Theory of Infrared and Raman Processes in Crystals: Selection Rules in Diamond and Zincblende*

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To analyze infrared and Raman processes in crystals, the normal-mode spectrum of the crystal can be idealized by a discrete set of oscillators. These belong to the critical points in the lattice vibration spectrum; such points can be determined group theoretically. This approach, plus the relevant space-group selection rules, is used to determine the active one-, two-, three-, and (some) four-phonon combination and overtone processes in diamond and zincblende structures. All two-phonon overtones are infrared dipole forbidden in the diamond structure, verifying a conjecture of Lax and Burstein. Two-phonon overtones of LO and LA modes at X are infrared dipole forbidden in zincblende. Analysis of three-phonon processes will enable unambiguous optical assignments of symmetry species to branches to be made in diamond and zincblende, thus resolving uncertainties at the critical points. Some selection rules for electric quadrupole and magnetic dipole processes are indicated: These may give rise to anisotropic optical absorption in cubic crystals.

INTRODUCTION

AN ideal crystal composed of N primitive cells with r distinct atoms per cell has $3Nr$ normal modes of vibration. These $3Nr$ modes are distributed in the relevant Brillouin zone, on $3r-3$ optic and 3 acoustic branches; in each branch the mode, or phonon, frequency depends parametrically upon the wave vector which can assume all values in, and on, the Brillouin zone. In order to carry out an analysis of optically active lattice vibration processes, we shall idealize the phonon spectrum, representing the $3Nr$ phonons by a much smaller number.

Following Born, we assume that only those phonons in each branch participate in optical processes which arise from regions where there is a high density of phonon states per unit wave vector interval. These regions, or points, are known as critical points in the phonon dispersion. At a critical point on a branch the phonon frequency as a function of wave vector has vanishing slope in one or more directions. Thus, the number of phonons in the crystal which can participate in optical processes is the sum of products of the numbers of critical points for that space group times the number of distinct branches at each critical point. Each of these phonons must be assigned to one of the irreducible representations of the crystal space group; i.e., it must belong to a crystal species (using molecular terminology). Using the relevant space-group theory, it is then possible to determine the optical activity permissible for such a system of crystal modes, allowing for the possibility of exciting one or more of these phonons.

Here we shall enumerate the space-group selection rules in the diamond and zincblende structures which are relevant to the analysis of infrared absorption and Raman scattering processes in those structures. The

specific application of these rules to the problem of unambiguously assigning symmetry species to the branches of the phonon spectrum will be discussed. Ambiguities arise, in both structures, in the *a priori* assignment of species to branch at zone points of high symmetry. These ambiguities can be resolved when appropriate experimental results are obtained, and interpreted, using the selection rules. The method of obtaining space-group selection rules, and the rules themselves were given without applications in a previous paper[1] to which reference should be made for details.

Previously, work on this problem has been reported by Winston and Halford.[2] These authors discussed underlying space-group theory in some detail, but did not obtain selection rules for multiphonon processes involving the crystal as a whole. Their interests were in the direction of applications to molecular-type crystals, and in effect they restricted attention to modes of infinite wavelength ($k=0$). More recently, Pollack and Satten[3] discussed the use of space-group theory in interpreting electron-phonon interaction effects in the optical spectra of paramagnetic ions in crystals. The approach these authors used has some similarity to ours, although their interests were in local effects.

While we shall enumerate and discuss the selection rules relevant to the detailed interpretation of lattice vibration spectra for these two space groups, we do not report here on numerical calculations of the phonon energies in particular materials. Such calculations require least-squares-type fitting of the observed features in the spectrum to the selection rules. A complete determination of the phonon spectrum at the critical points, using optical data requires *inter alia* (a) selection rules, (b) infrared absorption spectra, (c) Raman scattering spectra, (d) a theoretical estimate of the relative intensities of allowed processes of the same order (e.g., relative intensities of various allowed two-phonon proc-

[1] J. L. Birman, Phys. Rev. 127, 1093 (1962).
[2] H. Winston and R. Halford, J. Chem. Phys. 17, 607 (1949).
[3] S. A. Pollack and R. Satten, J. Chem. Phys. 36, 804 (1962); S. A. Pollack, Tech. Report No. 2 UCLA, 1960 (unpublished).

esses), and (e) a theoretical estimate of intensities of electric quadrupole and magnetic dipole transitions compared to electric dipole. The situation in these respects is analogous to the molecular case. Much work remains to be done before results of similar accuracy can be obtained for crystals, as for molecules. Some of these problems will be discussed below.

2. ACTIVE CRYSTAL VIBRATIONS

If we consider the crystal as a gigantic molecule, and assume the Born-Kármán cyclic boundary conditions, the symmetry group of a crystal is a finite space group. An active vibrational state of the crystal can then be excited, from the ground-vibrational state, by absorption of a single infrared quantum from the radiation field, or by the analogous one-quantum Raman scattering. We take the initial crystal vibrational state as the ground state: All vibrational quantum numbers are zero. For a different initial state the analysis can be modified, but the procedure is identical. In a multiphonon process, one electromagnetic quantum excites several crystal modes. In a two-phonon process if the two modes belong to different irreducible representations, one has a combination state[4]; if they are degenerate partners of the same space group irreducible representation, one has a first overtone state.[5] Higher order multiphonon processes may be pure combination states, pure overtone states, or some mixture, which is called a general combination.[6] We shall here take the phonon wave vector (in infrared and Raman processes) as zero. These conventions agree with the procedure used in the molecular (point group) case.[7]

