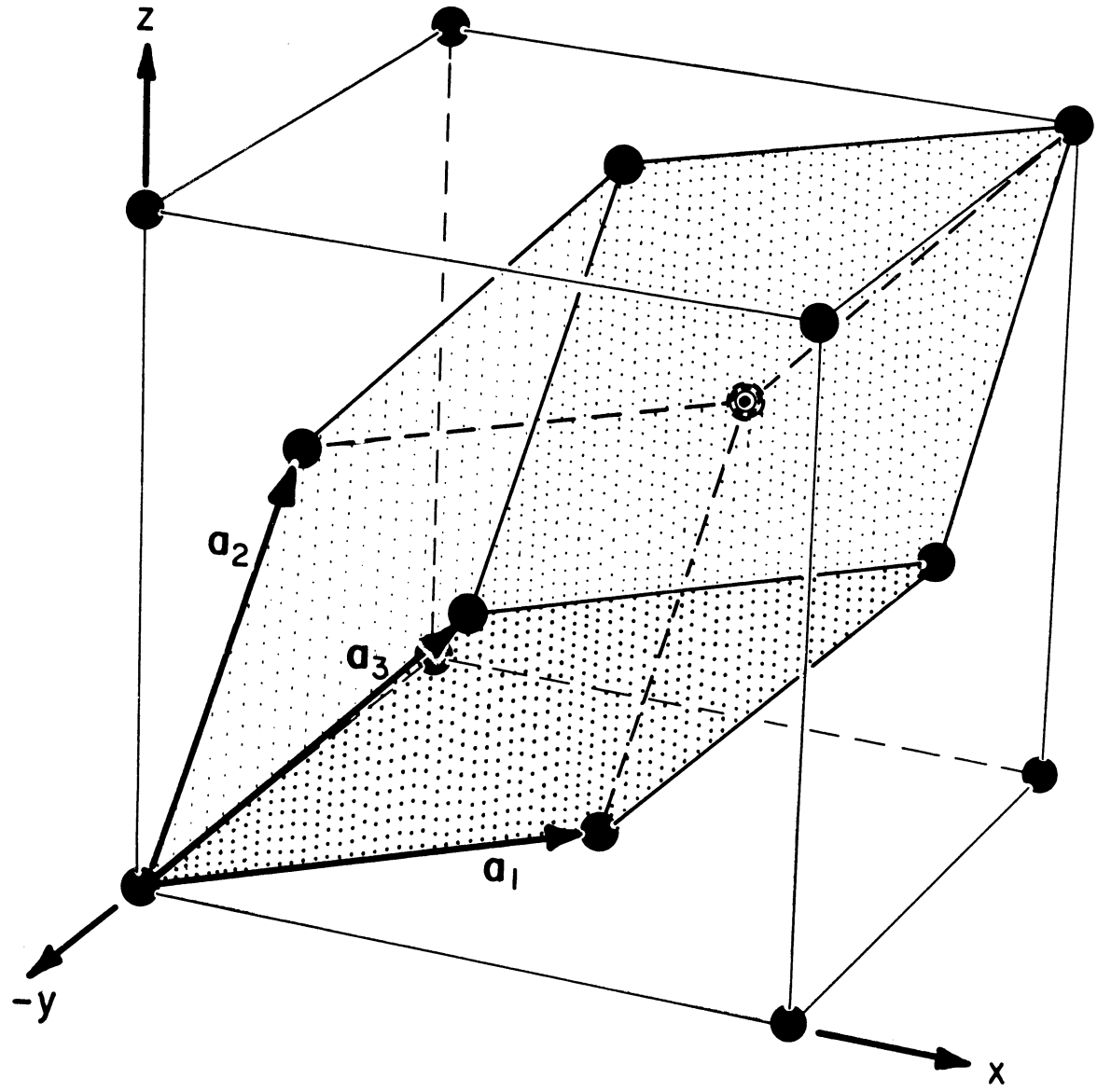


Figure 2. Primitive cell of the zinc-blende lattice and its relation to the cubic unit cell. Also shown are the basis vectors a_1, a_2, and a_3 of the direct lattice.

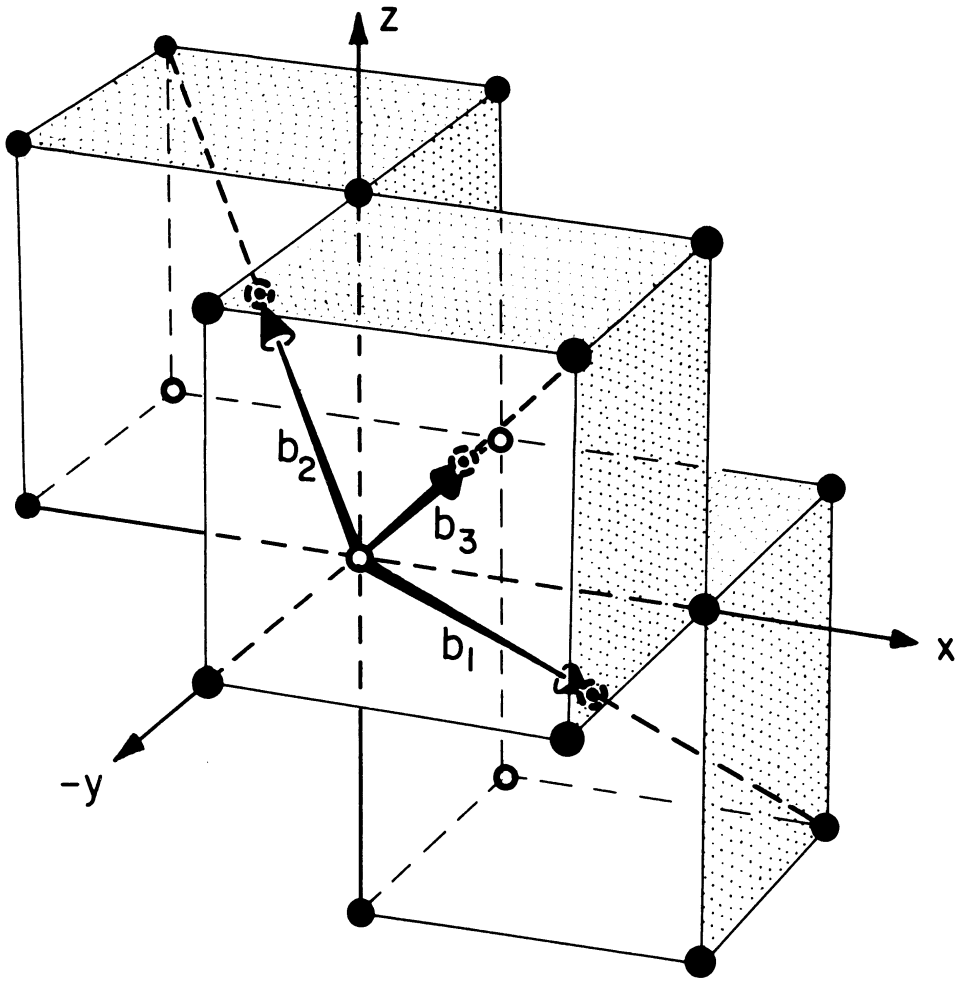


Figure 3. Portion of the reciprocal lattice of the zinc-blende structure. The basis vectors b_1, b_2, and b_3 are also shown

The first Brillouin zone is shown in Figure 4 with the symmetry points labelled essentially as in Figure 1 of Parmenter's paper.

The space group G of the zinc-blende lattice is $T_d^2(F\,\bar{4}3m)$, and the underlying point group G_o is $T_d(\bar{4}3m)$. The 24 elements of the group T_d are listed below and grouped into classes. The notation employed for the group elements follows the standard pattern, C denoting pure rotation, σ denoting reflections, and S standing for roto-reflections. The arguments and subscripts serve to specify the operation with respect to the cubic axes.

$$\{E\},\ \{C_3(111), C_3^{-1}(111), C_3(\bar{1}11), C_3^{-1}(\bar{1}11), C_3(\bar{1}\bar{1}1), C_3^{-1}(\bar{1}\bar{1}1),$$
$$C_3(1\bar{1}1), C_3^{-1}(1\bar{1}1)\},\ \{C_2(x), C_2(y), C_2(z)\},$$
$$\{S_4(x), S_4^{-1}(x), S_4(y), S_4^{-1}(y), S_4(z), S_4^{-1}(z)\},$$
$$\{\sigma_{xy}, \sigma_{yz}, \sigma_{zx}, \sigma_{\bar{x}y}, \sigma_{\bar{y}z}, \sigma_{\bar{z}x}\}\ .$$

The three-dimensional matrices corresponding to the various group operations are given below.

$$\underline{\underline{E}} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \underline{\underline{C_3}}(111) = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} \qquad \underline{\underline{C_3^{-1}}}(111) = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$$

$$\underline{\underline{C_3}}(\bar{1}11) = \begin{pmatrix} 0 & 0 & -1 \\ -1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \quad \underline{\underline{C_3^{-1}}}(\bar{1}11) = \begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & 1 \\ -1 & 0 & 0 \end{pmatrix} \quad \underline{\underline{C_3}}(\bar{1}\bar{1}1) = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & -1 \\ -1 & 0 & 0 \end{pmatrix}$$

$$\underline{\underline{C_3^{-1}}}(\bar{1}\bar{1}1) = \begin{pmatrix} 0 & 0 & -1 \\ 1 & 0 & 0 \\ 0 & -1 & 0 \end{pmatrix} \quad \underline{\underline{C_3}}(1\bar{1}1) = \begin{pmatrix} 0 & 0 & 1 \\ -1 & 0 & 0 \\ 0 & -1 & 0 \end{pmatrix} \quad \underline{\underline{C_3^{-1}}}(1\bar{1}1) = \begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & -1 \\ 1 & 0 & 0 \end{pmatrix}$$

$$\underline{\underline{C_2}}(x) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad \underline{\underline{C_2}}(y) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad \underline{\underline{C_2}}(z) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$S_4(x) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix} \qquad \underline{\underline{S_4^{-1}}}(x) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} \qquad \underline{\underline{S_4}}(y) = \begin{pmatrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$$

$$\underline{\underline{S}}_4^{-1}(y) = \begin{pmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{pmatrix} \qquad \underline{\underline{S}}_4(z) = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad \underline{\underline{S}}_4^{-1}(z) = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$\underline{\underline{\sigma}}_{xy} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \underline{\underline{\sigma}}_{yz} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \qquad \underline{\underline{\sigma}}_{zx} = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$$

$$\underline{\underline{\sigma}}_{\bar{x}y} = \begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \underline{\underline{\sigma}}_{\bar{y}z} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix} \qquad \underline{\underline{\sigma}}_{\bar{z}x} = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{pmatrix} \qquad (27)$$

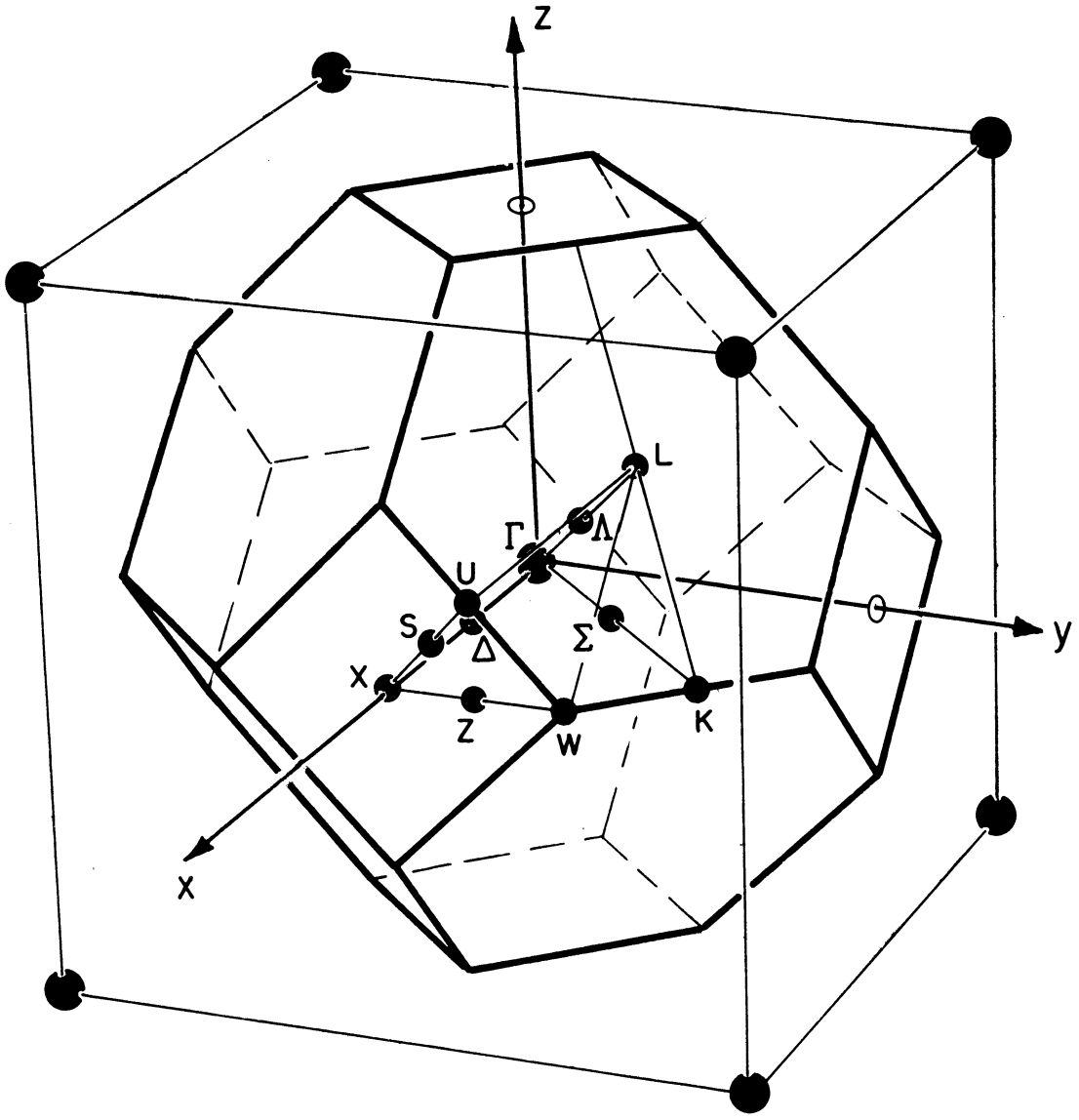


Figure 4. Central Brillouin zone and the symmetry points of the zone.

CHAPTER IV

RESULTS FOR ZINC-BLENDE STRUCTURE

The general considerations of Chapter II will now be applied to the various symmetry points in the irreducible portion of the Brillouin zone illustrated in Figure 5. This prism occupies 1/48 of the volume of the first zone, and the results for points in the rest of the zone may be obtained through the application of Eqs. (4) and (7).

