The form of the crystal polarizability and optical rotation tensors, Eqs. (29) and (37), are the same for both the one-molecule and one-electron basis sets. The one-electron basis set, which has been discussed here, has the average crystal field included in its defining equation. If the crystal field is approximated in the same way as the correlation interaction has been, then a set of molecular orbitals for an isolated molecule may be used as a basis for expressing Eqs. (29) and (37); the crystal-field interaction is included in the interaction matrix. The set of molecular orbitals represents the simplest computed basis set for a calculation of the optical properties of a molecular crystal or polymer.

The approximation of the intermolecular interaction as a dipole-dipole coupling is represented by

$$\Gamma(\mathbf{q})=\mathbf{P}_0\cdot\mathbf{d}(\mathbf{q})\cdot\mathbf{P}_0{}^{\dagger},$$

where

$$\mathbf{d}(\mathbf{q})=\sum_{\mathbf{h}}\mathbf{d}(\mathbf{h})e^{i\mathbf{q}\cdot\mathbf{h}},$$

and $\mathbf{d}(\mathbf{h})$ is the dipole interaction tensor between molecules separated by $\mathbf{h}$. Rhodes *et al.*[4,18] have shown that, with the use of the dipole approximation, the crystal polarizability may be expressed in terms of the molecular polarizability; the crystal optical rotation may be expressed in terms of the molecular optical rotation tensor also.

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Selection Rules for Anharmonic Interactions of Nearest Neighbors in Crystals with the Zinc Blende or Diamond Structure

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Selection rules are derived for multiple-phonon processes which are dominated by anharmonic interactions between nearest-neighbor lattice particles. These nearest-neighbor selection rules (NSR) are different from and supplementary to the usual group-theoretical selection rules. NSR for wave vectors at X or L are expressed in Born's (NSRB) and in Keating's (NSRK) formalism. The NSRB refer to anharmonic two-particle interactions; the NSRK allow interactions between two or more particles. The applicability of the NSR to various multiple-phonon processes—with emphasis on infrared two-phonon absorption—is investigated and the results of some relevant model calculations are given. Practical rules for further applications are proposed.

1. INTRODUCTION

We shall present a new type of selection rules for multiple-phonon interactions in crystals of the zinc-blende or diamond structure. These rules supplement the usual group-theoretical selection rules, and specify conditions under which anharmonic interactions between nearest-neighbor particles vanish.

Selection rules are commonly formulated for simple interaction expressions. If such an expression approximates a real interaction sufficiently well, then a forbidden (approximate) interaction will correspond to a real process of weak intensity. Infrared multiple-phonon absorption, for example, if forbidden by the group-theoretical selection rules (GSR) in the electric dipole approximation,[1] is extremely weak for all cases of practical interest.

The nearest-neighbor selection rules (NSR) to be derived here[2] are based on certain assumptions referring to the form of the anharmonic interactions and the magnitudes of the harmonic amplitudes. These assumptions, and the neglect of the contributions of higher-order neighbors to the anharmonicities, represent approximations to the situation in real materials. From our present state of knowledge we can suggest where and to what degree these approximations should be satisfied, but the validity of these approximations is not as well established as that for the GSR. If an interaction is forbidden by the NSR and the related real process is found

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[1] J. L. Birman, Phys. Rev. **131**, 1489 (1963).

[2] Some of the material of the present paper is discussed in greater detail in the following Foundational Research Projects Quarterly Reports: Naval Ordnance Laboratory Corona Report No. 688, p. 35, 1966 (unpublished); No. 705, p. 37, 1966 (unpublished); and No. 715, p. 39, 1967 (unpublished); Naval Ordnance Laboratory, Corona, California, and Naval Weapons Center Corona Laboratories Report No. TP 756, p. 9, 1968 (unpublished). These publications, hereafter referred to as N1, N2, N3, and N4, respectively, are available from the Clearinghouse for Federal Scientific and Technical Information, Springfield, Va. 22151, where they are listed as AD-645980, AD-651544, AD-655889, and AD-830635.

by experiment to be weak, we consider this as confirmation of the validity of our approximations and in this way learn something about the harmonic and anharmonic properties of the crystal.