A normal mode of vibration of a crystal $Q_{j,\kappa}{}^{(m)}$ is one of $(s \cdot l_m)$ degenerate partners,[1,8] transforming according to space group irreducible representation $\star k_j{}^{(m)}$. Here s is the number of arms in $\star k_j$, and l_m is the dimension of the allowable irreducible representation of $\mathcal{G}(k_j)/\mathcal{T}(k_j)$, and $\kappa = 1 \cdots (s l_m)$. If the occupation number of the mode $Q_{j,\kappa}{}^{(m)}$ is $n_j{}^{(m)}$, an integer, then a vibrational state of the crystal is completely specified in the harmonic approximation by giving the set $\{n_j{}^{(m)}\}$. The corresponding eigenfunction can be denoted

$$|n_j{}^{(m)}, n_{j'}{}^{(m')}, \cdots \rangle. \tag{2.1}$$

This eigenfunction transforms according to the reducible direct product representation

$$[\star k_j{}^{(m)}]_{(n_j{}^{(m)})} \otimes [\star k_{j'}{}^{(m')}]_{(n_{j'}{}^{(m')})} \otimes \cdots . \tag{2.2}$$

In (2.2),

$$[\star k_j{}^{(m)}]_{(n_j{}^{(m)})} \tag{2.3}$$

is the symmetrized $n_j{}^{(m)}$th Kronecker power of $\star k_j{}^{(m)}$. The representation (2.2) can be reduced to determine reduction coefficients

$$([k_j{}^{(m)}]_{(n_j{}^{(m)})}[k_{j'}{}^{(m')}]_{(n_{j'}{}^{(m')})} \cdots | k_{j''}{}^{(m'')}) . \tag{2.4}$$

Our published results include $n_j{}^{(m)} \leqslant 3$. As previously indicated, we choose the initial crystal vibrational state as the ground state

$$|0, 0, \cdots \rangle. \tag{2.5}$$

This function transforms as $\Gamma^{(1)}$ for each space group. We choose all representations as real.

The matrix element involved in an optical process is then of the form

$$\langle n_j{}^{(m)}, n_{j'}{}^{(m')}, \cdots | \mathfrak{O} | 0, 0, \cdots \rangle. \tag{2.6}$$

For infrared dipole absorption, the operator[9]

$$\mathfrak{O} \text{ is } \nabla ; \tag{2.7}$$

for Raman scattering,[10,11]

$$\mathfrak{O} \text{ is } \alpha , \tag{2.8}$$

where α is the polarizability tensor; for electric quadrupole absorption,

$$\mathfrak{O} \text{ is } \mathbf{Q} , \tag{2.9}$$

where $\mathbf{Q}$ is the quadrupole tensor; for magnetic dipole absorption

$$\mathfrak{O} \text{ is } \mathbf{M} , \tag{2.10}$$

where $\mathbf{M}$ is the magnetic dipole operator. The assumption of infinite-wavelength light means that the tensor operators (2.7)–(2.10) transform for each space group as $\Gamma^{(O)}$. This will be a reducible space-group representation, reducible into irreducible components each of which has wave vector (star) Γ.

3. ACTIVE VIBRATIONS IN DIAMOND

The necessary critical points[12] in the diamond structure phonon spectrum are for wave vectors Γ, X, L, W. In diamond itself (carbon with diamond structure), Phillips[13] has suggested an "accidental" critical point at Σ. In Table I we list: the wave vectors for the necessary critical points, the phonon branches, the irreducible representations (species) to which each branch may belong, and give the assignments preferred by Lax-Hopfield,[14] on the basis of central-force-type calculations of a type previously discussed by Herman.[15] While these

[4] E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill Book Company, Inc., New York, 1955), pp. 148–151, discuss the analogous molecular case.

[5] See Ref. 4, pp. 151–155 for discussion of the analogous molecular case.

[6] See Ref. 4 pp. 155–156 for discussion of the molecular case.

[7] Refs. 4, 5, and 6. Also, G. Herzberg, *Infrared and Raman Spectra of Polyatonic Molecules* (D. Van Nostrand Company Inc., New York, 1945), Chap. 3.

[8] E. P. Wigner, Nachr. Akad. Wiss. Göttingen, Math. Physik Kl. 2, 133 (1930).

[9] Ref. 4, pp. 159–161 discuss the molecular case.

[10] Ref. 4, pp. 161–162 discuss the molecular case.

[11] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, 1954), Secs. 48 and 49.

[12] L. Van Hove, Phys. Rev. **89**, 1189 (1953); and J. C. Phillips, *ibid*. **104**, 1263 (1956).

[13] J. C. Phillips, Phys. Rev. **111**, 147 (1959).

[14] M. Lax and J. J. Hopfield, Phys. Rev. **124**, 115 (1961). In Table I this is called L-H assignment.

[15] F. Herman, J. Phys. Chem. Solids **8**, 405 (1959).

assignments seem reasonable, they have not been checked by other force-field-type calculations[16] and, hence, must be considered tentative. We recall that inelastic neutron scattering can give the phonon-dispersion curves (phonon energy versus wave vector) but not the species to be assigned to each branch of the curve. As we shall point out below, study of the three-phonon region of active vibrations should enable assignments to be made. The Table emphasizes both the ambiguity in species assignment as well as (see footnote b to Table I) the lack of clear separation at $^\star W$ of branches into transverse and longitudinal. There are then a total of 11 different phonon frequencies to be assigned in a diamond structure material, assuming only the necessary critical points. (Note added in proof. This number will be increased if oscillators at "accidental" critical points are included. H. Bilz in private communication has indicated that Σ points need to be included for analysis of infrared and Raman processes in Si as well as C, thus increasing the number of phonons to 17.

TABLE I. Critical points and phonon species in O_h^7 and T_d^2.