We begin by noting that since T_d^2 is a symmorphic group, the $\underline{\underline{T}}$ matrices have nonzero diagonal boxes only, and have the typical form

$$\underline{\underline{T}}(\underline{v};\underline{\underline{R}}) = \begin{bmatrix} \Theta_1 \underline{\underline{R}} & 0 \\ 0 & \Theta_2 \underline{\underline{R}} \end{bmatrix}, \tag{28a}$$

where

$$\Theta_i = \exp\, i\underline{q}\cdot\left[\underline{x}(i) - \underline{\underline{R}}\,\underline{x}(i)\right], \quad i = 1,2. \tag{28b}$$

Clearly, $\Theta_1 = 1$ always since $\underline{x}(1) = 0$. The values for Θ_2 for the elements of $G_o(\underline{q})$ for $\underline{q}$ corresponding to the various symmetry points under consideration are listed in Table I. We begin the symmetry analysis with the point Δ.

Δ: $\underline{q} = 2\pi/a(\eta,0,0)$ $1 > \eta > 0$

The point group $G_o(\underline{q})$ associated with Δ has the elements $\{\underline{\underline{E}}\,|\,0\}$ $\{\underline{\underline{C}}_2(x)\,|\,0\}$ $\{\underline{\underline{\sigma}}_{yz}\,|\,0\}$, $\{\underline{\underline{\sigma}}_{\bar{y}z}\,|\,0\}$, and is isomorphous to the molecular point group C_{2v}. The $\underline{\underline{T}}$ matrices are:

$$\underline{\underline{T}}(\Delta;\underline{\underline{E}}) = \begin{pmatrix} \underline{\underline{E}} & 0 \\ 0 & \underline{\underline{E}} \end{pmatrix}$$

$$\underline{\underline{T}}(\Delta;C_2(x)) = \begin{pmatrix} \underline{\underline{C}}_2(x) & 0 \\ 0 & \underline{\underline{C}}_2(x) \end{pmatrix}$$

$$\underline{\underline{T}}(\Delta;\underline{\underline{\sigma}}_{yz}) = \begin{pmatrix} \underline{\underline{\sigma}}_{yz} & 0 \\ 0 & \underline{\underline{\sigma}}_{yz} \end{pmatrix}$$

$$\underline{\underline{T}}(\Delta;\underline{\underline{\sigma}}_{\bar{y}z}) = \begin{pmatrix} \underline{\underline{\sigma}}_{\bar{y}z} & 0 \\ 0 & \underline{\underline{\sigma}}_{\bar{y}z} \end{pmatrix} \tag{29}$$

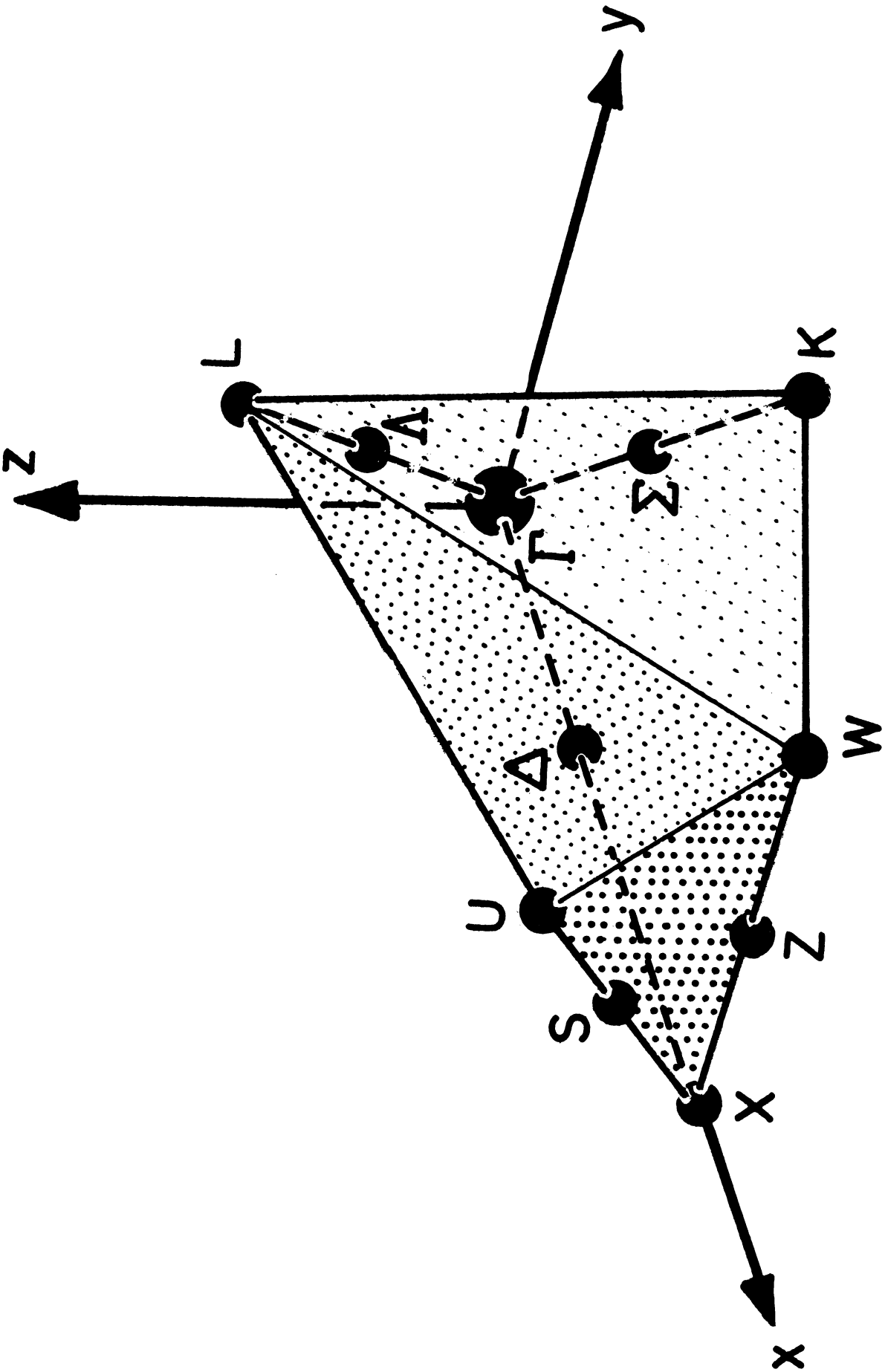


Figure 5. Irreducible prism of the Brillouin zone.

TABLE I

PHASE FACTORS USED IN CONSTRUCTING THE MULTIPLIER REPRESENTATIONS FOR VARIOUS SYMMETRY POINTS

Point	$\underline{q}$	Operation	$\underline{\underline{R}}\,\underline{x}(2)$	$\underline{q}\cdot[\underline{x}(2) - \underline{\underline{R}}\,\underline{x}(2)]$	Θ_2
Γ	$(0,0,0)$	All 24		0	1
X	$\frac{2\pi}{a}(1,0,0)$	E	$(\frac{1}{4},\frac{1}{4},\frac{1}{4})a$	0	1
		$C_2(x)$	$(\frac{1}{4},-\frac{1}{4},-\frac{1}{4})a$	0	1
		$C_2(y)$	$(-\frac{1}{4},\frac{1}{4},-\frac{1}{4})a$	π	-1
		$C_2(z)$	$(-\frac{1}{4},-\frac{1}{4},\frac{1}{4})a$	π	-1
		$S_4(x)$	$(-\frac{1}{4},\frac{1}{4},-\frac{1}{4})a$	π	-1
		$S_4^{-1}(x)$	$(-\frac{1}{4},-\frac{1}{4},\frac{1}{4})a$	π	-1
		σ_{yz}	$(\frac{1}{4},\frac{1}{4},\frac{1}{4})a$	0	1
		$\sigma_{\bar{y}z}$	$(\frac{1}{4},\frac{1}{4},\frac{1}{4})a$	0	1
Δ	$\frac{2\pi}{a}(\eta,0,0)$	E	$(\frac{1}{4},\frac{1}{4},\frac{1}{4})a$	0	1
		$C_2(x)$	$(\frac{1}{4},-\frac{1}{4},-\frac{1}{4})a$	0	1
		σ_{yz}	$(\frac{1}{4},\frac{1}{4},\frac{1}{4})a$	0	1
		$\sigma_{\bar{y}z}$	$(\frac{1}{4},\frac{1}{4},\frac{1}{4})a$	0	1
Λ	$\frac{\pi}{a}(\eta,\eta,\eta)$	E	$(\frac{1}{4},\frac{1}{4},\frac{1}{4})a$	0	1
		$C_3(111)$	$(\frac{1}{4},\frac{1}{4},\frac{1}{4})a$	0	1
		$C_3^{-1}(111)$	$(\frac{1}{4},\frac{1}{4},\frac{1}{4})a$	0	1
		σ_{xy}	$(\frac{1}{4},\frac{1}{4},\frac{1}{4})a$	0	1
		σ_{yz}	$(\frac{1}{4},\frac{1}{4},\frac{1}{4})a$	0	1
		σ_{xz}	$(\frac{1}{4},\frac{1}{4},\frac{1}{4})a$	0	1

TABLE I (Concluded)

Point	$\underline{q}$	Operation	$\underline{\underline{R}}\,\underline{x}(2)$	$\underline{q}\cdot[\underline{x}(2) - \underline{\underline{R}}\,\underline{x}(2)]$	Θ_2
Z	$\frac{2\pi}{a}(1,\eta,0)$	E	$(\frac{1}{4},\frac{1}{4},\frac{1}{4})a$	0	1
		$C_2(y)$	$(-\frac{1}{4},\frac{1}{4},-\frac{1}{4})a$	π	-1
W	$\frac{2\pi}{a}(1,\frac{1}{2},0)$	E	$(\frac{1}{4},\frac{1}{4},\frac{1}{4})a$	0	1
		$S_4(y)$	$(-\frac{1}{4},-\frac{1}{4},\frac{1}{4})a$	$\frac{3\pi}{2}$	-i
		$S_4^{-1}(y)$	$(\frac{1}{4},-\frac{1}{4},-\frac{1}{4})a$	$\frac{\pi}{2}$	i
		$C_2(y)$	$(-\frac{1}{4},\frac{1}{4},-\frac{1}{4})a$	π	-1
Σ	$\frac{2\pi}{a}(\eta,\eta,0)$	E	$(\frac{1}{4},\frac{1}{4},\frac{1}{4})a$	0	1
		σ_{xy}	$(\frac{1}{4},\frac{1}{4},\frac{1}{4})a$	0	1
S	$\frac{2\pi}{a}(1,\eta,\eta)$	E	$(\frac{1}{4},\frac{1}{4},\frac{1}{4})a$	0	1
		σ_{yz}	$(\frac{1}{4},\frac{1}{4},\frac{1}{4})a$	0	1

The irreducible representations for this group and the number of times they occur in the reducible representation $\{\underline{\underline{T}}(\Delta;\underline{\underline{R}})\}$ are listed in Table II.

TABLE II

IRREDUCIBLE MULTIPLIER REPRESENTATIONS OF THE GROUP $G_o(\Delta)$

	E	$C_2(x)$	σ_{yz}	$\sigma_{\bar{y}z}$	$n(\Delta_i)$
Δ_1	1	1	1	1	2
Δ_2	1	1	-1	-1	0
Δ_3	1	-1	-1	1	2
Δ_4	1	-1	1	-1	2
Tr $\underline{\underline{T}}$	6	-2	2	2	

The dynamical matrix can be written quite generally as

$$\underline{\underline{D}}(\underline{q}) = \begin{bmatrix} \underline{\underline{D}}\left(\frac{q}{11}\right) & \underline{\underline{D}}\left(\frac{q}{12}\right) \\ \underline{\underline{D}}^{\dagger}\left(\frac{q}{12}\right) & \underline{\underline{D}}\left(\frac{q}{22}\right) \end{bmatrix} \tag{30}$$

where $\kappa = 1, 2$ denotes positive ion and negative ion, respectively. Next, taking $\underset{\sim}{q} = \Delta$ and $\underline{\underline{R}} = \underline{\underline{\sigma}}_{yz}$ and using Eq. (9a) we obtain,

$$\begin{bmatrix} D_{xx}\left(\frac{\Delta}{\kappa\kappa'}\right) & D_{xy}\left(\frac{\Delta}{\kappa\kappa'}\right) & D_{xz}\left(\frac{\Delta}{\kappa\kappa'}\right) \\ D_{yx}\left(\frac{\Delta}{\kappa\kappa'}\right) & D_{yy}\left(\frac{\Delta}{\kappa\kappa'}\right) & D_{yz}\left(\frac{\Delta}{\kappa\kappa'}\right) \\ D_{xz}\left(\frac{\Delta}{\kappa\kappa'}\right) & D_{zy}\left(\frac{\Delta}{\kappa\kappa'}\right) & D_{zz}\left(\frac{\Delta}{\kappa\kappa'}\right) \end{bmatrix} = \begin{bmatrix} D_{xx}\left(\frac{\Delta}{\kappa\kappa'}\right) & D_{xz}\left(\frac{\Delta}{\kappa\kappa'}\right) & D_{xy}\left(\frac{\Delta}{\kappa\kappa'}\right) \\ D_{zx}\left(\frac{\Delta}{\kappa\kappa'}\right) & D_{zz}\left(\frac{\Delta}{\kappa\kappa'}\right) & D_{zy}\left(\frac{\Delta}{\kappa\kappa'}\right) \\ D_{yx}\left(\frac{\Delta}{\kappa\kappa'}\right) & D_{yz}\left(\frac{\Delta}{\kappa\kappa'}\right) & D_{yy}\left(\frac{\Delta}{\kappa\kappa'}\right) \end{bmatrix}$$

With $\underline{\underline{R}} = \underline{\underline{\sigma}}_{yz}$, however, we obtain

$$\begin{bmatrix} D_{xx}(\overset{\Delta}{\alpha\alpha'}) & D_{xy}(\overset{\Delta}{\alpha\alpha'}) & D_{xz}(\overset{\Delta}{\alpha\alpha'}) \\ D_{yx}(\overset{\Delta}{\alpha\alpha'}) & D_{yy}(\overset{\Delta}{\alpha\alpha'}) & D_{yz}(\overset{\Delta}{\alpha\alpha'}) \\ D_{zx}(\overset{\Delta}{\alpha\alpha'}) & D_{zy}(\overset{\Delta}{\alpha\alpha'}) & D_{zz}(\overset{\Delta}{\alpha\alpha'}) \end{bmatrix} = \begin{bmatrix} D_{xx}(\overset{\Delta}{\alpha\alpha'}) & -D_{xz}(\overset{\Delta}{\alpha\alpha'}) & -D_{xy}(\overset{\Delta}{\alpha\alpha'}) \\ -D_{zx}(\overset{\Delta}{\alpha\alpha'}) & D_{zz}(\overset{\Delta}{\alpha\alpha'}) & D_{zy}(\overset{\Delta}{\alpha\alpha'}) \\ -D_{yx}(\overset{\Delta}{\alpha\alpha'}) & D_{yz}(\overset{\Delta}{\alpha\alpha'}) & D_{yy}(\overset{\Delta}{\alpha\alpha'}) \end{bmatrix}$$

From these we find:

$$D_{xy}(\overset{\Delta}{\alpha\alpha'}) = D_{xz}(\overset{\Delta}{\alpha\alpha'}) = 0 \quad ,$$

$$D_{yy}(\overset{\Delta}{\alpha\alpha'}) = D_{zz}(\overset{\Delta}{\alpha\alpha'}) \quad ,$$

and

$$D_{yz}(\overset{\Delta}{\alpha\alpha'}) = D_{zy}(\overset{\Delta}{\alpha\alpha'}) \quad .$$

The remaining elements in $G_o(\Delta)$ do not provide any further simplification in $\underline{\underline{D}}(q)$. We may thus write it as

$$\underline{\underline{D}}(\Delta) = \begin{bmatrix} A & 0 & 0 & G & 0 & 0 \\ 0 & B & C & 0 & H & J \\ 0 & C & B & 0 & J & H \\ G^* & 0 & 0 & D & 0 & 0 \\ 0 & H^* & J^* & 0 & E & F \\ 0 & J^* & H^* & 0 & F & E \end{bmatrix} \qquad (31a)$$

avoiding the subscripts. Here A, B, C, D, E, and F are completely real.