The confinement of the NSR to nearest neighbors refers to the anharmonic interactions only; the harmonic interaction remains unrestricted, i.e., it may extend up to neighbors of arbitrary order. For crystals of the diamond structure, all we have to know about the harmonic properties are the correct phonon representations. This information, which is also required for the GSR, is of a rather general nature but not trivial; the correct representation assignments in diamond have been determined only recently.[3] For crystals of the zinc-blende structure, the NSR require more detailed information on the harmonic properties: First, a distinction must be drawn between "normal" and "anomalous" crystals. This distinction is similar to that of the group-theoretical representations in diamond but goes beyond the usual group-theoretical considerations for zinc blende; after dispatching preliminaries in Sec. 2, we shall present this subject in Sec. 3. Second, for the NSR to be applicable, the two kinds of particles in the crystal must oscillate with amplitudes of the same magnitude in certain of the modes under consideration; the plausibility of such behavior will be discussed later in the paper (Sec. 8).

The phase factors of the particle displacements are derived in Sec. 4, and in Secs. 5 and 6 they lead to the NSR, the topic of our presentation. The NSR are expressed in Sec. 5 by employing a description of the anharmonicity in the traditional Born formalism.[4] For certain later applications it will be convenient to make use of Keating's formalism[5,6]; the NSR will be adapted to that formalism in Sec. 6. The various selection rules are compared in Sec. 7.

The last five sections serve as an investigation of the applicability of the NSR. Section 8 discusses the harmonic amplitude ratios in zinc-blende structures. Section 9 shows the applicability of the NSR to a model of the third-order potential, which is related to the matrix elements of two-phonon absorption in Sec. 10. The relevance of the NSR to various experimental results is discussed in Sec. 11. Finally, in Sec. 12, we employ the NSR for some tentative predictions.

The general considerations of this paper refer to all crystals with diamond or zinc-blende structures, but where numerical data and estimates are involved we shall confine our discussions to diamond, Si, Ge, and the compounds of Al, Ga, and In with P, As, and Sb. Among the crystals with zinc-blende structure, the actual comparison of the NSR with experiment will be further restricted to GaAs because of the inadequacy of data for the other compounds.

Throughout this paper we shall consider the crystal lattice to be built up from rigid particles. This should not affect the formal generality of our approach, since for a lattice of deformable particles, such as the shell model, the shell displacements can be expressed by the core displacements and eliminated, thus leading to an equivalent rigid particle model.

2. DYNAMIC EQUATIONS

Let $\mathbf{r}(l\kappa)$ be the equilibrium position of the lattice particle $(l\kappa)$, where κ is one of the two lattice sites α or β in the elementary cell l of the zinc-blende or diamond lattice. The position vector from lattice site $(0\kappa')$ to $(l\kappa)$ is designated by $\mathbf{r}(l\kappa,0\kappa')$, and α and β are chosen such that $\mathbf{r}(0\beta,0\alpha)=\frac{1}{4}\,a(1,1,1)$, with a the lattice constant.

The displacement of the particle $(l\kappa)$ from its equilibrium position may be built up by superposition of terms of the form

$$\mathbf{u}(l\kappa|\mathbf{q}j)=\mathbf{w}(\kappa|\mathbf{q}j)\exp[i\mathbf{q}\cdot\mathbf{r}(l\kappa)], \qquad (2.1)$$

where the mode $(\mathbf{q}j)$ is characterized by the wave vector $\mathbf{q}$ and the branch label j. The polarization vectors $\mathbf{w}$, together with the angular eigenfrequencies ω, may be obtained from[4,7]

$$m_\kappa\omega(\mathbf{q}j)^2\mathbf{w}(\kappa|\mathbf{q}j)=\sum_{\kappa'}\mathbf{C}(\mathbf{q}|\kappa,\kappa')\cdot\mathbf{w}(\kappa'|\mathbf{q}j), \qquad (2.2)$$

where m_κ is the mass of the particle at lattice site κ, and the tensors $\mathbf{C}$ are given by

$$\mathbf{C}(\mathbf{q}|\kappa,\kappa')=\sum\nolimits_l \mathbf{\Phi}(l\kappa,0\kappa')\exp[-i\mathbf{q}\cdot\mathbf{r}(l\kappa,0\kappa')]. \qquad (2.3)$$

The $\mathbf{\Phi}$'s are the harmonic force constant tensors.