Critical points	Diamond Phonon	Species	L-H[a] assignment
Γ	$O(\Gamma)$	$\Gamma^{(25+)}$	
$^\star X$	$TO(X)$	$^\star X^{(4)}$ or $^\star X^{(3)}$	$^\star X^{(4)}$
	$L(X)=LO(X)=LA(X)$	$^\star X^{(1)}$	
	$TA(X)$	$^\star X^{(3)}$ or $^\star X^{(4)}$	$^\star X^{(3)}$
$^\star L$	$TO(L)$	$^\star L^{(3-)}$ or $^\star L^{(3+)}$	$^\star L^{(3-)}$
	$LO(L)$	$^\star L^{(1+)}$ or $^\star L^{(2-)}$	$^\star L^{(1+)}$
	$LA(L)$	$^\star L^{(2-)}$ or $^\star L^{(1+)}$	$^\star L^{(2-)}$
	$TA(L)$	$^\star L^{(3+)}$ or $^\star L^{(3-)}$	$^\star L^{(3+)}$
$^\star W$	$O_1(W), A_1(W)$ $O_2(W)=A_2(W)^b$	$^\star W^{(m)}$, $m=1, 2$	

Critical points	Zincblende Phonon	Species
Γ	$O(\Gamma)$	$\Gamma^{(15)}$
$^\star X$	$TO(X)$	$^\star X^{(5)}$
	$LO(X)$	$^\star X^{(1)}$ or $^\star X^{(3)}$
	$LA(X)$	$^\star X^{(1)}$ or $^\star X^{(3)}$
	$TA(X)$	$^\star X^{(5)}$
$^\star L$	$TO(L)$	$^\star L^{(3)}$
	$LO(L)$	$^\star L^{(1)}$
	$LA(L)$	$^\star L^{(1)}$
	$TA(L)$	$^\star L^{(3)}$
$^\star W$	$O_1(W), O_2(W), O_3(W)$ $A_1(W), A_2(W), A_3(W)^b$	$^\star W^{(m)}$, $m=1, 2, 3, 4$

a See Ref. 14.
b Contrary to some implications in the literature (especially Ref. 13) there is no division of the modes at $^\star W$ into transverse and longitudinal, either in zincblende or diamond. The only justification for this usage, in the case of diamond, resides in the fact that in the two parameter approximation (in which α and $\beta \neq 0$ in Ref. 15), the three branches at $^\star W$ (each is 12-fold degenerate with $s = 6$, $l_m = 2$) are degenerate with the branches at X. Thus, we prefer the usage here $O_j(W)$ or $A_j(W)$ for optic or acoustic branches, respectively.

16 M. Musgrave and J. Pople, Proc. Roy. Soc. (London) A268, 474 (1962) have proposed a valence force field for diamond; T. Shimanouchi, M. Tsuboi, and T. Miyazawa, J. Chem. Phys. 35, 1957 (1961) have also discussed methods which could be used to calculate the phonon spectrum in diamond structure.

TABLE II. Two-phonon processes in diamond structure.

Species	Activity	Type
	Overtones	
$[\Gamma^{(25+)}]_{(2)}$	R	$2O(\Gamma)$
$[^\star X^{(4)}]_{(2)}$	R	$2TO(X)$
$[^\star X^{(1)}]_{(2)}$	R	$2L(X)$
$[^\star X^{(3)}]_{(2)}$	R	$2TA(X)$
$[^\star L^{(3-)}]_{(2)}$	R	$2TO(L)$
$[^\star L^{(1+)}]_{(2)}$	R	$2LO(L)$
$[^\star L^{(2-)}]_{(2)}$	R	$2LA(L)$
$[^\star L^{(3+)}]_{(2)}$	R	$2TA(L)$
$[^\star W^{(1)}]_{(2)}$	R	$2O_1(W); 2A_1(W)$
$[^\star W^{(2)}]_{(2)}$	R	$2O_2(W)=2A_2(W)$
	Combinations	
$^\star X^{(4)} \otimes ^\star X^{(1)}$	$D; R(dp)$	$TO(X)+L(X)$
$^\star X^{(4)} \otimes ^\star X^{(3)}$	$D; R(dp)$	$TO(X)+TA(X)$
$^\star X^{(1)} \otimes ^\star X^{(3)}$	$D; R(dp)$	$L(X)+TA(X)$
$^\star L^{(3-)} \otimes ^\star L^{(1+)}$	D	$TO(L)+LO(L)$
$^\star L^{(3-)} \otimes ^\star L^{(2-)}$	$R(dp)$	$TO(L)+LA(L)$
$^\star L^{(3-)} \otimes ^\star L^{(3+)}$	$D(2)$	$TO(L)+TA(L)$
$^\star L^{(1+)} \otimes ^\star L^{(2-)}$	D	$LO(L)+LA(L)$
$^\star L^{(1+)} \otimes ^\star L^{(3+)}$	$R(dp)$	$LO(L)+TA(L)$
$^\star L^{(2-)} \otimes ^\star L^{(3+)}$	D	$LA(L)+TA(L)$
$^\star W^{(1)} \otimes ^\star W^{(1)}$	$D; R$	a
$^\star W^{(1)} \otimes ^\star W^{(2)}$	$D(2); R(dp)$	
$^\star W^{(2)} \otimes ^\star W^{(2)}$	$D; R$	a

a In these lines the two branches, which have the same symmetry, are assumed distinct. Since there are three branches at this point in the zone, but only two distinct species, two of the branches must belong to the same species. The combinations which will occur are then $O_1(W)+A_1(W)$; $O_1(W)+O_2(W)$; and $A_1(W)+A_2(W)$. See footnote a to Table I.

I thank Professor Bilz for sending his results prior to publication.)