The matrix given in (31a) must be consistent with the general requirement that

$$D_{\alpha\beta}\begin{pmatrix} q \\ \nu\,\nu' \end{pmatrix} = D^{*}_{\alpha\beta}\begin{pmatrix} -q \\ \nu\,\nu' \end{pmatrix} . \qquad (9c)$$

As noted earlier, this condition in some instances provides further simplifications (see remarks after 9b). Let us explore this possibility. Now the operation $\underline{\underline{C}}_2(y)$ takes $\underset{\sim}{q}$ to $-\underset{\sim}{q}$ if $\underset{\sim}{q}$ is along Δ.* Therefore,

$$\underline{\underline{D}}\begin{pmatrix} -q \\ \| \end{pmatrix} = \underline{\underline{C}}_2(y)\,\underline{\underline{D}}\begin{pmatrix} q \\ \| \end{pmatrix}\underline{\underline{C}}_2(y) \qquad (\underset{\sim}{q} \text{ along } \Delta)$$

(see Eq. (9a)). This together with (31) above gives us

$$D_{yz}\begin{pmatrix} q \\ \| \end{pmatrix} = C = D^{*}_{yz}\begin{pmatrix} -q \\ \| \end{pmatrix} = -C^{*} .$$

Since C is real, this means

$$C = 0$$

In a similar fashion, we can show

$$F = 0$$

The element J, however, does not vanish. Noting the additional simplifications deduced above, we may write (31a) as

$$\underline{\underline{D}}(\Delta) = \begin{bmatrix} A & 0 & 0 & G & 0 & 0 \\ 0 & B & 0 & 0 & H & J \\ 0 & 0 & B & 0 & J & H \\ G^{*} & 0 & 0 & D & 0 & 0 \\ 0 & H^{*} & J^{*} & 0 & E & 0 \\ 0 & J^{*} & H^{*} & 0 & 0 & E \end{bmatrix} \qquad (31b)$$

*In general, the requirement is that $\underline{\underline{S}}\underset{\sim}{q}$ be equal to $-\underset{\sim}{q} + \underset{\sim}{G}$.

Our task now is to block diagonalize the matrix above and for this purpose we need $\underset{\sim}{S}(q)$. Let us first construct the projection operators $\mathcal{P}^{\Delta_1}$, $\mathcal{P}^{\Delta_3}$, and $\mathcal{P}^{\Delta_4}$. Using Eq. (17), the matrices in (27) and (29) and Table II, we get

$$\mathcal{P}^{\Delta_1} = \frac{1}{4}\left[\begin{array}{ccc|ccc} 4 & 0 & 0 & & & \\ 0 & 0 & 0 & & \mathbf{0} & \\ 0 & 0 & 0 & & & \\ \hline & & & 4 & 0 & 0 \\ & \mathbf{0} & & 0 & 0 & 0 \\ & & & 0 & 0 & 0 \end{array}\right] \tag{32}$$

$$\mathcal{P}^{\Delta_3} = \frac{1}{4}\left[\begin{array}{ccc|ccc} 0 & 0 & 0 & & & \\ 0 & 2 & -2 & & \mathbf{0} & \\ 0 & -2 & 2 & & & \\ \hline & & & 0 & 0 & 0 \\ & \mathbf{0} & & 0 & 2 & -2 \\ & & & 0 & -2 & 2 \end{array}\right] \tag{33}$$

$$\mathcal{P}^{\Delta_4} = \frac{1}{4}\left[\begin{array}{ccc|ccc} 0 & 0 & 0 & & & \\ 0 & 2 & 2 & & \mathbf{0} & \\ 0 & 2 & 2 & & & \\ \hline & & & 0 & 0 & 0 \\ & \mathbf{0} & & 0 & 2 & 2 \\ & & & 0 & 2 & 2 \end{array}\right] \tag{34}$$

Using these projection matrices, we obtain the following symmetry vectors.

$$\Delta_1: \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \end{bmatrix} \quad \Delta_3: \begin{bmatrix} 0 \\ 1/\sqrt{2} \\ -1/\sqrt{2} \\ 0 \\ 0 \\ 0 \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 1/\sqrt{2} \\ -1/\sqrt{2} \end{bmatrix} \quad \Delta_4: \begin{bmatrix} 0 \\ 1/\sqrt{2} \\ 1/\sqrt{2} \\ 0 \\ 0 \\ 0 \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 1/\sqrt{2} \\ 1/\sqrt{2} \end{bmatrix} \tag{35}$$

From these we find the transformation matrix $\underline{\underline{S}}(\underset{\sim}{q})$ to be,

$$\underline{\underline{S}}(\Delta) = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1/\sqrt{2} & 0 & 1/\sqrt{2} & 0 \\ 0 & 0 & -1/\sqrt{2} & 0 & 1/\sqrt{2} & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/\sqrt{2} & 0 & 1/\sqrt{2} \\ 0 & 0 & 0 & -1/\sqrt{2} & 0 & 1/\sqrt{2} \end{bmatrix} \begin{matrix} \\ \\ \\ \\ \\ \\ \end{matrix} \begin{matrix} \\ \\ \\ \\ \\ \\ \end{matrix} \begin{matrix} \\ \\ \\ \\ \\ \\ \end{matrix}$$

$$\underbrace{}_{\Delta_1} \quad \underbrace{}_{\Delta_3} \quad \underbrace{}_{\Delta_4}$$

(36)

and the block diagonal form $\underline{\underline{D}}'(\underset{\sim}{q})$ of the dynamical matrix to be

$$\underline{\underline{D}}'(\Delta) = \left[\begin{array}{cc|cc|cc} A & G & 0 & 0 & 0 & 0 \\ G^* & D & 0 & 0 & 0 & 0 \\ \hline 0 & 0 & B & H-J & 0 & 0 \\ 0 & 0 & H^*-J^* & E & 0 & 0 \\ \hline 0 & 0 & 0 & 0 & B & H+J \\ 0 & 0 & 0 & 0 & H^*+J^* & E \end{array}\right] \begin{matrix} \\ \\ \\ \\ \\ \\ \end{matrix} \begin{matrix} \\ \\ \\ \\ \\ \\ \end{matrix} \begin{matrix} \leftarrow \Delta_1 \\ \\ \leftarrow \Delta_3 \\ \\ \leftarrow \Delta_4 \\ \\ \end{matrix}$$

(37)

By diagonalizing successively the three 2 x 2 blocks in (37) above, we may obtain $\omega^2(\Delta;\Delta_1 1)$, $\omega^2(\Delta;\Delta_1 2)$, etc. Thus

$$\omega^2(\Delta;\Delta_i a) = \frac{\alpha_{11}+\alpha_{22}}{2} + \frac{(2a-3)}{2}\left\{(\alpha_{11}+\alpha_{22})^2 - 4(\alpha_{11}\alpha_{22}-|\alpha_{12}|^2)\right\}^{1/2} \quad (38a)$$

where for Δ_1,

$$\alpha_{11} = A \ , \ \alpha_{22} = D \ , \ \alpha_{12} = G \ ; \quad (38b)$$

for Δ_3,

$$\alpha_{11} = B \ , \ \alpha_{22} = E \ , \ \alpha_{12} = H - J \ ; \quad (38c)$$

and for Δ_4,

$$\alpha_{11} = B \ , \ \alpha_{22} = E \ , \ \alpha_{12} = H + J \ . \quad (38d)$$

The index a takes on the values 1 and 2 corresponding to the two occurrences of each of the representations Δ_1, Δ_3, and Δ_4.

The eigenvectors in each case can be written as

$$A_i(a)\underline{\Psi}(\Delta;\Delta_i 1) + B_i(a)\underline{\Psi}(\Delta;\Delta_i 2) \ . \quad (39)$$

Substituting this and the corresponding frequency into Eq. (1), we have

$$\alpha_{11} A_i(a) + \alpha_{12} B_i(a) = \omega^2(\Delta;\Delta_i a) A_i(a)$$

$$\alpha_{12}^* A_i(a) + \alpha_{22} B_i(a) = \omega^2(\Delta;\Delta_i a) B_i(a) \ . \quad (40a)$$

Also,

$$|A_i(a)|^2 + |B_i(a)|^2 = 1 \tag{40b}$$

Solving these for $A_i(a)$ and $B_i(a)$,

$$A_i(a) = \frac{\alpha_{12}}{\{|\alpha_{12}|^2 + (\alpha_{11} - \omega^2)\}^{1/2}} \; ; \; B_i(a) = -\frac{(\alpha_{11} - \omega^2)}{\alpha_{12}} A_i(a) \; . \tag{41}$$

Finally we test for possible extra degeneracies due to time reversal symmetry. Since Δ is within the zone, we apply the criteria of (i), p. 8. The elements $\underline{\underline{A}}$ which send $\underset{\sim}{q}$ to $-\underset{\sim}{q}$ are $\underline{\underline{C}}_2(z)$, $\underline{\underline{C}}_2(y)$, $\underline{\underline{S}}_4^{-1}(\mathbf{x})$, and $\underline{\underline{S}}_4(\mathbf{x})$. Therefore

$$Q = \frac{1}{4} \sum_A \chi^{\Delta_i}(A^2)$$

$$= \frac{1}{4} \left\{ \chi^{\Delta_i}(\underline{\underline{E}}) + \chi^{\Delta_i}(\underline{\underline{E}}) + \chi^{\Delta_i}(\underline{\underline{C}}_2(x)) + \chi^{\Delta_i}(\underline{\underline{C}}_2(x)) \right\}$$

= 1 for Δ_1
= 0 for Δ_3
= 0 for Δ_4.

Thus Δ_3 and Δ_4 are related by time reversal symmetry,[2] and as is to be expected, both occur in $\{\underline{\underline{T}}\}$ the same number of times. By examining the symmetry vectors, we note that the Δ_1 modes are longitudinal while Δ_3 and Δ_4 are transverse.

X: $\underset{\sim}{q} = 2\pi/a(1,0,0)$

The point group $G_0(\underset{\sim}{q})$ is isomorphous to the molecular point group V_d and has the elements $\{\underline{\underline{E}}|0\}$, $\{\underline{\underline{C}}_2(\kappa)|0\}$, $\{\underline{\underline{C}}_2(y)|0\}$ $\{\underline{\underline{C}}_2(z)|0\}$, $\{\underline{\underline{S}}_4(x)|0\}$ $\{\underline{\underline{S}}_4^{-1}(x)|0\}$, $\{\underline{\underline{\sigma}}_{yz}|0\}$ $\{\underline{\underline{\sigma}}_{\bar{y}z}|0\}$. The $\underline{\underline{T}}$ matrices may be written down readily using Table I and the three-dimensional matrices in (27). The irreducible representations and the number of times each occurs in the reducible representation are given in Table III. The dynamical matrix after simplifications has the form

TABLE III

IRREDUCIBLE MULTIPLIER REPRESENTATIONS OF THE GROUP $G_o(X)$

	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	$S_4(x)$	$S_4^{-1}(x)$	σ_{yz}	$\sigma_{\bar{y}z}$	$n(X_i)$
X_1	1	1	1	1	1	1	1	1	1
X_2	1	1	1	1	-1	-1	-1	-1	0
X_3	1	-1	-1	1	-1	-1	1	1	1
X_4	1	-1	-1	1	1	1	-1	-1	0
X_5	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$	$\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & -1 \\ -1 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$	2
Tr $\underline{\underline{T}}$	6	0	0	-2	0	0	2	2	

$$\underline{\underline{D}}(X) = \left[\begin{array}{ccc|ccc} A & 0 & 0 & 0 & 0 & 0 \\ 0 & B & 0 & 0 & 0 & E \\ 0 & 0 & B & 0 & E & 0 \\ \hline 0 & 0 & 0 & C & 0 & 0 \\ 0 & 0 & E^* & 0 & D & 0 \\ 0 & E^* & 0 & 0 & 0 & D \end{array}\right] \tag{42}$$

while the matrix $\underline{\underline{S}}(X)$ constructed from the symmetry vectors has the form

$$\underline{\underline{S}}(X) = \begin{array}{c} \begin{array}{cccccc} X_1 & X_3 & & X_5 & & \end{array} \\ \left[\begin{array}{cccccc} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{array}\right] \end{array} \tag{43}$$

From these two matrices, we obtain the block diagonal form as

$$\underline{\underline{D}}'(X) = \left[\begin{array}{c|c|cc|c} C & 0 & 0 & 0 & \leftarrow X_1 \\ \hline 0 & A & 0 & 0 & \leftarrow X_3 \\ \hline 0 & 0 & \begin{array}{cc} B & E \\ E^* & D \end{array} & 0 & \leftarrow X_5 \\ \hline 0 & 0 & 0 & \begin{array}{cc} B & E \\ E^* & D \end{array} & \leftarrow X_5 \end{array}\right] \tag{44}$$

The frequencies for X_1 and X_3 are:

$$\omega^2(X; X_1) = C$$

$$\omega^2(X; X_3) = A \tag{45}$$

The two frequencies for X_5 are given by (38a) with

$$\alpha_{11} = B$$

$$\alpha_{12} = E$$

$$\alpha_{22} = D \tag{46}$$

The eigenvectors are:

$$X_1: \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \end{bmatrix} \qquad X_3: \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \tag{47}$$

Those for X_5 are given by Eq. (41) with the definitions of α_{11}, etc., as in (46). Observe that in both X_1 and X_3, which occur only once, one species of atoms is stationary. This is consistent with the general observation of Elliott and Thorpe[9] that "if a representation occurs only once, then only one species is involved in that mode." Also note that both X_1 and X_3 refer to longitudinal modes. The "optic" or the "acoustic" nature of the mode depends upon the relative values of C and A. The modes belonging to X_5 involve motions of both atoms, and are transverse. Time reversal does not introduce any additional degeneracies.