We shall confine our considerations to the points X and L with wave vectors $(2\pi/a)(1,0,0)$ and $(\pi/a)(1,1,1)$, respectively. Because of the symmetry of the zinc-blende lattice, the secular equation factorizes at these points. With $\mathbf{q}$ at X or L, and a mode of polarization P equal to L (longitudinal) or T (transverse), we obtain

$$AB=c(\mathbf{q}\mathrm{P})^2, \qquad (2.4)$$

with

$$\begin{aligned} A&=a(\mathbf{q}\mathrm{P})-m_\alpha\omega^2,\\ B&=b(\mathbf{q}\mathrm{P})-m_\beta\omega^2. \end{aligned} \qquad (2.5)$$

The a, b, and c are real and are related to (2.3) by

$$\begin{aligned} a(X\mathrm{L})&=C_{11}(X|\alpha,\alpha),\\ a(X\mathrm{T})&=C_{22}(X|\alpha,\alpha),\\ a(L\mathrm{L})&=C_{11}(L|\alpha,\alpha)+2C_{12}(L|\alpha,\alpha),\\ a(L\mathrm{T})&=C_{11}(L|\alpha,\alpha)-C_{12}(L|\alpha,\alpha), \end{aligned} \qquad (2.6)$$

by a corresponding set for the b's with α replaced by β,

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[3] G. Dolling and R. A. Cowley, Proc. Phys. Soc. (London) **88**, 463 (1966).

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

[5] P. N. Keating, Phys. Rev. **145**, 637 (1966).

[6] P. N. Keating, Phys. Rev. **149**, 674 (1966).

[7] L. Merten, Z. Naturforsch. **13a**, 662, 1067 (1958).

and by

$$\begin{aligned} &c(X\mathrm{L})=0,\\ &c(X\mathrm{T})=-iC_{23}(X\,|\,\alpha,\beta),\\ &c(L\mathrm{L})=e^{-i3\pi/4}[C_{11}(L\,|\,\alpha,\beta)+2C_{12}(L\,|\,\alpha,\beta)],\\ &c(L\mathrm{T})=e^{-i3\pi/4}[C_{11}(L\,|\,\alpha,\beta)-C_{12}(L\,|\,\alpha,\beta). \end{aligned} \tag{2.7}$$

In the case of diamond symmetry, the above equations remain correct and, in addition, each a is equal to the corresponding b.

3. NORMALITY

Our NSR will be seen to depend on the signs of A, B, and $c(\mathbf{q}\mathrm{P})$. According to (2.4) the signs of A and B are the same for a given mode. If ω_{A} (A = acoustical) and ω_{O} (O = optical) are a pair of solutions of (2.4), then, with $\omega_{\mathrm{A}}<\omega_{\mathrm{O}}$, it follows that A and B are positive for the acoustical mode and negative for the optical mode. This leaves open the question of the signs of $c(X\mathrm{T})$, $c(L\mathrm{L})$, and $c(L\mathrm{T})$. Note that $c(X\mathrm{L})$ vanishes, so the question of its sign does not arise.

In crystals of diamond structure, symmetry leaves a choice in the assignment of group-theoretical irreducible representations[1] to the modes at L and the transverse modes at X. It is easy to see that this choice is directly and unambiguously related to the signs of $c(\mathbf{q}\mathrm{P})$. The correct representation assignments depend on the values of the force constants. Fitting of a shell model[3] to neutron scattering data gives for Si and Ge the assignments shown in Table I, while in diamond the assignments for LA(L) and LO(L) are interchanged[3]; this switch in the assignments is connected to an inversion of the sign of the corresponding c; that is, $c(L\mathrm{L})$ in diamond is positive.

We define crystals with

$$c(X\mathrm{T})<0,\quad c(L\mathrm{L})<0,\quad c(L\mathrm{T})>0, \tag{3.1}$$

as normal. This means that Si and Ge are normal, while diamond, for the longitudinal modes at L, is anomalous.

For crystals with zinc-blende structure, we define normality by the same inequalities (3.1) as for diamond structures. However, zinc-blende symmetry gives only one possible irreducible representation for each of the modes of interest[1]; the zinc-blende representations therefore do not characterize the signs of the $c(\mathbf{q}\mathrm{P})$.

It is instructive to specialize for a moment on a crystal of diamond symmetry with an harmonic interaction consisting of nearest-neighbor central and noncentral forces, characterized by parameters α and β, respectively.[5,8] We find for this model

$$\begin{aligned} &c(X\mathrm{T})=-4(\alpha-\beta),\\ &c(L\mathrm{L})=-2(\alpha-3\beta),\\ &c(L\mathrm{T})=4\alpha. \end{aligned} \tag{3.2}$$

Stability requires that α and β be positive. If the central force is dominant, then (3.1) is satisfied and the crystal is normal.

TABLE I. Signs of $c(\mathbf{q}\mathrm{P})$ and irreducible representations for the phonon modes in Si and Ge.