In the diamond structure O_h^7 the operator

$$\nabla \text{ transforms as } \Gamma^{(15-)}, \qquad (3.1)$$

the tensor

$$\alpha \text{ transforms as } \Gamma^{(1+)} \oplus \Gamma^{(12+)} \oplus \Gamma^{(25+)}. \qquad (3.2)$$

Thus, an infrared absorption process is dipole allowed from the ground vibrational state (2.5) to the final vibrational state (2.1), if among the reduction coefficients (2.4), the term $(|\Gamma^{(15-)}) \neq 0$. If, in the reduction of (2.5), the coefficient $(|\Gamma^{(15-)})$ equals m, we shall indicate this in our Tables as $D(m)$, thus conveying dipole allowed and multiplicity, m. If, in carrying out a reduction of (2.2), any of the coefficients $(|\Gamma^{(1+)})$ or $(|\Gamma^{(12+)})$, or $(|\Gamma^{(25+)})$ are nonzero the process is Raman allowed. In the Tables this will be indicated as R. As in the molecular case,[4,7] if in the direct product (2.2) $(|\Gamma^{(1+)})=0$, but either $(|\Gamma^{(12+)})$ or $(|\Gamma^{(25+)}) \neq 0$ the process is active in Raman scattering but gives rise to depolarized scattered radiation; such a case will be indicated as $R(dp)$.

3.1. One-Phonon Processes

As is well known the optic branch phonon at Γ is Raman active in diamond. This is the only one-phonon activity permitted.

TABLE III. Three-phonon processes in diamond structure.