Λ: $\underset{\sim}{q} = \pi/a(\eta, \eta, \eta)$ $1 > \eta > 0$

$G_o(\underset{\sim}{q})$ is isomorphous to the point group C_{3v}, and its irreducible representations are given in Table IV. Also presented in the table are the

occurrences of the irreducible representations in the reducible representation formed by the $\underline{\underline{T}}$ matrices.

TABLE IV

IRREDUCIBLE MULTIPLIER REPRESENTATIONS OF THE GROUP $G_o(\Lambda)$

	E	$C_3(111)$	$C_3^{-1}(111)$	σ_{xy}	σ_{yz}	σ_{xz}	$n(\Lambda_i)$
Λ_1	1	1	1	1	1	1	2
Λ_2	1	1	1	-1	-1	-1	0
Λ_3	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ +\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & +\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & +\frac{\sqrt{3}}{2} \\ +\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	2
$\mathrm{Tr}\,\underline{\underline{T}}$	6	0	0	2	2	2	

The dynamical matrix for this point can be written as

$$\underline{\underline{D}}(\Lambda) = \begin{bmatrix} A & B & B & E & F & F \\ B & A & B & F & E & F \\ B & B & A & F & F & E \\ E^* & F^* & F^* & C & D & D \\ F^* & E^* & F^* & D & C & D \\ F^* & F^* & E^* & D & D & C \end{bmatrix} \tag{48}$$

while the $\underline{\underline{S}}$ matrix has the form

$$\underline{\underline{S}}(\Lambda) = \begin{bmatrix} 1/\sqrt{3} & 0 & 1/\sqrt{6} & 0 & 1/\sqrt{2} & 0 \\ 1/\sqrt{3} & 0 & 1/\sqrt{6} & 0 & -1/\sqrt{2} & 0 \\ 1/\sqrt{3} & 0 & -\sqrt{\frac{2}{3}} & 0 & 0 & 0 \\ 0 & 1/\sqrt{3} & 0 & 1/\sqrt{6} & 0 & 1/\sqrt{2} \\ 0 & 1/\sqrt{3} & 0 & 1/\sqrt{6} & 0 & 1/\sqrt{2} \\ 0 & 1/\sqrt{3} & 0 & -\sqrt{\frac{2}{3}} & 0 & 0 \end{bmatrix} \quad \begin{matrix} \\ \\ \\ \\ \\ \\ \end{matrix} \quad \begin{matrix} \\ \\ \\ \\ \\ \\ \end{matrix}$$

Λ_1 Λ_3

(49)

Upon transforming $\underline{\underline{D}}(\Lambda)$ using $\underline{\underline{S}}(\Lambda)$, we obtain the block diagonal form $\underline{\underline{D}}'(\Lambda)$ as

$$\underline{\underline{D}}'(\Lambda) = \left[\begin{array}{cc|cc|cc} A+2B & E+2F & & & & \\ E^*+2F^* & C+2D & 0 & & 0 & \\ \hline & & A-B & E-F & & \\ 0 & & E^*-F^* & C-D & 0 & \\ \hline & & & & A-B & E-F \\ 0 & & 0 & & E^*-F^* & C-D \end{array}\right] \quad \begin{matrix} \\ \\ \leftarrow \Lambda_1 \\ \\ \leftarrow \Lambda_3 \\ \\ \leftarrow \Lambda_3 \end{matrix}$$

(50)

The eigenfrequencies and eigenvectors resulting from these 2 x 2 blocks may as before be obtained from Eqs. (38a) and (41), respectively, with

$$\alpha_{11} = A + 2B$$

$$\alpha_{22} = C + 2D$$

$$\alpha_{12} = E + 2F \tag{51}$$

for Λ_1, and

$$\alpha_{11} = A - B$$

$$\alpha_{22} = C - D$$

$$\alpha_{12} = E - F \tag{52}$$

for Λ_3.

Time reversal does not introduce any additional degeneracies.

L: $\underset{\sim}{q} = \pi/a(1,1,1)$

The results for the point L which is on the zone boundary in the (111) direction are identical with those deduced above for Λ, a general point in the same direction. This follows from the fact that $G_o(\underset{\sim}{q})$ is the same for both points

Z: $\underset{\sim}{q} = 2\pi/a(1,\eta,0)$ $0 < \eta < 0.5$

The group $G_o(\underset{\sim}{q})$ for this point has just two elements, E and $C_2(y)$. The $\underline{\underline{T}}$ matrices are readily written down using the rotation matrices in (27) and the phase factors in Table I. The character table and the break-up of the reducible representation are shown in Table V.

TABLE V

IRREDUCIBLE MULTIPLIER REPRESENTATIONS OF THE GROUP $G_o(Z)$

	E	$C_2(y)$	$n(Z_i)$
Z_1	1	1	3
Z_2	1	-1	3
Tr $\underline{\underline{T}}$	6	0	

The dynamical matrix assumes the form

$$\underline{\underline{D}}(Z) = \begin{bmatrix} A & 0 & 0 & 0 & K & 0 \\ 0 & B & 0 & L & 0 & M \\ 0 & 0 & C & 0 & N & 0 \\ 0 & L^* & 0 & D & 0 & 0 \\ K^* & 0 & N^* & 0 & E & 0 \\ 0 & M^* & 0 & 0 & 0 & F \end{bmatrix} \tag{53}$$

where $K^* = -e^{+i\pi\eta_K}$, $L^* = -e^{+i\pi\eta_L}$, $M^* = e^{+i\pi\eta_M}$, $N^* = e^{+i\pi\eta_N}$.

For $\underline{\underline{S}}(Z)$ we have

$$\underline{\underline{S}}(Z) = \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{bmatrix} \begin{matrix} \\ \\ \\ \\ \\ \\ \end{matrix} \quad \begin{matrix} \underbrace{} \\ Z_1 \end{matrix} \quad \begin{matrix} \underbrace{} \\ Z_2 \end{matrix} \tag{54}$$

The resulting block diagonal form is

$$\underline{\underline{D}}'(Z) = \left[\begin{array}{ccc|ccc} B & L & M & & & \\ L^* & D & 0 & & 0 & \\ M & 0 & F & & & \\ \hline & & & A & 0 & K \\ & 0 & & 0 & C & N \\ & & & K^* & N^* & E \end{array}\right] \tag{55}$$

The two 3 x 3 matrices above must be diagonalized to obtain the three frequencies belonging to Z_1 and the three frequencies belonging to Z_2. Time reversal does not introduce any extra degeneracies.

W: $\underset{\sim}{q} = 2\pi/a(1,1/2,0)$

The point W has higher symmetry than Z, there being four elements in $G_o(\underset{\sim}{q})$, which is isomorphous to S_4. The character table and the reduction of the $\underline{\underline{T}}$ matrices are given in Table VI.

TABLE VI

IRREDUCIBLE MULTIPLIER REPRESENTATIONS OF THE GROUP $G_o(W)$

	E	$S_4(y)$	$S_4^{-1}(y)$	$C_2(y)$	$n(W_i)$
W_1	1	1	1	1	1
W_2	1	-1	-1	1	2
W_3	1	i	-i	-1	2
W_4	1	-i	i	-1	1
Tr $\underline{\underline{T}}$	6	(-1+i)	(-1-i)	0	

Following the usual procedure, we find the dynamical matrix $\underline{\underline{D}}(W)$ to be

$$\underline{\underline{D}}(W) = \begin{bmatrix} A & 0 & 0 & 0 & K & 0 \\ 0 & B & 0 & L & 0 & L^* \\ 0 & 0 & A & 0 & K & 0 \\ 0 & L^* & 0 & D & 0 & 0 \\ K^* & 0 & K^* & 0 & E & 0 \\ 0 & L & 0 & 0 & 0 & D \end{bmatrix} \tag{56}$$

with $K^* = -iK$, $L^* = -iL$.

The $\underline{\underline{S}}(W)$ matrix has the form

$$\underline{\underline{S}}(W) = \begin{bmatrix} 0 & 0 & 0 & 1/\sqrt{2} & 0 & 1/\sqrt{2} \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -i/\sqrt{2} & 0 & i/\sqrt{2} \\ 1/\sqrt{2} & 0 & 1/\sqrt{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ -i/\sqrt{2} & 0 & i/\sqrt{2} & 0 & 0 & 0 \end{bmatrix} \begin{matrix} \uparrow & & & & & \uparrow \\ W_1 & & W_2 & & W_3 & W_4 \end{matrix} \tag{57}$$

The resulting block diagonal matrix is

$$\underline{\underline{D}}'(W) = \left[\begin{array}{c|cc|c} D & 0 & 0 & 0 \\ \hline 0 & \begin{matrix} B & \sqrt{2}L \\ \sqrt{2}L^* & D \end{matrix} & 0 & 0 \\ \hline 0 & 0 & \begin{matrix} A & \sqrt{2}K \\ \sqrt{2}K^* & E \end{matrix} & 0 \\ \hline 0 & 0 & 0 & A \end{array}\right] \begin{matrix} \leftarrow W_1 \\ \leftarrow W_2 \\ \leftarrow W_3 \\ \leftarrow W_4 \end{matrix} \tag{58}$$

The eigenfrequencies for the modes W_1 and W_4 are given simply as

$$\omega^2(W_1) = D$$
$$\omega^2(W_4) = A \tag{59}$$

Those for W_2 and W_3 are found by solving the appropriate 2 x 2 blocks as in Eq. (38a), i.e., for W_2 we take

$$\alpha_{11} = B$$

$$\alpha_{22} = D$$

and

$$\alpha_{12} = \sqrt{2}\, L \qquad (60a)$$

while for W_3 we take

$$\alpha_{11} = A$$

$$\alpha_{22} = E$$

and

$$\alpha_{12} = \sqrt{2}\, K \qquad (60b)$$

Regarding extra degeneracies due to time reversal, Parmenter[2] remarks that W_3 and W_4 are degenerate. However, application of criterion (ii) on p. 9 shows that for W_3,

$$Q = \frac{1}{4}\left\{ \chi^{W_3}(C_2^2(z)) + \chi^{W_3}(C_2^2(x)) \right.$$

$$\left. + \chi^{W_3}(\sigma_{zx}^2) + \chi^{W_3}(\sigma_{\bar{z}x}^2) \right\}$$

$$= \frac{1}{4}\left\{ 4\, \chi^{W_3}(E) \right\} = 1 \,.$$

Thus W_3 cannot be related by time reversal degeneracy to any other representation. The same can be shown to be true for W_4. It is worth noting that if W_3 and W_4 were degenerate, we would expect them to occur the same number of times in the reducible representation which, as seen in Table VI, they do not.

Σ: $\underset{\sim}{q} = 2\pi/a(\dot{\eta}, \eta, 0)$. $0 < \eta < 0.75$

The point group $G_o(q)$ is very simple having just two elements $\{\underline{\underline{E}}|0\}$ and $\{\underline{\underline{\sigma}}_{xy}|0\}$, and is isomorphous to the molecular point group C_s. The irreducible representations and their occurrences in the reducible representation furnished by $\underline{\underline{T}}$ matrices are given in Table VII.

TABLE VII

IRREDUCIBLE MULTIPLIER REPRESENTATIONS OF THE GROUP $G_o(\Sigma)$

	E	σ_{xy}	$n(\Sigma_i)$
Σ_1	1	1	4
Σ_2	1	-1	2
Tr $\underline{\underline{T}}$	6	2	

The dynamical matrix after simplification has the form

$$\underline{\underline{D}}(\Sigma) = \begin{bmatrix} A & C & D & J & L & M \\ C & A & D & L & J & M \\ -D & -D & B & N & N & K \\ J^* & L^* & N^* & E & G & H \\ L^* & J^* & N^* & G & E & H \\ M^* & M^* & K^* & -H & -H & F \end{bmatrix} \tag{61}$$

where $J^* = Je^{+i2\pi\eta}$, $L^* = Le^{+i2\pi\eta}$, $M^* = -Me^{+i2\pi\eta}$, $N^* = -Ne^{+i2\pi\eta}$, and $K^* = Ke^{i2\pi\eta}$. The matrix $\underline{\underline{S}}$ which serves to bring $\underline{\underline{D}}(\Sigma)$ above into block diagonal form is found to be

$$\underline{\underline{S}}(\Sigma) = \begin{bmatrix} 1/\sqrt{2} & 0 & 0 & 0 & 1/\sqrt{2} & 0 \\ 1/\sqrt{2} & 0 & 0 & 0 & -1/\sqrt{2} & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1/\sqrt{2} & 0 & 0 & 0 & 1/\sqrt{2} \\ 0 & 1/\sqrt{2} & 0 & 0 & 0 & -1/\sqrt{2} \\ 0 & 0 & 0 & 1 & 0 & 0 \end{bmatrix} \quad \begin{matrix} \\ \\ \\ \\ \\ \\ \end{matrix} \quad \begin{matrix} \\ \\ \\ \\ \\ \\ \end{matrix}$$

Σ_1 Σ_2

(62)

The block diagonal matrix is

$$\underline{\underline{D}}'(\Sigma) = \left[\begin{array}{cccc|cc} \sqrt{2}(A+C) & \sqrt{2}(J+L) & \sqrt{2}D & \sqrt{2}M & 0 & 0 \\ \sqrt{2}(J^*+L^*) & \sqrt{2}(E+G) & \sqrt{2}N^* & \sqrt{2}H & 0 & 0 \\ -\sqrt{2}D & \sqrt{2}N & B & K & 0 & 0 \\ -\sqrt{2}M^* & -\sqrt{2}H & K^* & F & 0 & 0 \\ \hline 0 & 0 & 0 & 0 & \sqrt{2}(A-C) & \sqrt{2}(J-L) \\ 0 & 0 & 0 & 0 & \sqrt{2}(J^*-L^*) & \sqrt{2}(E-G) \end{array}\right] \begin{matrix} \\ \\ \\ \\ \\ \\ \end{matrix} \begin{matrix} \\ \\ \leftarrow \Sigma_1 \\ \\ \\ \\ \end{matrix} \begin{matrix} \\ \\ \\ \\ \leftarrow \Sigma_2 \\ \\ \end{matrix} .$$

(63)

The frequencies and eigenvectors for the 2 x 2 block (corresponding to species Σ_2) may be determined using Eqs. (38a) and (41) with

$$\begin{aligned} \alpha_{11} &= \sqrt{2}(A-C) , \\ \alpha_{22} &= \sqrt{2}(E-G) , \\ \alpha_{12} &= \sqrt{2}(J-L) . \end{aligned} \qquad (64)$$

The solutions for the 4 x 4 block are too lengthy to be given here. They may, however, be found easily for any given problem through the use of a computer.