Species	Activity	Type[a]	Species	Activity	Type[a]
Overtones			**Simple combinations**		
$[\Gamma^{(25+)}]_{(3)}$	R	$3O(\Gamma)$	$\star W^{(1)} \otimes \star W^{(1)} \otimes \star X^{(4)}$	$D(3); R$	$TO(X)+$
$[\star X^{(4)}]_{(3)}$	R	$3TO(X)$	$\otimes \star X^{(1)}$	$D(3); R$	$L(X)+$ } c
$[\star X^{(1)}]_{(3)}$	$D; R$	$3L(X)$	$\otimes \star X^{(3)}$	$D(3); R$	$TA(X)+$
$[\star X^{(3)}]_{(3)}$	D	$3TA(X)$	$\star W^{(1)} \otimes \star W^{(2)} \otimes \star X^{(4)}$	$D(3); R$	$TO(X)+$
$[\star L^{(m)}]_{(3)}$	No activity		$\otimes \star X^{(1)}$	$D(3); R$	$L(X)+$ } b
$[\star W^{(m)}]_{(3)}$	No activity		$\otimes \star X^{(3)}$	$D(3); R$	$TA(X)+$
Simple combinations			**General combinations**		
$\star X^{(4)} \otimes \star X^{(1)} \otimes \Gamma^{(25+)}$	$D(2); R$	$TO(X)+L(X)+O(\Gamma)$	$[\star X^{(4)}]_{(2)} \otimes \Gamma^{(25+)}$	$D; R$	$2TO(X)+O(\Gamma)$
$\star X^{(4)} \otimes \star X^{(3)} \otimes \Gamma^{(25+)}$	$D(3); R$	$TO(X)+TA(X)+O(\Gamma)$	$[\star X^{(1)}]_{(2)} \otimes \Gamma^{(25+)}$	$D(2); R$	$2L(X)+O(\Gamma)$
$\star X^{(1)} \otimes \star X^{(3)} \otimes \Gamma^{(25+)}$	$D(2); R$	$L(X)+TA(X)+O(\Gamma)$	$[\star X^{(3)}]_{(2)} \otimes \Gamma^{(25+)}$	$D(2); R$	$2TA(X)+O(\Gamma)$
$\star X^{(4)} \otimes \star X^{(1)} \otimes \star X^{(3)}$	$D(3); R$	$TO(X)+L(X)+TA(X)$	$[\star X^{(4)}]_{(2)} \otimes \star X^{(1)}$	$D(2); R$	$2TO(X)+L(X)$
$\star L^{(3-)} \otimes \star L^{(1+)} \otimes \Gamma^{(25+)}$	$D(3)$	$TO(L)+LO(L)+O(\Gamma)$	$\otimes \star X^{(3)}$	$D(2); R$	$+TA(X)$
$\star L^{(3-)} \otimes \star L^{(2-)} \otimes \Gamma^{(25+)}$	R	$TO(L)+LA(L)+O(\Gamma)$	$[\star X^{(1)}]_{(2)} \otimes \star X^{(4)}$	$D; R$	$2L(X)+TO(X)$
$\star L^{(3-)} \otimes \star L^{(3+)} \otimes \Gamma^{(25+)}$	$D(6)$	$TO(L)+TA(L)+O(\Gamma)$	$\otimes \star X^{(3)}$	$D(2); R$	$+TA(X)$
$\star L^{(1+)} \otimes \star L^{(2-)} \otimes \Gamma^{(25+)}$	$D(2)$	$LO(L)+LA(L)+O(\Gamma)$	$[\star X^{(3)}]_{(2)} \otimes \star X^{(4)}$	$D; R$	$2TA(X)+TO(X)$
$\star L^{(1+)} \otimes \star L^{(3+)} \otimes \Gamma^{(25+)}$	R	$LO(L)+TA(L)+O(\Gamma)$	$\otimes \star X^{(1)}$	$D(2); R$	$+L(X)$
$\star L^{(2-)} \otimes \star L^{(3+)} \otimes \Gamma^{(25+)}$	$D(3)$	$LA(L)+TA(L)+O(\Gamma)$	$[\star L^{(3-)}]_{(2)} \otimes \Gamma^{(25+)}$	R	$2TO(L)+O(\Gamma)$
$\star L^{(3-)} \otimes \star L^{(1+)} \otimes \star X^{(4)}$	$D(3); R$	$TO(L)+LO(L)+TO(X)$	$[\star L^{(1+)}]_{(2)} \otimes \Gamma^{(25+)}$	R	$2LO(L)+O(\Gamma)$
$\otimes \star X^{(1)}$	$D(3); R$	$+L(X)$	$[\star L^{(2-)}]_{(2)} \otimes \Gamma^{(25+)}$	R	$2LA(L)+O(\Gamma)$
$\otimes \star X^{(3)}$	$D(3); R$	$+TA(X)$	$[\star L^{(3+)}]_{(2)} \otimes \Gamma^{(25+)}$	R	$2TA(L)+O(\Gamma)$
$\star L^{(3-)} \otimes \star L^{(2-)} \otimes \star X^{(4)}$	$D(3); R$	$TO(L)+LA(L)+TO(X)$	$[\star L^{(3-)}]_{(2)} \otimes \star X^{(4)}$	$D(3); R$	$2TO(L)+TO(X)$
$\otimes \star X^{(1)}$	$D(3); R$	$+L(X)$	$\otimes \star X^{(1)}$	$D(3); R$	$+L(X)$
$\otimes \star X^{(3)}$	$D(3); R$	$+TA(X)$	$\otimes \star X^{(3)}$	$D(3); R$	$+TA(X)$
$\star L^{(3-)} \otimes \star L^{(3+)} \otimes \star X^{(4)}$	$D(6); R$	$TO(L)+TA(L)+TO(X)$	$[\star L^{(1+)}]_{(2)} \otimes \star X^{(4)}$	$D; R(dp)$	$2LO(L)+TO(X)$
$\otimes \star X^{(1)}$	$D(6); R$	$+L(X)$	$\otimes \star X^{(1)}$	$D; R$	$+L(X)$
$\otimes \star X^{(3)}$	$D(6); R$	$+TA(X)$	$\otimes \star X^{(3)}$	$D; R(dp)$	$+TA(X)$
$\star L^{(1+)} \otimes \star L^{(2-)} \otimes \star X^{(4)}$	$D; R$	$LO(L)+LA(L)+TO(X)$	$[\star L^{(2-)}]_{(2)} \otimes \star X^{(4)}$	$D; R(dp)$	$2LA(L)+TO(X)$
$\otimes \star X^{(1)}$	$D(2); R$	$+L(X)$	$\otimes \star X^{(1)}$	$D; R$	$+L(X)$
$\otimes \star X^{(3)}$	$D(2); R$	$+TA(X)$	$\otimes \star X^{(3)}$	$D; R(dp)$	$+TA(X)$
$\star L^{(1+)} \otimes \star L^{(3+)} \otimes \star X^{(4)}$	$D(3); R$	$LO(L)+TA(L)+TO(X)$	$[\star L^{(3+)}]_{(2)} \otimes \star X^{(4)}$	$D(3); R$	$2TA(L)+TO(X)$
$\otimes \star X^{(1)}$	$D(3); R$	$+L(X)$	$\otimes \star X^{(1)}$	$D(3); R$	$+L(X)$
$\otimes \star X^{(3)}$	$D(3); R$	$+TA(X)$	$\otimes \star X^{(3)}$	$D(3); R$	$+TA(X)$
$\star L^{(2-)} \otimes \star L^{(3+)} \otimes \star X^{(4)}$	$D(3); R$	$LA(L)+TA(L)+TO(X)$	$[\star W^{(1)}]_{(2)} \otimes \Gamma^{(25+)}$	$D(2); R$	$O(\Gamma)+\{b$
$\otimes \star X^{(1)}$	$D(3); R$	$+L(X)$	$[\star W^{(2)}]_{(2)} \otimes \Gamma^{(25+)}$	$D(2); R$	$O(\Gamma)+\{b$
$\otimes \star X^{(3)}$	$D(3); R$	$+TA(X)$	$[\star W^{(1)}]_{(2)} \otimes \star X^{(4)}$	$D(2); R$	$TO(X)+$
$\star W^{(1)} \otimes \star W^{(1)} \otimes \Gamma^{(25+)}$	$D(5); R$	$O_1(W)+O_2(W)^b$	$\otimes \star X^{(1)}$	$D(2); R$	$L(X)+$ } d
$\star W^{(1)} \otimes \star W^{(2)} \otimes \Gamma^{(25+)}$	$D(5); R$	$O(\Gamma)+\begin{cases} O_1(W)+O_2(W)^b \\ O_1(W)+A_1(W)^b \\ A_1(W)+A_2(W)^b \end{cases}$	$\otimes \star X^{(3)}$	$D(3); R$	$LA(X)+$

[a] Where possible, we follow Lax-Hopfield assignments as given in Ref. 14.
[b] See footnotes to Tables I and II regarding ambiguity in assigning species to branches at W.
[c] The two phonons of same symmetry must come from different branches. The same rule obtains if the different branches of the same symmetry are $\star W^{(2)}$.
[d] Refer to footnote b. Also note that the same selection rule holds for $\star W^{(2)}$. Thus, each of the three $\star X^{(m)}$ phonons may combine with the first overtone of each of the three $\star W^{(m)}$ phonons.

3.2. Two-Phonon Processes

The case of a single infrared photon being absorbed and simultaneously producing two phonons has been examined in the diamond structure by several authors.[17] In Table II we list all active two-phonon overtones and combinations which can arise from the phonon branches at the critical points. In the two-phonon case, only phonons from branches with the same star can arise, since we neglect the finite wavelength of light. In

[17] M. Lax and E. Burstein, Phys. Rev. **97**, 39 (1955); M. J. Stephen, Proc. Phys. Soc. (London) **71**, 485 (1957). The full space group theory was not utilized in these papers.

Table II we use the Lax-Hopfield assignments to label the branches.

As first result we note that all two-phonon overtones are infrared dipole forbidden, Raman allowed in diamond. This result follows from the complete reduction of the appropriate symmetrized square representations. Note, in particular, that in the reduction of the ordinary and the symmetrized Kronecker square of states $\star X^{(1)}$, $\star X^{(3)}$, $\star X^{(4)}$, $\star W^{(1)}$, and $\star W^{(2)}$ both even and odd representations occur. (See Tables VI and VIII of Ref. 1). Thus, the parity argument advanced by Lax and Burstein (for the infrared result) which was based on an

oversimplified one-dimensional model of the diamond structure is not applicable, even though their conjecture is verified by the complete analysis. This point will again be discussed when we present our results for the zincblende structure: *vide infra*. All the infrared dipole forbidden two-phonon overtones may give rise to quadrupole absorption in addition to Raman scattering. We return to this point later.

Two-phonon combination infrared absorption should gives rise to ten "lines" in the diamond structure, in the approximation in which we are working: namely that the crystal has eleven fundamental oscillators. The "lines" originating from branches $\star X^{(m)}$ are both infrared dipole and Raman active. (These "lines" are actually bands.[18])

3.3. Three-Phonon Processes

In Table III we list the active three-phonon processes, including overtones, combinations, and general states.

A necessary, but not sufficient, condition for activity of a three-phonon process is that the direct product of the stars must contain Γ. We are thus no longer restricted to three states all with the same star. For example, two-phonon states $\star X^{(m)}$ and $\star X^{(m')}$ may combine with the Raman state $\Gamma^{(25+)}$; states $\star L^{(m)}$ and $\star L^{(m')}$ may combine with $\star X^{(m'')}$, etc. There are very many three-phonon processes which are infrared active in diamond, and this should give rise to a considerable complexity in the details of the absorption spectrum in this energy region. It is thus desirable to obtain the highest resolution possible in absorption experiments carried out in this region, in order to obtain useful results.

A most interesting result in the three-phonon region concerns the three-phonon overtones: $[\star X^{(3)}]_{(3)}$ and $[\star X^{(4)}]_{(3)}$. The former is infrared dipole allowed only, the latter Raman active only. Since one of the ambiguities in the diamond phonon spectrum concerns assignment of TO or TA to $\star X^{(3)}$ or $\star X^{(4)}$, we see that this selection rule can provide an unambiguous optical resolution of the uncertainty. The situation is quite analogous to that obtaining in the molecular case,[7] where overtone and combination bands can be used to resolve ambiguities of assignments.

3.4. Higher Order Effects: Quadrupole and Magnetic Dipole

Recently there has been interest in anisotropic optical absorption effects which may occur in cubic crystals due to violation of the electric dipole selection rules by higher order processes,[19] e.g., electric quadrupole, or magnetic dipole. Normally violations of the dipole selection rules are neglected, in the study of molecular

TABLE IV. Two-phonon processes in zincblende.

Species	Activity	Type
	Overtones	
$[\Gamma^{(15)}]_{(2)}$	$D; R$	$2O(\Gamma)$
$[\star X^{(5)}]_{(2)}$	$D; R$	$2TO(X)$ and $2TA(X)$
$[\star X^{(1)}]_{(2)}$	R }	$2LO(X)$ and $2LA(X)$
$[\star X^{(3)}]_{(2)}$	R	
$[\star L^{(3)}]_{(2)}$	$D(2); R$	$2TO(L)$ and $2TA(L)$
$[\star L^{(1)}]_{(2)}$	$D; R$	$2LO(L)$ and $2LA(L)$
$[\star W^{(m)}]_{(2)}$ $m=1, 2, 3, 4$	R }	$2O_1(W); 2O_2(W); 2O_3(W);$ $2A_1(W); 2A_2(W); 2A_3(W)$
	Combinations	
$\star X^{(5)} \otimes \star X^{(1)}$	$D; R(dp)$ }	$TO(X)+LO(X); TO(X)+LA(X);$
$\otimes \star X^{(3)}$	$D; R(dp)$ }	$TA(X)+LO(X); TA(X)+LA(X)$
$\otimes \star X^{(5)}$	$D; R$	$TO(X)+TA(X)$
$\star X^{(3)} \otimes \star X^{(1)}$	$D; R$	$LO(X)+LA(X)$
$\star L^{(3)} \otimes \star L^{(1)}$	$D; R(dp)$	$TO(L)+LO(L); TO(L)+LA(L);$ $TA(L)+LO(L); TA(L)+LA(L)$
$\star L^{(3)} \otimes \star L^{(3)}$	$D; R$	$TO(L)+TA(L)$
$\star L^{(1)} \otimes \star L^{(1)}$	$D; R$	$LO(L)+LA(L)$
$\star W^{(1)} \otimes \star W^{(1)}$	R	
$\star W^{(2)} \otimes \star W^{(2)}$	R	
$\star W^{(3)} \otimes \star W^{(3)}$	R	
$\star W^{(4)} \otimes \star W^{(4)}$	R	
$\star W^{(1)} \otimes \star W^{(2)}$	$D; R(dp)$	a
$\star W^{(1)} \otimes \star W^{(3)}$	$D; R(dp)$	
$\star W^{(1)} \otimes \star W^{(4)}$	$D; R(dp)$	
$\star W^{(2)} \otimes \star W^{(3)}$	$D; R(dp)$	
$\star W^{(2)} \otimes \star W^{(4)}$	$D; R(dp)$	
$\star W^{(3)} \otimes \star W^{(4)}$	$D; R(dp)$	

a In listing these combinations it is not possible to be more specific because of ambiguity of assignments at $\star W$. However, in this list of combinations, it is to be noted that the two phonons participating, even if of the same symmetry, must arise from different branches.

infrared absorption.[20] It is not at all obvious, failing a quantitative estimate, that neglect of quadrupole, or magnetic dipole, absorption is justified in a solid. We note that the relevant tensor operator for quadrupole transition, Q, transforms in O_h^7 as does α (3.2). Transitions which are Raman allowed should also be quadrupole allowed. We thus suggest an experimental search, in the two-phonon overtone region, for anisotropic infrared absorption.[21]

The magnetic dipole operator M, transforms in O_h^7 as the irreducible representation $\Gamma^{(15+)}$. Selection rule for such transitions can easily be obtained from the Table in Ref. 1. As with the quadrupole transitions specific enumeration of such allowed processes will not be given pending either theoretical estimates of intensities or experimental verification, of anisotropic absorption.