K: $q = 2\pi/a(0.75,0.75,0)$

The results deduced above for Σ are applicable to the point K as well and indeed beyond K up to the point $2\pi/a(1,1,0)$.

S: $q = 2\pi/a(1,\eta,\eta)$

The results for S are very similar to those just deduced for Σ. The wave vector group has two elements $\{\underline{\underline{E}}|0\}$, $\{\underline{\underline{\sigma}}_{yz}|0\}$, with the following character table.

TABLE VIII

IRREDUCIBLE MULTIPLIER REPRESENTATIONS OF THE GROUP $G_o(S)$

	E	σ_{yz}	$n(S_i)$
S_1	1	1	4
S_2	1	-1	2
Tr $\underline{\underline{T}}$	6	2	

The dynamical matrix is

$$\underline{\underline{D}}(S) = \begin{bmatrix} A & C & C & J & L & L \\ -C & B & D & N & K & M \\ -C & D & B & N & M & K \\ J^* & N^* & N^* & E & G & G \\ L^* & K^* & M^* & -G & F & H \\ L^* & M^* & K^* & -G & H & F \end{bmatrix}, \tag{65}$$

with $J^* = e^{+i2\pi\eta}J$, $L^* = -e^{+i2\pi\eta}L$, $M^* = e^{+i2\pi\eta}M$, and $N^* = -e^{+i2\pi\eta}N$, and after transformation by the matrix

$$\underline{\underline{S}}(S) = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1/\sqrt{2} & 0 & 1/\sqrt{2} & 0 \\ 0 & 0 & 1/\sqrt{2} & 0 & -1/\sqrt{2} & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/\sqrt{2} & 0 & 1/\sqrt{2} \\ 0 & 0 & 0 & 1/\sqrt{2} & 0 & -1/\sqrt{2} \end{bmatrix} \quad \begin{matrix} \\ \\ \\ \\ \\ \\ \end{matrix} \quad \begin{matrix} \\ \\ \\ \\ \\ \\ \end{matrix}$$

$$\underbrace{\qquad\qquad}_{S_1} \qquad \underbrace{\qquad}_{S_2}$$

(66)

assumes the form

$$\underline{\underline{D}}'(S) = \left[\begin{array}{cccc|c} A & J & C\sqrt{2} & L\sqrt{2} & \\ J & E & N^*\sqrt{2} & G\sqrt{2} & \\ -C\sqrt{2} & N\sqrt{2} & B+D & K+M & 0 \\ L^*\sqrt{2} & -G\sqrt{2} & K^*+M^* & F^*+H^* & \\ \hline & & & & B-D \;\; K-M \\ & 0 & & & K^*-M^* \;\; F-H \end{array}\right]$$

(67)

which we note is very similar to that for Σ.

$\underline{\underline{\Gamma}}$: $\underset{\sim}{q} = (0,0,0)$

Finally we turn to the most symmetric point in the Brillouin zone, namely the center. At this point, the point group is the full tetrahedral group T_d

having 24 elements. The character table and the decomposition of the reducible representation are given in Table IX. From this we see that corresponding to $\underset{\sim}{q} = 0$ there must be two triplets each belonging to the representation Γ_{15}. One of these corresponds to the acoustic modes of zero frequency. The remaining triply degenerate mode is the optic frequency. Experimentally, however, in zinc-blende type crystals two distinct frequencies are seen at $q = 0$ instead of a single frequency. It would seem from this that there is some contradiction. It turns out, however, that the splitting that is observed (which incidentally is due to coulombic effects*) is at values of $\underset{\sim}{q}$ which though small are yet not identically equal to zero. At $\underset{\sim}{q} \equiv 0$ there is in fact a triple degeneracy. For a further discussion of this problem, see the article by Warren[6] and the references cited therein.

TABLE IX

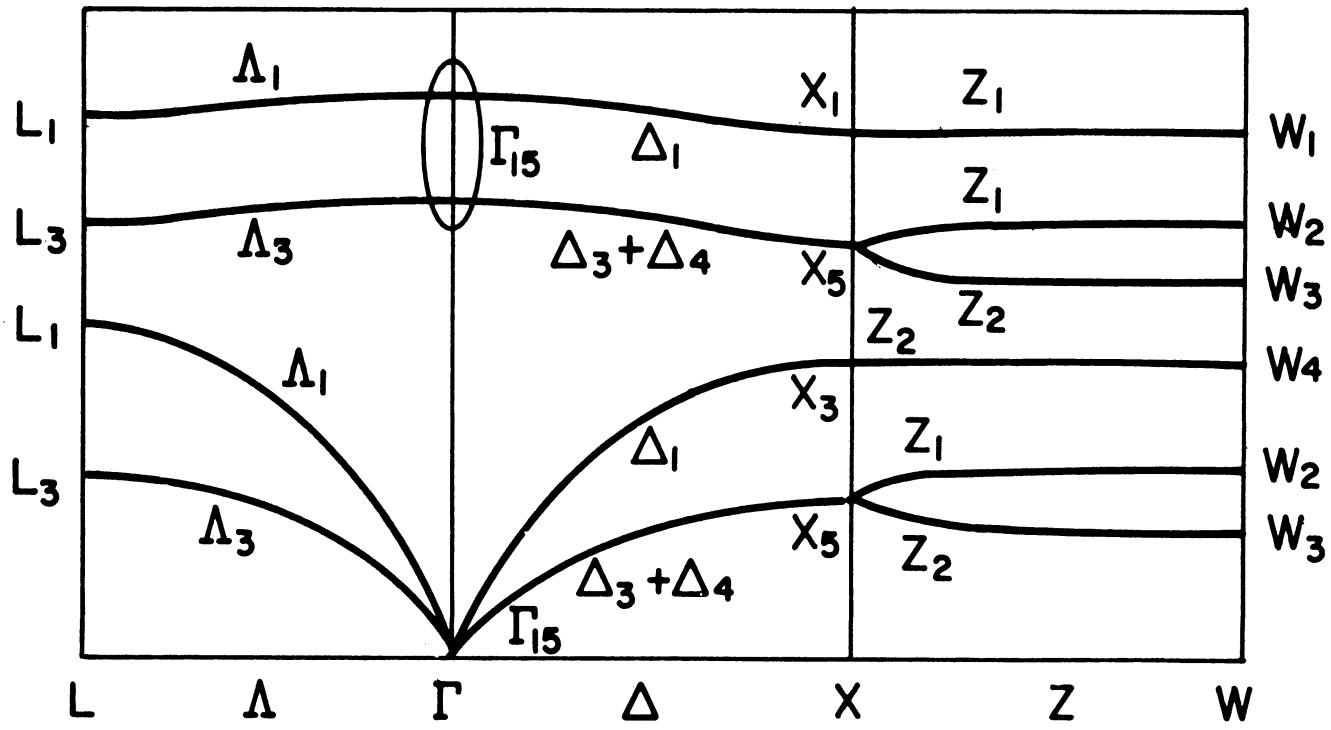
CHARACTER TABLE FOR THE GROUP $G_o(\Gamma)$

	E	$8C_3$	$3C_2$	$6S_4$	6σ	$n(\Gamma_i)$
Γ_1	1	1	1	1	1	0
Γ_2	1	1	1	-1	-1	0
Γ_{12}	2	-1	2	0	0	0
Γ_{15}	3	0	-1	-1	1	2
Γ_{25}	3	0	-1	1	-1	0
Tr $\underline{\underline{T}}$	6	0	-2	-2	2	

This concludes the discussion of the symmetry of the dynamical matrix at various symmetry points in the Brillouin zone.

The manner in which the representations change as we move in reciprocal space is indicated in Table X taken from the work of Parmenter. Using this table and the results deduced above, we sketch schematically in Figure 6 the dispersion relations for the zinc-blende structure. In some directions and points there is more than one way of doing the labelling, and only one of the possibilities has been indicated in the figure. For example, at X, the top Δ_1 branch could go over to either X_1 or X_3 while the bottom Δ_1 goes over to either X_3 or X_1. We indicate one of the two possible choices. Similar considerations

*The behavior of the optic modes at small values of $\underset{\sim}{q}$ is a topic in itself.[10,11]



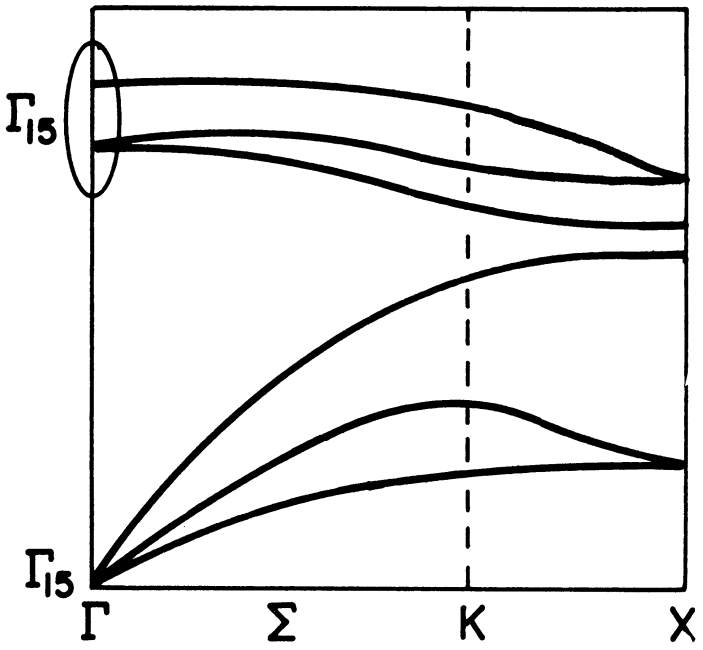


Figure 6. Schematic plot of the dispersion relations for the zinc-blende lattice. At point X, the labelling of X_1 and X_3 is ambiguous and is model dependent. Similar ambiguities exist at Z and W.

TABLE X

COMPATIBILITY TABLES CONNECTING REPRESENTATIONS AT DIFFERENT SYMMETRY POINTS

$\Gamma \rightarrow \Delta$		$\Delta \rightarrow X$		$X \rightarrow Z$		$Z \rightarrow W$	
Γ_1	Δ_1	Δ_1	X_1, X_3	X_1	Z_1	Z_1	W_1, W_2
Γ_2	Δ_2	Δ_2	X_2, X_4	X_2	Z_1	Z_2	W_3, W_4
Γ_{12}	$\Delta_1 + \Delta_2$	Δ_3	X_5	X_3	Z_2		
Γ_{15}	$\Delta_1 + \Delta_3 + \Delta_4$	Δ_4		X_4	Z_2		
Γ_{25}	$\Delta_2 + \Delta_3 + \Delta_4$			X_5	$Z_1 + Z_2$		
$\Gamma \rightarrow \Lambda$		$\Gamma \rightarrow \Sigma$		$X \rightarrow S$			
Γ_1	Λ_1	Γ_1	Σ_1	X_1	S_1		
Γ_2	Λ_2	Γ_2	Σ_2	X_2	S_2		
Γ_{12}	Λ_3	Γ_{12}	$\Sigma_1 + \Sigma_2$	X_3	S_1		
Γ_{15}	$\Lambda_1 + \Lambda_3$	Γ_{15}	$2\Sigma_1 + \Sigma_2$	X_4	S_2		
Γ_{25}	$\Lambda_2 + \Lambda_3$	Γ_{25}	$\Sigma_1 + 2\Sigma_2$	X_5	$S_1 + S_2$		

have been used at Z, W. As noted earlier this ambiguity can be reduced only by explicit numerical calculations of the dispersion curves based on suitable force constant models. It is also of some interest to compare the representations of the zinc-blende lattice with those of two related lattice structures, viz., face center lattice (space group O_h^5) and the diamond lattice (space group O_h^7). Such a comparison has been made by Parmenter and his results are reproduced in Table XI.

TABLE XI

COMPATABILITY TABLES FOR THE REPRESENTATIONS OF THE SINGLE GROUPS CONNECTING THE ZINC BLENDE (T_d^2) WITH THE FACE-CENTERED-CUBIC (O_h^5) AND THE DIAMOND (O_h^7) STRUCTURES

T_d^2	O_h^5	T_d^2	O_h^7
Γ_1	Γ_1 or Γ_2'	Γ_1	Γ_1 or Γ_2'
Γ_2	Γ_2 or Γ_1'	Γ_2	Γ_2 or Γ_1'
Γ_{12}	Γ_{12} or Γ_{12}'	Γ_{12}	Γ_{12} or Γ_{12}'
Γ_{15}	Γ_{15} or Γ_{25}'	Γ_{15}	Γ_{15} or Γ_{25}'
Γ_{25}	Γ_{25} or Γ_{15}'	Γ_{25}	Γ_{25} or Γ_{15}'
Δ_1	Δ_1 or Δ_2'	Δ_1	Δ_1 or Δ_2'
Δ_2	Δ_2 or Δ_1'	Δ_2	Δ_2 or Δ_1'
Δ_3, Δ_4	Δ_5	Δ_3, Δ_4	Δ_5
Λ_1	Λ_1	Λ_1	Λ_1
Λ_2	Λ_2	Λ_2	Λ_2
Λ_3	Λ_3	Λ_3	Λ_3
Σ_1	Σ_1 or Σ_3	Σ_1	Σ_1 or Σ_3
Σ_2	Σ_2 or Σ_4	Σ_2	Σ_2 or Σ_4
Z_1	Z_1 or Z_2	Z_1, Z_2	Z_1
Z_2	Z_3 or Z_4		
X_1	X_1 or X_2'	X_1, X_3	X_1
X_2	X_2 or X_1'		
X_3	X_3 or X_4'	X_2, X_4	X_2
X_4	X_4 or X_3'		
X_5	X_5 or X_5'	X_5	X_3 or X_4
W_1	W_1 or W_2	W_1, W_3	W_1
W_2	W_1' or W_2'		
W_3, W_4	W_3	W_2, W_4	W_2

CHAPTER V

SELECTION RULES IN OPTICAL SPECTRA

In this chapter, we shall discuss selection rules for two phonon absorption in zinc-blende type crystals. Several methods[3,12,13] for obtaining these have been reported in the literature. We follow the techniques of MV as they lead not only to the selection rules but to the complete structure of the dipole moment operator as well. Similar techniques for obtaining the structure of the polarizability tensor which controls Raman scattering are also discussed.