4. ACTIVE VIBRATIONS IN ZINCBLENDE

The critical points in the zincblende-structure[22] phonon spectrum are at Γ, X, L, W. In Table I we list

[18] R. F. Wallis and A. A. Maraduddin, paper presented at the International Conference on Semiconductors, Exeter, 1962 (to be published). Also M. Born and K. Huang, Ref. 11, Chap. 7.

[19] R. J. Elliott, Phys. Rev. **124**, 340 (1961).

[20] G. Herzberg, Ref. 7, p. 380; E. B. Wilson, *et al.* Ref. 4, p. 39, and footnote 2, p. 607.

[21] Also noted in the talk given at the APS meeting in New York, January 1962. See J. L. Birman, Bull. Am. Phys. Soc. **7**, 65 (1962).

[22] R. H. Parmenter, Phys. Rev. **100**, 573 (1955), especially p. 579, second paragraph.

TABLE V. (*continued*)

Species	Activity	Type
	Simple combinations	
$\star W^{(m)} \otimes \star W^{(m')} \otimes \star X^{(m'')}$	$D; R$	All combinations of TO(X), or TA(X), or LO(X), or LA(X) and phonons from two distinct branches of $\star W$ are allowed.
	General combinations	
$[\star X^{(5)}]_{(2)} \otimes \Gamma^{(15)}$	$D(4); R$	2TO(X)+O(Γ); 2TA(X)+O(Γ).
$[\star X^{(1)}]_{(2)} \otimes \Gamma^{(15)}$	$D(2); R$ ⎫	O(Γ)+LO(X);
$[\star X^{(3)}]_{(2)} \otimes \Gamma^{(15)}$	$D(2); R$ ⎬	O(Γ)+LA(X)
$[\star X^{(5)}]_{(2)} \otimes \star X^{(5)}$	$D(3); R$	2TO(X)+TA(X)[b]; 2TA(X)+TO(X)[b]
$\otimes \star X^{(1)}$	$D(2); R$ ⎫	2TO(X)+LO(X); 2TO(X)+LA(X);
$\otimes \star X^{(3)}$	$D(2); R$ ⎬	2TA(X)+LO(X); 2TA(X)+LA(X)
$[\star X^{(1)}]_{(2)} \otimes \star X^{(5)}$	$D; R(dp)$ ⎫	2LO(X)+TO(X); 2LO(X)+TA(X);
$\otimes \star X^{(3)}$	$D; R(dp)$ ⎬	2LO(X)+LA(X)
$[\star X^{(3)}]_{(2)} \otimes \star X^{(5)}$	$D; R(dp)$ ⎬	2LA(X)+TO(X); 2LA(X)+TA(X);
$\otimes \star X^{(1)}$	$D; R(dp)$ ⎭	2LA(X)+LO(X)
$[\star L^{(3)}]_{(2)} \otimes \Gamma^{(15)}$	$D(5); R$	2TO(L)+O(Γ); 2TA(L)+O(Γ)
$[\star L^{(1)}]_{(2)} \otimes \Gamma^{(15)}$	$D(2); R$	2LO(L)+O(Γ); 2LA(L)+O(Γ)
$[\star L^{(3)}]_{(2)} \otimes \star X^{(5)}$	$D(7); R$	2TO(L)+TO(X); 2TO(L)+TA(X); 2TA(L)+TO(X); 2TA(L)+TA(X)
$\otimes \star X^{(1)}$	$D(3); R$ ⎫	2TO(L)+LO(X); 2TO(L)+LA(X);
$\otimes \star X^{(3)}$	$D(3); R$ ⎬	2TA(L)+LO(X); 2TA(L)+LA(X)
$[\star W^{(m)}]_{(2)} \otimes \Gamma^{(15)}$ $m=1, 2, 3, 4$	$D(2); R$	All combinations of O(Γ) and phonon overtones of $\star W^{(m)}$ are allowed.
$[\star W^{(m)}]_{(2)} \otimes \star X^{(m')}$	$D; R$	All combinations of TO(X), or TA(X), or LA(X), or TA(X) and phonon overtones of $\star W^{(m)}$ are allowed.

[b] Here two $\star X^{(5)}$ modes are from the same branch, the third is from the other branch of symmetry $\star X^{(5)}$.

4.2. Two-Phonon Processes

The selection rules for active two-phonon processes are given in Table IV. Noteworthy results are the prohibition of two-phonon overtones of states $\star X^{(1)}$ and $\star X^{(3)}$ in infrared absorption. These are the longitudinal optic and acoustic branch states at $\star X$. [These are the states which "originate" from the state $\star X^{(1)}$ of diamond; this is the degenerate longitudinal state (LO and LA coincide) which is split when the diamond structure is imagined perturbed to produce zincblende. (Ref. 22, Table XV).] These overtones will be Raman active, however. The overtones of the transverse states are allowed; both of these (optic and acoustic) transform as $\star X^{(5)}$. Other forbidden two-phonon overtones are for states $\star W^{(m)}$, for $m=1, 2, 3, 4$, which originate from the corresponding diamond states.

In view of the currency of arguments about selection rules based on the one-dimensional model and conjecture of Lax and Burstein,[17] it seems worthwhile to emphasize again that the selection rules follow from the entire space-group analysis.[23] In particular, the presence or absence of inversion, or inversion plus a fractional translation, in the space group is not simply related to activity or inactivity of two-phonon overtones. Thus, in zincblende which has no inversion symmetry certain overtones are forbidden. In diamond only for these irreducible representations for which the factor group $\mathcal{G}(\mathbf{k}_j)/T(\mathbf{k}_j)$ is a direct product group of inversion times a smaller group, can parity arguments be invoked. The important states $\star X^{(m)}$ and $\star W^{(m)}$ are of indefinite (mixed) parity and give rise to even plus odd representations when direct products are reduced.

4.3. Three-Phonon Processes

In Table V the active three-phonon states are listed. One notes that, as in diamond, very few three-phonon overtones are infrared active. A large number of three-

phonon processes are active, however, as simple or general combinations.

5. DISCUSSION AND SUMMARY

Infrared lattice vibration spectra have recently been reported for several materials with diamond,[24] and zincblende[25] structures. With few exceptions (e.g., the work of Hardy and Smith[24]) the interpretations of the spectra which have been given ignore the dispersion of phonon energy in each branch. That is, single characteristic energies are assigned to each branch (e.g., TO energy, etc.) and the locations of features in the spectrum are correlated with sums and/or differences of these few parameters. The temperature dependence of the spectrum is used as an auxiliary guide. The Lax-Burstein conjecture has been used as a selection rule for both structures. An impressive example of the fit of many features in the spectrum by few parameters is provided by the recent work of Turner and Reese.[25]

A deeper examination indicates, however, that the situation is far from satisfactory. For example, Hardy and Smith[24] were unable to derive a consistent set of fundamental phonon energies for diamond, even for the limited spectral region which came into their purview; a similar difficulty was encountered by Johnson[24] for silicon. The demarcation by the former authors of "two-phonon" or "three-phonon" energy regions seems not to take account of the likelihood, for example, that a combination like 2TA+LA phonons (from appropriately chosen stars) will occur at energy less than two Raman phonons, i.e., in their "two-phonon" region. Certain of the assignments of Turner and Reese[25] are not consistent with the selection rules for zincblende. Thus, the 2LO assignment (Ref. 25) line 1, Table II must refer to two phonons of symmetry $\star L^{(1)}$, but then the 3LO assignment (Ref. 25) line 9, Table III is incorrect, since $[\star L^{(1)}]_{(3)}$ is inactive. Other examples could be cited of inconsistencies or incompleteness in assignments but this is not our purpose. Finally, the neglect of phonon dispersion is *a priori* unsatisfactory in any theory of lattice absorption.

It seems evident that the quantitative study of lattice vibration spectra of crystals is in its infancy.[26] In principle, this powerful tool can provide us with precise values of the phonon energies, at least at the critical points in the spectrum. The use of selection rules, such as those derived here for the two space groups diamond and zincblende, is a first and necessary step in this study. Having enumerated the relevant selection rules here, we hope to return later to their systematic application to interpretation of spectra.

Among the problems remaining are the estimation of relative intensities of various active processes. To procede in this direction will require better understanding of the mechanism or mechanisms[18] by which multiphonon processes are activated, so that the relevant matrix elements can be calculated. An experimental result, which may be relevant here is the detailed structure one observes in the infrared absorption spectra of zincblende crystals compared to diamond. Compare, for example, the two- and three-phonon regions in AlSb, reported by Turner and Reese,[25] with the same regions in Si and C.[24]

In summary, there seems every reason to expect that the combination of high resolution infrared absorption spectroscopy, and Raman scattering, data (the latter perhaps made easier by available laser sources) may provide significant keys by which the phonon dispersions in solids can be determined. In the interpretation of these data, space-group selection rules will surely play as central a role as in the molecular case.

[24] For carbon (diamond) see J. R. Hardy and S. D. Smith, Phil. Mag. **6**, 1163 (1961), and paper presented at the International Meeting on Semiconductors, Exeter, 1962 (to be published); for silicon, F. A. Johnson, Proc. Phys. Soc. (London) **73**, 265 (1959); for germanium, B. N. Brockhouse and P. K. Iyengar, Phys. Rev. **111**, 747 (1958); also see thesis by J. F. Hirshberg, Syracuse University, 1958 (unpublished) available from University Microfilms Im. Ann Arbor; M. J. Stephen, Proc. Phys. Soc. (London) **71**, 485 (1958).

[25] For GaP see D. Kleinman, W. Spitzer, Phys. Rev. **118**, 110 (1960); InSb, S. Fray, F. A. Johnson, and R. Jones, Proc. Phys. Soc. (London) **76**, 939 (1960); SiC, W. Spitzer and D. Kleinman, Phys. Rev. **113**, 127 (1959); AlSb, W. Turner, W. Reese, *ibid.* **127**, 126 (1962); GaAs, W. Cochran, S. J. Fray, F. A. Johnson, J. Quarrington, and N. Williams, Suppl. J. Appl. Phys. **32**, 2102 (1961); and ZnS, T. Deutch, in *Proceedings of the International Conference on the Physics of Semiconductors at Exeter, 1962* (Institute of Physics and the Physical Society, London, 1962), pp. 505–512.

[26] For a recent review of infrared spectra of solids see S. S. Mitra, in *Solid State Physics*, edited by F. Seitz, and D. Turnbull (Academic Press Inc., New York, 1962), Vol. 13, p. 2; Some accounts of Raman spectra of solids are given by S. Mizushima, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. 26, p. 171.

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