A. INFRARED ABSORPTION

Among the methods frequently employed for the study of phonons in crystals are infrared absorption and Raman scattering. In an infrared experiment, one examines the absorption of a thin slice of the crystal as a function of the frequency of the incident radiation, and looks for resonances in the absorption. These resonances arise due to the interaction between the photons and phonons, and are subject to the conservation laws:

Energy of photon $\hbar\omega$ = algebraic sum of energies of all phonons contributing to the resonance.

Momentum of photon $\hbar Q \approx 0$ (for infrared radiation)
$= \hbar \times$ (vector sum of wave vectors of all phonons involved in the resonance).

In a one phonon resonance, for example, we will have

$$\hbar\omega = \hbar\omega_j(\underline{q})$$
$$\underline{Q} \approx 0$$
$$= \underline{q} \tag{68}$$

Since in ZnS type crystals there are only two nonzero frequencies at $q \approx 0$ (see Figure 6), one phonon resonance does not lead to much information. On the other hand, for two phonon processes the conservation equations take the form

(sum mode) $\hbar\omega = \hbar\omega_j(\underline{q}) + \hbar\omega_{j'}(\underline{q}')$

(difference mode) $= \hbar\omega_j(\underline{q}) - \hbar\omega_{j'}(\underline{q}')$

$$\underline{Q} \approx 0$$
$$= \underline{q} + \underline{q}'$$

(69)

and clearly many combinations are possible. Therefore it should be possible to say more about the phonon spectrum from a study of two phonon absorption than from one phonon absorption. Figure 7 shows the absorption curve for ZnS as observed by Deutsch.[14] We see at least six prominent transmission dips, and the question naturally arises as to which phonons are responsible for these. To answer this question, it is necessary to consider briefly the cross section for photon absorption. This is proportional to

$$\left\langle \sum_n \left| \int X_n^*(\underline{x})\, \underline{M}(\underline{x})\, X_m(\underline{x})\, d\underline{x} \right|^2 \delta(E_n - E_m - \hbar\omega) \right\rangle \quad (70)$$

Ave. over initial states m

Here $X_m(\underset{\sim}{x})$ and $X_n(\underset{\sim}{x})$ denote the crystal vibrational wave functions in the vibrational states m and n respectively, and $\underset{\sim}{M}$ is the dipole moment operator. Expand $\underset{\sim}{M}$ in a power series of nuclear displacements as follows:

$$\underline{M}(\underline{x}) = \underline{M}^{(0)}(\underline{x}) + \underline{M}^{(1)}(\underline{x}) + \underline{M}^{(2)}(\underline{x}) + \cdots \quad , \quad (71)$$

where

$$M_\alpha^{(1)}(\underline{x}) = \sum_{\ell\kappa\beta} M_{\alpha,\beta}\begin{pmatrix}\ell\\ \kappa\end{pmatrix} u_\beta\begin{pmatrix}\ell\\ \kappa\end{pmatrix}$$

$$M_\alpha^{(2)}(\underline{x}) = \frac{1}{2}\sum_{\substack{\ell\kappa\beta\\ \ell'\kappa'\gamma}} M_{\alpha,\beta\gamma}\begin{pmatrix}\ell\ell'\\ \kappa\kappa'\end{pmatrix} u_\beta\begin{pmatrix}\ell\\ \kappa\end{pmatrix} u_\gamma\begin{pmatrix}\ell'\\ \kappa'\end{pmatrix} \quad (72)$$

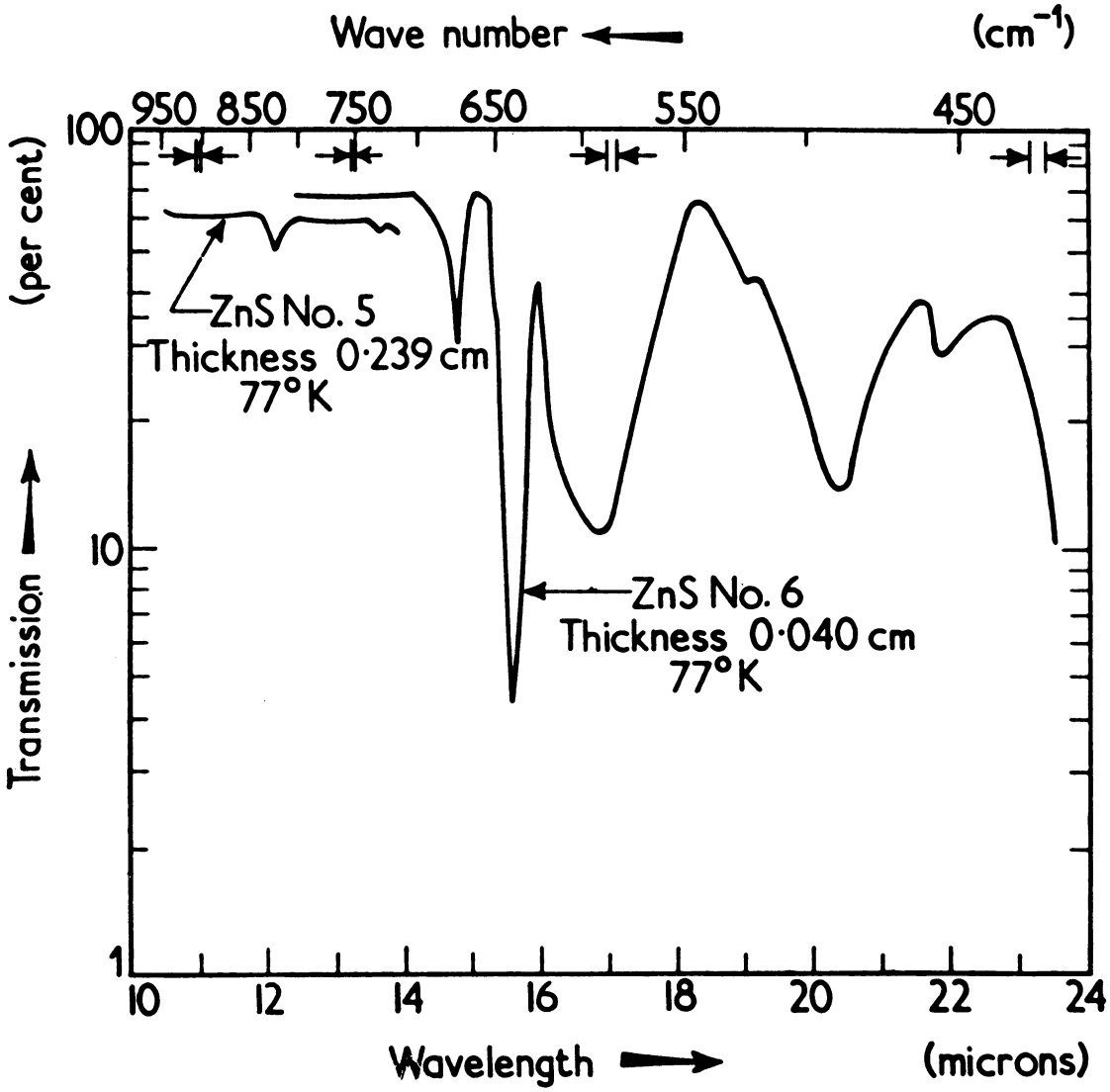


Figure 7. Transmission of zinc sulphide. Data of Deutsch.[14] (Reproduced from Proc. Internat. Conf. on the Physics of Semiconductors, Exeter, 1962.)

and so on, with $\underset{\sim}{U}\binom{\ell}{\kappa}$ denoting the displacement of the atom at $\binom{\ell}{\kappa}$. In two phonon absorption, we are interested in the part $\underset{\sim}{M}^2(\underset{\sim}{x})$ of $\underset{\sim}{M}(\underset{\sim}{x})$. On account of the translational periodicity of the crystal,

$$M_{\alpha,\beta\gamma}\binom{\ell\,\ell'}{\kappa\,\kappa'} = M_{\alpha,\beta\gamma}\binom{0\;\; \ell'-\ell=\bar{\ell}}{\kappa\;\;\kappa'}$$

$$= M_{\alpha,\beta\gamma}\binom{-\bar{\ell}\;\; 0}{\kappa\;\;\kappa'} \quad . \tag{73}$$

Using this fact and the familiar normal coordinate expansion for $\underset{\sim}{U}\binom{\ell}{\kappa}$,(10)

$$\underset{\sim}{u}\binom{\ell}{\kappa} = (Nm_\kappa)^{-\frac{1}{2}} \sum_{\underset{\sim}{q}j} \underset{\sim}{e}(\kappa, \underset{\sim}{q}j)\, Q\binom{\underset{\sim}{q}}{j}\, e^{i\,\underset{\sim}{q}\cdot\underset{\sim}{x}(\ell)} ,$$

where N is the number of primitive cells in the lattice, and $Q(\underset{\sim}{q}_j)$ is the normal coordinate appropriate to the mode $(\underset{\sim}{q}, j)$, we can express M^2_α as

$$M^{(2)}_\alpha = \frac{1}{2} \sum_{\underset{\sim}{q}\underset{\sim}{q}'jj'} M_\alpha\binom{\underset{\sim}{q}\;\underset{\sim}{q}'}{j\;j'}\, Q\binom{\underset{\sim}{q}}{j}\, Q\binom{\underset{\sim}{q}'}{j'}\, \Delta(\underset{\sim}{q}+\underset{\sim}{q}')$$

$$= \frac{1}{2} \sum_{\underset{\sim}{q}jj'} M_\alpha\binom{\underset{\sim}{q}\;-\underset{\sim}{q}}{j\;j'}\, Q\binom{\underset{\sim}{q}}{j}\, Q^+\binom{\underset{\sim}{q}}{j'} \tag{74a}$$

$$= \frac{1}{2} \sum_{\underset{\sim}{q}jj'} M_\alpha\binom{-\underset{\sim}{q}\;\underset{\sim}{q}}{j\;j'}\, Q^+\binom{\underset{\sim}{q}}{j}\, Q\binom{\underset{\sim}{q}}{j'} \quad . \tag{74b}$$

In Eqs. (74a) and (74b) above,

$$M_\alpha\binom{\underset{\sim}{q}\;\underset{\sim}{q}'}{j\;j'} = \sum'_{\substack{\ell'\kappa\beta \\ \kappa'\gamma}} M_{\alpha,\beta\gamma}\binom{\ell\,\ell'}{\kappa\,\kappa'}\, \frac{e_\beta(\kappa,\underset{\sim}{q}j)\, e_\gamma(\kappa',\underset{\sim}{q}'j')}{\sqrt{m_\kappa\, m_{\kappa'}}}$$

$$(\times)\ \exp i\,\underset{\sim}{q}'\cdot\left[\underset{\sim}{x}(\ell') - \underset{\sim}{x}(\ell)\right] \tag{75}$$

In obtaining them, we have made use of the results (10)

$$e_\alpha^*(x, \underline{q}\, j) = e_\alpha(x, -\underline{q}\, j)$$

$$Q^*\left(\frac{q}{j}\right) = Q\left(\frac{-q}{j}\right)$$

and

$$\sum_{\ell} \exp i\, \underline{q} \cdot \underline{x}(\ell) = N \Delta(\underline{q}) \quad . \tag{76}$$

Observe that the momentum conservation $(\underline{q} + \underline{q}') = 0$ expressed in Eq. (69) arises through the Δ function above.

On introducing (74) into (70) and further expressing $Q(\frac{q}{j})$ in terms of annihilation and creation operators $a_{\underset{\sim}{qj}}$ and $a^+_{\underset{\sim}{qj}}$ as

$$Q\left(\frac{q}{j}\right) = \left(\frac{\hbar}{2\omega_j(\underline{q})}\right)^{1/2} \left[a_{\underline{q}j} + a^+_{-\underline{q}j}\right] \tag{77}$$

and then using the following properties,

$$a_{\underline{q}j} \,|\, n_j(\underline{q}) \rangle = 0 \quad , \quad n_j(\underline{q}) = 0 \quad ,$$

$$a_{\underline{q}j} \,|\, n_j(\underline{q}) \rangle = (n_j(\underline{q}))^{1/2} \,|\, n_j(\underline{q}) - 1 \rangle \quad , \quad n_j(\underline{q}) \neq 0 \quad ,$$

$$a^+_{\underline{q}j} \,|\, n_j(\underline{q}) \rangle = (n_j(\underline{q}) + 1)^{1/2} \,|\, n_j(\underline{q}) + 1 \rangle \quad ,$$

$$a^+_{\underline{q}j}\, a_{\underline{q}j} \,|\, n_j(\underline{q}) \rangle = n_j(\underline{q}) \,|\, n_j(\underline{q}) \rangle \quad ,$$

$$\left[a_{\underline{q}j}\, ,\, a_{\underline{q}'j'}\right] = \left[a^+_{\underline{q}j}\, ,\, a^+_{\underline{q}'j'}\right] = 0 \quad ,$$

$$[a_{\underline{q}j}, a^{+}_{\underline{q}'j'}] = \delta_{jj'}\,\Delta(\underline{q}-\underline{q}'),$$

and,
$$\langle n_j(\underline{q})\rangle = \left[\exp\left(\frac{\hbar\omega_j(\underline{q})}{k_B T}\right) - 1\right]^{-1}, \tag{78}$$

we find that the absorption cross section for the difference band, for example, is

$$\propto \sum_{\underline{q}jj'} \left|\underline{M}\begin{pmatrix} -\underline{q} & \underline{q} \\ j & j' \end{pmatrix}\right|^2 \{\langle n_j(\underline{q})\rangle[\langle n_{j'}(\underline{q})\rangle + 1] -$$

$$\langle n_{j'}(\underline{q})\rangle[\langle n_j(\underline{q})\rangle + 1]\} \frac{1}{\omega_j(\underline{q})\,\omega_{j'}(\underline{q})}$$

$$(\times)\,\delta[\omega_j(\underline{q}) - \omega_{j'}(\underline{q}) - \omega]$$

$$\propto \sum_{jj'} \int_{S(\omega)} ds \left|\underline{M}\begin{pmatrix} -\underline{q} & \underline{q} \\ j & j' \end{pmatrix}\right|^2 \{\langle n_{j'}(\underline{q})\rangle - \langle n_j(\underline{q})\rangle\}$$

$$(\times)\,\frac{1}{\omega_j(\underline{q})\,\omega_{j'}(\underline{q})}\,\frac{1}{|\nabla\omega|_{\omega=\omega_j(\underline{q})-\omega_{j'}(\underline{q})}} \tag{79}$$

The integration above is over a constant frequency surface. A similar expression may be written down for the summation band.[15]

From Eq. (79) we see the following:

(i) A given pair of phonons $(-\underset{\sim}{q}, j)$ and $(\underset{\sim}{q}, j')$ can combine and contribute to a difference band only if there is at least one nonvanishing element of $M(\begin{smallmatrix} -\underset{\sim}{q} & \underset{\sim}{q} \\ j & j' \end{smallmatrix})$. This is the statement of the selection rule.

(ii) If there is a nonvanishing element in $M(\begin{smallmatrix} -\underset{\sim}{q} & \underset{\sim}{q} \\ j & j' \end{smallmatrix})$, then the two branches j and j' can combine for all values of $\underset{\sim}{q}$ from the zone center to the zone boundary resulting in a continuum in the absorption spectrum.

(iii) The continuous spectrum will have singularities whenever $|\nabla\omega|_{\omega=\omega_j(\underset{\sim}{q})-\omega_{j'}(\underset{\sim}{q})}$.

In ZnS type crystals $|\nabla\omega_j(\underset{\sim}{q})|$ vanishes at Γ, L. X, and W[2] (see also Figure 6). Hence singularities in two phonon absorption spectra may be expected due to combination of the "critical" point phonons, i.e., those at Γ, L, X, and W. We shall now employ group theoretical considerations to determine the structure of M at these points.

We note first that

$$M_\alpha^*\left(\begin{smallmatrix} -\underset{\sim}{q} & \underset{\sim}{q} \\ j & j' \end{smallmatrix}\right) = M_\alpha\left(\begin{smallmatrix} \underset{\sim}{q} & -\underset{\sim}{q} \\ j & j' \end{smallmatrix}\right) = M_\alpha\left(\begin{smallmatrix} -\underset{\sim}{q} & \underset{\sim}{q} \\ j' & j \end{smallmatrix}\right) \tag{80}$$

s result is easily obtained from the definition of $M_\alpha(\begin{smallmatrix} -\underset{\sim}{q} & \underset{\sim}{q} \\ j & j' \end{smallmatrix})$ as given in (75) and the properties quoted in (76). Next we observe that under a space up operation S_m, the triad $M_{\mu,\nu\rho}(\begin{smallmatrix} \ell & \ell' \\ \kappa & \kappa' \end{smallmatrix})$ transforms as

$$M_{\alpha,\beta\gamma}\left(\begin{smallmatrix} \ell_1 & \ell_2 \\ \varkappa_1 & \varkappa_2 \end{smallmatrix}\right) = \sum_{\varkappa\varkappa'\mu\nu\rho} S_{\mu\alpha} S_{\nu\beta} S_{\rho\gamma} M_{\mu\nu\rho}\left(\begin{smallmatrix} \ell & \ell' \\ \varkappa & \varkappa' \end{smallmatrix}\right)$$
$$(\times)\ \delta\left(\varkappa, S_m[\varkappa_1]\right)\delta\left(\varkappa', S_m[\varkappa_2]\right), \tag{81}$$

where

$$S_m \underline{\chi}\left(\begin{smallmatrix} \ell_1 \\ \varkappa_1 \end{smallmatrix}\right) = \underline{\chi}\left(\begin{smallmatrix} \ell \\ \varkappa \end{smallmatrix}\right)$$

and

$$S_m \underline{\chi}\left(\begin{smallmatrix} \ell_2 \\ \varkappa_2 \end{smallmatrix}\right) = \underline{\chi}\left(\begin{smallmatrix} \ell' \\ \varkappa' \end{smallmatrix}\right), \tag{82}$$

and the δ's merely reinforce the fact that the sublattices κ_1 and κ_2 go to κ and κ', respectively. Also from (82) above we have

$$\underline{X}(\ell_1) = S_m^{-1}\,\underline{X}\begin{pmatrix}\ell\\ \kappa\end{pmatrix} - \underline{X}(\kappa_1)$$

$$= \underline{\underline{S}}^{-1}\underline{X}(\ell) + S_m^{-1}\underline{X}(\kappa) - \underline{X}(\kappa_1) \qquad (83)$$

and a similar expression for $\underline{X}(\ell_2)$. Therefore using (81) and (83), we can readily establish that

$$M_\alpha\begin{pmatrix}-\underline{q} & \underline{q}\\ j & j'\end{pmatrix} = \sum_{\substack{\ell_2\kappa_1\beta\\ \kappa_2\gamma}} M_{\alpha,\beta\gamma}\begin{pmatrix}\ell_1\ell_2\\ \kappa_1\kappa_2\end{pmatrix}\left(m_{\kappa_1}m_{\kappa_2}\right)^{-\frac{1}{2}}$$

$$\times\; e^*_\beta(\kappa_1\,\underline{q}\,j)\,e_\gamma(\kappa_2\,\underline{q}\,j')\exp -i\,\underline{q}\cdot[\underline{X}(\ell') - \underline{X}(\ell)] \qquad (84a)$$

$$= \sum_\mu S_{\mu\alpha}\left\{\sum_{\substack{\ell'\kappa\nu\\ \kappa'\rho}} \frac{M_{\mu,\nu\rho}\begin{pmatrix}\ell\,\ell'\\ \kappa\,\kappa'\end{pmatrix}}{(m_\kappa m_{\kappa'})^{1/2}}\exp -i\,\underline{\underline{S}}\,\underline{q}\cdot[\underline{X}(\ell) - \underline{X}(\ell')]\right\}$$

$$\times\left\{\sum_{\kappa_1\beta}\Gamma^*_{\nu\beta}(\kappa\kappa_1\,|\,\underline{q};S_m)\,e^*_\beta(\kappa_1\,\underline{q}\,j)\right\}$$

$$\times\left\{\sum_{\kappa_2\gamma}\Gamma_{\rho\gamma}(\kappa'\kappa_2\,|\,\underline{q};S_m)\,e_\gamma(\kappa_2\,\underline{q}\,j')\right\}. \qquad (84b)$$

If S_m is not a member of the group of the wave vector, then from Eq. (4) we have

$$\sum_{\kappa_2 \gamma} \Gamma_{\rho\gamma}(\kappa'\kappa_2 | \underline{q}; S_m) e_\gamma(\kappa_2, \underline{q} j') = e_\rho(\kappa', \underline{\underline{S}}\, \underline{q}\, j'), \quad (85)$$

which helps us to recast (84b) above in the form

$$M_\alpha \begin{pmatrix} -\underline{q} & \underline{q} \\ j & j' \end{pmatrix} = \sum_\mu S_{\mu\alpha} M_\mu \begin{pmatrix} -\underline{\underline{S}}\,\underline{q} & \underline{\underline{S}}\,\underline{q} \\ j & j' \end{pmatrix}$$

$$S_m \notin G_o(\underline{q}) \quad (86a)$$

or more compactly as

$$\underline{\underline{M}}(-\underline{q}, \underline{q}) = \underline{\underline{S}}\, \underline{\underline{M}}(-\underline{\underline{S}}\,\underline{q}, \underline{\underline{S}}\,\underline{q}) . \quad (86b)$$

Compare this with (7) which is a similar relationship for the dynamical matrix.

If S_m is a member of $G_o(\underline{q})$ (in which we shall, as in Chapter I, denote it by R_m), then (84b) leads to an expression somewhat different from (86). We recall from Chapter I that

$$\underline{\underline{\Gamma}}(\underline{q}; R_m)\, \underline{\underline{e}}(\underline{q} j)$$

$$= \exp -i\underline{q}\cdot[\underline{v}(R) + \underline{\chi}(m)]\, \underline{\underline{T}}(\underline{q}, \underline{\underline{R}})\, \underline{\underline{e}}(\underline{q}, sa\lambda)$$

$$= \exp -i\underline{q}\cdot[\underline{v}(R) + \underline{\chi}(m)] \sum_{\lambda_1=1}^{f_s} \tau^{(s)}_{\lambda_1\lambda}\, \underline{\underline{e}}(\underline{q}, sa\lambda_1) . \quad (87)$$

This helps us to write (84b) in the form

$$M_\alpha\begin{pmatrix} -\underline{q} & \underline{q} \\ j & j' \end{pmatrix} = M_\alpha\begin{pmatrix} -\underline{q} & \underline{q} \\ sa\lambda & s'a'\lambda' \end{pmatrix}$$

$$= \sum_\mu R_{\mu\alpha} \sum_{\lambda_1\lambda_2} \left[\tau^{(s)}_{\lambda,\lambda}(R)\right]^* \left[\tau^{(s')}_{\lambda_2\lambda'}(R)\right] M_\mu\begin{pmatrix} -\underline{q} & \underline{q} \\ sa\lambda_1 & s'a'\lambda_2 \end{pmatrix}. \quad (88)$$

Results (80) and (88) are applicable to all crystals, and of these the last one determines the interrelations among the $3 \times (3n)^2$ elements of $\underset{\sim}{M}(-\underline{q},\underline{q})$ for a given q. Observe that (88) plays a role similar to Eq. (9a) which determines interrelations between the elements of $\underline{\underline{D}}$.

We will now use Eq. (88) to establish the structure of $\underset{\sim}{M}$ at point X. Let us first write

$$M_x(\underline{q}=X\,;\, sa\lambda, s'a'\lambda') \equiv M_x\begin{pmatrix} -\underline{q} & \underline{q} \\ sa\lambda & s'a'\lambda' \end{pmatrix}_{\underline{q}=X}$$

in the form of the following 6×6 ($3n \times 3n$) array, where we have made use of the Hermitian property (80).

M_x	X_1	X_3	$X_5 11$	$X_3 12$	$X_5 21$	$X_5 22$
X_1	a_1	a_{21}	a_{20}	a_{18}	a_{15}	a_{11}
X_3	a^*_{21}	a_2	a_{19}	a_{17}	a_{14}	a_{10}
$X_5 11$	a^*_{20}	a^*_{19}	a_3	a_{16}	a_{13}	a_9
$X_5 12$	a^*_{18}	a^*_{17}	a^*_{16}	a_4	a_{12}	a_8
$X_5 21$	a^*_{15}	a^*_{14}	a^*_{13}	a^*_{12}	a_5	a_7
$X_5 22$	a^*_{11}	a^*_{10}	a^*_9	a^*_8	a^*_7	a_6

Next consider one of the operations of $G_o(\underset{\sim}{q})$ say $C_2(y)$. Using the 3 x 3 matrix for $C_2(\bar{y})$ as given in Eq. (27) and the irreducible representations found in Table III in Eq. (88) we may write

$$M_x(\underline{q}=x, x_1, x_1) = a_1$$

$$- \sum_\nu \left[\underline{\underline{C}}_2(y)\right]_{\nu x} (1)(1) M_\nu(\underline{q}=x, x_1, x_1)$$

$$= -M_x(\underline{q}=x, x_1, x_1) = 0$$

In a similar fashion

$$M_x(\underline{q}=x, x_5 11, x_5 11) = a_3$$

$$= \sum_\nu \left[\underline{\underline{C}}_2(y)\right]_{\nu x} \sum_{\lambda_1\lambda_2} \left[\tau^{x_5}_{\lambda_1\lambda}(C_2(y))\right]^* \left[\tau^{x_5}_{\lambda_2\lambda'}(C_2(y))\right]$$

$$(x)\ M_\nu(\underline{q}=x, x_5 11, x_5 11)$$

$$= -M_x(\underline{q}=x, x_5 11, x_5 11) = 0$$

In this way we finally determine the matrix M_x to be

M_x	X_1	X_3	$X_5 11$	$X_5 12$	$X_5 21$	$X_5 22$
X_1	0	a_{21}	0	a_{18}	0	a_{11}
X_3	a_{21}^*	0	a_{19}	0	a_{14}	0
$X_5 11$	0	a_{19}^*	0	a_{16}	0	a_9
$X_5 12$	a_{18}^*	0	a_{16}^*	0	a_{12}	0
$X_5 21$	0	a_{14}^*	0	a_{12}^*	0	a_7
$X_5 22$	a_{11}^*	0	a_9^*	0	a_7^*	0

which we shall write as

M_x	X_1	X_3	X_{511}	X_{512}	X_{521}	X_{522}
X_1	0	a	0	b	0	c
X_3	a^*	0	d	0	e	0
X_{511}	0	d^*	0	f	0	g
X_{512}	b^*	0	f^*	0	h	0
X_{521}	0	e^*	0	h^*	0	j
X_{522}	c^*	0	g^*	0	j^*	0

there being only 9 nonvanishing elements instead of the 21 we started with. Results for M_y and M_z are presented below.

It should be noted that while the elements of M_y and M_z are related among themselves, they are not related to those of M_x. This is a reflection of the fact that in the group $G_0(X)$ there is no element which interchanges x components of $\underset{\sim}{q}$ with y and z components whereas there are elements (e.g., σ_{yz}) which mix the y and z components.

M_y	X_1	X_3	X_{511}	X_{512}	X_{521}	X_{522}
X_1	0	A	$-B$	0	$-C$	0
X_3	A^*	0	0	$-D$	0	$-E$
X_{511}	$-B$	0	0	F^*	0	H
X_{512}	0	$-D^*$	F	0	G	0
X_{521}	$-C^*$	0	0	G^*	0	J^*
X_{522}	0	$-E^*$	H^*	0	J	0

M_y	X_1	X_3	X_{511}	X_{512}	X_{521}	X_{522}
X_1	0	A	0	B	0	C
X_3	A^*	0	D	0	E	0
X_{511}	0	D^*	0	F	0	G
X_{512}	B	0	F^*	0	H	0
X_{521}	0	E^*	0	H^*	0	J
X_{522}	C^*	0	G^*	0	J^*	0

Results for the points L and W are given in Table XII. Similar but less detailed results obtained earlier by Birman[3] are summarized in Table XIII. It can be seen readily that his results are in agreement with ours if one notes that a combination is allowed (insofar as an unpolarized beam experiment is concerned) if there is at least one nonzero element corresponding to that combination in any of the three matrices M_x, M_y, M_z.

One point worthy of note here is that the structure of $\underset{\sim}{M}$ is dependent on the form of the irreducible representation. For example, the elements of M_x, M_y, and M_z involving L_3 depend upon the matrices chosen for that representation. However, the squares of the elements summed over the degenerate partners (which is what is relevant to an experiment) must be representation independent. Thus

$$\sum_{\lambda=1}^{2} |M_x(\underline{q}=L, L_1 1, L_3 \lambda)|^2$$

$$= \sum_{\lambda=1}^{2} |M_y(\underline{q}=L, L_1 1, L_3 \lambda)|^2$$

$$= \sum_{\lambda=1}^{2} |M_z(\underline{q}=L, L_1 1, L_3 \lambda)|^2$$

TABLE XII

THE FORM OF THE MATRICES $M_\alpha(qsa\lambda s'a'\lambda')$ FOR POINTS L AND W.
THE MATRICES FOR POINT Λ HAVE THE SAME FORM AS FOR POINT L

M_x	L_11	L_12	L_311	L_312	L_321	L_322
L_11	a_1	a_5	a_7	$\sqrt{3}a_7$	a_9	$\sqrt{3}a_9$
L_12	a_5^*	a_2	a_{10}	$\sqrt{3}a_{10}$	a_3	$\sqrt{3}a_8$
L_311	a_7^*	a_{10}^*	a_3	0	a_6	0
L_312	$\sqrt{3}a_7^*$	$\sqrt{3}a_{10}^*$	0	a_3	0	a_6
L_321	a_9^*	a_8^*	a_6	0	a_4	0
L_322	$\sqrt{3}a_9$	$\sqrt{3}a_8$	0	a_6^*	0	a_4

M_x	W_1	W_21	W_22	W_31	W_32	W_4
W_1				b_1	b_4	b_6
W_21		0		b_7	b_2	b_5
W_22				b_9	b_8	b_3
W_31	b_1	b_7^*	b_9^*			
W_32	b_4^*	b_2^*	b_8^*		0	
W_4	b_6^*	b_5^*	b_3^*			

M_y	L_11	L_12	L_311	L_312	L_321	L_322
L_11	a_1	a_5	a_7	$-\sqrt{3}a_7$	a_9	$-\sqrt{3}a_9$
L_12	a_5^*	a_2	a_{10}	$-\sqrt{3}a_{10}$	a_8	$-\sqrt{3}a_8$
L_311	a_7^*	a_{10}^*	a_3	0	a_6	0
L_312	$-\sqrt{3}a_7^*$	$-\sqrt{3}a_{10}^*$	0	a_3	0	a_6
L_321	a_9^*	a_8^*	a_6^*	0	a_4	0
L_322	$-\sqrt{3}a_9^*$	$-\sqrt{3}a_8^*$	0	a_6^*	0	a_4

M_y	W_1	W_21	W_22	W_31	W_32	W_4
W_1	0	C_1	C_2			
W_21	C_1^*	0	0		0	
W_22	C_2^*	0	0			
W_31				0	0	C_3
W_22		0		0	0	C_4
W_4				C_3^*	C_4^*	0

M_z	L_11	L_12	L_311	L_312	L_321	L_322
L_11	a_1	a_5	$-2a_7$	0	$-2a_9$	0
L_12	a_5^*	a_2	$-2a_{10}$	0	$-2a_8$	0
L_311	$-2a_7^*$	$-2a_{10}^*$	a_3	0	a_6	0
L_312	0	0	0	a_3	0	a_6
L_321	$-2a_9^*$	$-2a_8^*$	a_6^*	0	a_4	0
L_322	0	0	0	a_6^*	0	a_4

M_z	W_11	W_21	W_22	W_31	W_32	W_4
W_11				$-ib_1$	$-ib_4$	ib_6
W_21		0		ib_7	ib_2	$-ib_5$
W_22				ib_9	ib_8	$-ib_3$
W_31	$+ib_1^*$	$-ib_7^*$	$-ib_9^*$			
W_32	$+ib_4^*$	$-ib_2^*$	$-ib_8^*$		0	
W_4	$-ib_6^*$	ib_5^*	ib_3^*			

TABLE XIII

SUMMARY OF TWO-PHONON INFRARED ABSORPTION SELECTION RULES DEDUCED BY BIRMAN[3]

Symmetry Point	Species	Type
X	$X_1 \otimes X_5$	TO(X) + LO(X); TO(X) + LA(X)
	$X_3 \otimes X_5$	TA(X) + LO(X); TA(X) + LA(X)
	$X_5 \otimes X_5$	2TO(X); 2TA(X); TO(X) + TA(X)
W	$W_1 \otimes W_2$	
	$W_1 \otimes W_3$	
	$W_1 \otimes W_4$	
	$W_2 \otimes W_3$	
	$W_2 \otimes W_4$	
	$W_3 \otimes W_4$	
L	$L_1 \otimes L_1$	2LO(L); 2LA(L); LO(L) + LA(L)
	$L_3 \otimes L_3$	2TO(L); 2TA(L); TO(L) + TA(L)
	$L_3 \otimes L_1$	TO(L) + LO(L); TO(L) + LA(L); TA(L) + LO(L); TA(L) + LA(L)

as is to be intuitively expected for the (111) direction, and this is precisely what one finds with another form of the representation L_3 given below.

E	C_3	C_3^{-1}	σ_{xy}	σ_{yz}	σ_{xz}
$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \omega & 0 \\ 0 & \omega^2 \end{pmatrix}$	$\begin{pmatrix} \omega^2 & 0 \\ 0 & \omega \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & \omega \\ \omega^2 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & \omega^2 \\ \omega & 0 \end{pmatrix}$

$\omega = e^{-i\frac{2\pi}{3}}$

Given a knowledge of such selection rules and some idea of the phonon dispersion curves based on model calculations or experimental results for a similar material it is possible to assign features of an absorption curve (such as Figure 7) to various combination processes and thus to deduce the critical frequencies. For example, Johnson[15] deduces the following critical frequencies for ZnS based on the curve in Figure 7.

Γ	LO	366 cm^{-1}
	TO	338
L	TO	321
	LO	272
	LA	227
X	TO	305
	LO	275
	LA	221

(89)

B. RAMAN SCATTERING

We consider now briefly two phonon processes in Raman scattering. We recall that in a Raman scattering experiment monochromatic light of frequency ω and wave vector $\underset{\sim}{Q}(\approx 0)$ is allowed to be scattered by the crystal and the scattered beam frequency analyzed. The scattered spectrum shows both lines of higher (anti-Stokes) and lower (Stokes) frequency due to interaction with phonons, and as in the case of infrared absorption, the conservation rules are

Change in energy of photon = $\hbar\Omega$

$= \hbar\Omega' - \hbar\omega = \pm$ (algebraic sum of phonon energies)
(+ anti-Stokes process)
(- Stokes process)

Change in momentum of photon ≈ 0

$= \hbar$ (vector sum of wave vectors of participating phonons).

For two phonon processes this becomes

$$\hbar(\omega' - \omega) = \pm \hbar[\omega_j(\underline{q}) + \omega_{j'}(\underline{q})] \quad \begin{cases} \text{SUM MODE} \\ +\text{Anti-stokes}, -\text{Stokes} \end{cases}$$

$$= \pm \hbar[\omega_j(\underline{q}) - \omega_{j'}(\underline{q})] \quad \begin{cases} \text{DIFFERENCE MODE} \\ +\text{Anti-Stokes}, -\text{Stokes} \end{cases}$$

$$\underline{q} + \underline{q}' \approx 0$$

As in the case of infrared absorption, two phonon processes lead to a continuum with singularities due to combination of critical phonons.

If radiation with an electric vector $\underset{\sim}{E}$ is Raman scattered, and if κ denotes the polarization of the scattered radiation, then the cross section for scattering

$$I(\omega') \propto \sum_{\alpha,\beta,\gamma,\delta} n_\alpha n_\gamma I_{\alpha\beta,\gamma\delta} E_\beta E_\delta \qquad (90)$$

where

$$I_{\alpha\beta,\gamma\delta} = \left\langle \sum_n \langle m | P^*_{\alpha\beta} | n \rangle \langle n | P_{\gamma\delta} | m \rangle \delta(E_n - E_m + \hbar\Omega) \right\rangle_{\text{Ave. over initial states } m} \qquad (91)$$

The tensor $\underline{P}$ above is the polarizability tensor and as with $\underset{\sim}{M}$ earlier, may be expanded in powers of nuclear displacements as follows:

$$P_{\alpha\beta}(\underline{X}) = P^{(0)}_{\alpha\beta}(\underline{X}) + P^{(1)}_{\alpha\beta}(\underline{X}) + P^{(2)}_{\alpha\beta}(\underline{X}) + \ldots \qquad (92)$$

The term of interest to us is the second order term given by

$$P^{(2)}_{\alpha\beta}(\underline{X}) = \frac{1}{2} \sum_{\substack{\gamma\delta \\ \ell\ell'\kappa\kappa'}} P_{\alpha\beta,\gamma\delta} \begin{pmatrix} \ell & \ell' \\ \kappa & \kappa' \end{pmatrix} u_\gamma \begin{pmatrix} \ell \\ \kappa \end{pmatrix} u_\delta \begin{pmatrix} \ell' \\ \kappa' \end{pmatrix} \tag{93}$$

Expressed in terms of normal coordinates, this becomes

$$P^{(2)}_{\alpha\beta}(\underline{X}) = \frac{1}{2} \sum_{\underline{q}jj'} P_{\alpha\beta} \begin{pmatrix} -\underline{q} & \underline{q} \\ j & j' \end{pmatrix} Q^\dagger \begin{pmatrix} \underline{q} \\ j \end{pmatrix} Q \begin{pmatrix} \underline{q} \\ j \end{pmatrix} \tag{94}$$

where

$$P_{\alpha\beta} \begin{pmatrix} -\underline{q} & \underline{q} \\ j & j' \end{pmatrix} = \sum_{\substack{\ell'\kappa\gamma \\ \kappa'\delta}} P_{\alpha\beta,\gamma\delta} \begin{pmatrix} \ell & \ell' \\ \kappa & \kappa' \end{pmatrix} \frac{e^*_\gamma(\kappa\, \underline{q}\, j)\, e_\delta(\kappa'\, \underline{q}\, j')}{(m_\kappa\, m_{\kappa'})^{1/2}}$$

$$(\times) \exp - i\, \underline{q} \left[\underline{X}(\ell) - \underline{X}(\ell')\right] \tag{95}$$

Compare with Eq. (75). In arriving at (94), use has been made of translational invariance analogous to (73).

$$P_{\alpha\beta,\gamma\delta} \begin{pmatrix} \ell & \ell' \\ \kappa & \kappa' \end{pmatrix} = P_{\alpha\beta,\gamma\delta} \begin{pmatrix} 0 & \ell' - \ell = \bar{\ell} \\ \kappa & \kappa' \end{pmatrix}$$

$$= P_{\beta,\gamma\delta} \begin{pmatrix} -\bar{\ell} & 0 \\ \kappa & \kappa' \end{pmatrix} \tag{96}$$

The cross section may now be evaluated in a straight-forward manner by substituting for the normal coordinates in terms of annihilation and creation operators and evaluating the thermal average as before. As in the case of infrared absorption, we have summation and difference bands both in Stokes and anti-Stokes processes. For example, the cross section for difference band in anti-Stokes process is proportional to

$$\sum_{\alpha\beta\gamma\delta} n_\alpha n_\gamma E_\beta E_\delta \sum_{jj'} \int_{S(\Omega)} P^*_{\alpha\beta}\begin{pmatrix} -\underline{q} & \underline{q} \\ j & j' \end{pmatrix} P_{\gamma\delta}\begin{pmatrix} -\underline{q} & \underline{q} \\ j & j' \end{pmatrix}$$

$$(\times)\ \frac{1}{\omega_j(\underline{q})\,\omega_{j'}(\underline{q})}\ \frac{\{\langle n_j(\underline{q})\rangle\langle n_{j'}(\underline{q})\rangle + \langle n_j(\underline{q})\rangle\}}{|\nabla\Omega|_{\Omega=\omega_j(\underline{q})-\omega_{j'}(\underline{q})}}\, dS \qquad (97)$$

The selection rules are thus determined by the structure of $P_{\alpha\beta}\begin{pmatrix} -\underline{q} & \underline{q} \\ j & j' \end{pmatrix}$.

A relation connecting the different elements of $P_{\alpha\beta}$ may now be obtained as we did earlier for M_α. We observe that $P_{\alpha\beta,\gamma\delta}\begin{pmatrix} l_1 & l_2 \\ \kappa_1 & \kappa_2 \end{pmatrix}$ transforms under S_m as

$$P_{\alpha\beta,\gamma\delta}\begin{pmatrix} l_1 l_2 \\ \kappa_1 \kappa_2 \end{pmatrix} = \sum_{\mu\nu\rho\sigma\kappa\kappa'} S_{\mu\alpha} S_{\nu\beta} S_{\rho\gamma} S_{\sigma\delta}\, P_{\mu\nu,\rho\sigma}\begin{pmatrix} l\, l' \\ \kappa\, \kappa' \end{pmatrix}$$

$$(\times)\ \delta(\kappa, S_m[\kappa_1])\ \delta(\kappa', S_m[\kappa_2])\ . \qquad (98)$$

With the help of (98), we may write down the analogue of (84), i.e.,

$$P_{\alpha\beta}\begin{pmatrix} -\underline{q} & \underline{q} \\ j & j' \end{pmatrix} = \sum_{\mu\nu} S_{\mu\alpha} S_{\nu\beta} \sum_{\substack{l' \\ \kappa\kappa' \\ \rho\sigma}} \frac{P_{\mu\nu,\rho\sigma}\begin{pmatrix} l\, l' \\ \kappa\, \kappa' \end{pmatrix}}{(m_\kappa m_{\kappa'})^{1/2}}$$

$$(\times)\ \exp -i \sum \underline{q} \cdot [\underline{X}(l) - \underline{X}(l')]\ (\times)$$

$$(x)\left\{\sum_{x_1\gamma}\Gamma^{*}_{\rho\gamma}(x x_1|\underline{q};S_m)\,e^{*}_{\gamma}(x_1\,\underline{q}\,j)\right\}$$

$$(x)\left\{\sum_{x_2\delta}\Gamma_{\gamma\delta}(x' x_2|\underline{q};S_m)\,e_{\delta}(x_2\,\underline{q}\,j')\right\} \qquad (99)$$

or

$$P_{\alpha\beta}\begin{pmatrix}-\underline{q} & \underline{q}\\ j & j'\end{pmatrix}=\sum_{\mu\nu}{}' S_{\mu\alpha}\,S_{\nu\beta}\,P_{\mu\nu}\begin{pmatrix}-\underline{S}\,\underline{q} & \underline{S}\,\underline{q}\\ j & j'\end{pmatrix} \qquad (100)$$

if $S_m \notin G(\underline{q})$.

For $S_m \in G_o(\underline{q})$, we obtain

$$P_{\alpha\beta}\begin{pmatrix}-\underline{q} & \underline{q}\\ s a\lambda & s' a'\lambda'\end{pmatrix}=\sum_{\mu\nu}{}' R_{\mu\alpha}\,R_{\nu\beta}$$

$$(x)\sum_{\lambda_1,\lambda_2}\left[\tau^{(s)}_{\lambda,\lambda_1}(\underline{q};\underline{\underline{R}})\right]^{*}\left[\tau^{(s')}_{\lambda_2\lambda}(\underline{q};\underline{\underline{R}})\right]P_{\mu\nu}\begin{pmatrix}-\underline{q} & \underline{q}\\ s a\lambda_1 & s' a'\lambda_2\end{pmatrix} \qquad (101)$$

which is similar in content to Eq. (88) and may be employed to determine the structure of $P_{\alpha\beta}$.

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