Mode	Representation	Mode	Representation	Sgn $c(\mathbf{q}\mathrm{P})$
TA(X)	$X^{(3)}$	TO(X)	$X^{(4)}$	$-$
LA(L)	$L^{(2-)}$	LO(L)	$L^{(1+)}$	$-$
TA(L)	$L^{(3+)}$	TO(L)	$L^{(3-)}$	$+$

If the simple model on which (3.2) is based is applicable, then a material becomes anomalous for $\beta/\alpha>\frac{1}{3}$. For β/α in diamond, Si and Ge, Keating[5] gives the values of 0.66, 0.29, and 0.32, respectively. These values agree with the above statement that Si and Ge are normal but diamond is anomalous. An analysis of the elastic constants of GaAs (see Appendix) yields $\beta/\alpha=0.25$, hence we expect GaAs to be normal.

We see that an anomalous crystal is characterized by unusually large noncentral forces; such forces give an unusually small ratio c_{12}/c_{11} of the elastic constants.[5] For the simple model discussed above, the critical ratio is $c_{12}/c_{11}=\frac{1}{3}$. For diamond, Si, and Ge, the ratio of the elastic constants[5] has the values 0.12, 0.39, and 0.37, respectively, which agrees with our above classification of these materials. Elastic constants have been reported[9] for all compounds of Al, Ga, and In with P, As, and Sb, except for AlAs and InP. The ratios c_{12}/c_{11} for the measured compounds are equal to or larger than those for Si and Ge. We see no reason why AlAs and InP should deviate from this behavior and expect all of the III-V compounds to be normal.

4. PHASE FACTORS

Our NSR are based on the fact that, once the normality of the crystal has been determined, the phase differences of the oscillations of the particles for the modes of interest are independent of the values of the force constants.

Suppressing the arguments for a moment, we designate the magnitude of a displacement vector (2.1) by u and define $\hat{u}=\mathbf{u}/u$. For $\mathbf{q}$ at L, we find from Sec. 2 that the vectors $\hat{u}$ at adjacent lattice sites can be related by a scalar phase factor χ:

$$\hat{u}(0\beta\,|\,\mathbf{q}j)=\chi(0\beta,l\alpha\,|\,\mathbf{q}j)\hat{u}(l\alpha\,|\,\mathbf{q}j). \tag{4.1}$$

For the longitudinal modes at X, we identify such a phase factor with its limit for $\mathbf{q}\rightarrow X$ along Δ. For the transverse modes at X, relation (4.1) can be established if the polarization vectors are chosen in Σ directions.

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[8] It should lead to no confusion that the letters α and β, which have previously been introduced to distinguish the two lattice sites, will here and later also be used for various force constants.

[9] See the review by J. R. Drabble, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic Press Inc., New York, 1966), Vol. 2, p. 75; measurements on GaP have been reported by R. Weil and W. O. Groves, J. Appl. Phys. **39**, 4049 (1968).

TABLE II. Phase factors of particle (0β) relative to its nearest neighbors $(l\alpha)$, numbered as in Fig. 1, with wave vector $\mathbf{q}$ at X or L in a normal crystal of zinc-blende or diamond structure.

$\mathbf{q}$	l	LA	LO	TA1	TA2	TO1	TO2
X	0 or 1	i	$-i$	1	-1	-1	1
	2 or 3	$-i$	i	-1	1	1	-1
L	0	1	-1	-1	-1	1	1
	1,2, or 3	-1	1	1	1	-1	-1

The values of the phase factors in a normal crystal for $\mathbf{q}$ at $X(2\pi/a,0,0)$ and $L(\pi/a,\pi/a,\pi/a)$ are presented in Table II, where the nearest neighbors of (0β) are enumerated as in Fig. 1. The transverse modes 1 and 2 at X refer to polarizations along [0,1,1] and [0,1,−1], respectively; for the transverse branches at L, the choice of modes 1 and 2 is irrelevant. If the behavior of the crystal in a certain mode is anomalous, then the value given for the phase factor of that mode must be multiplied by -1.

Of particular interest is the situation where $\chi=1$, which means that the two particles related by this phase factor oscillate in phase.

5. NSR IN BORN'S FORMALISM (NSRB)

An anharmonic interaction of, say, third order may be written in Born's formalism[4] as

$$H=\frac{1}{3!}\sum H_{ii'i''}(l\kappa,l'\kappa',l''\kappa'')\times u_i(l\kappa)u_{i'}(l'\kappa')u_{i''}(l''\kappa''),\quad(5.1)$$

where $u_i(l\kappa)$ is the i component of the displacement of particle $(l\kappa)$ and the sum runs over all labels. The generalization of (5.1) to arbitrary order is obvious. An expression of this general form may represent a scalar, such as an anharmonic potential, a vector, such as a second-order dipole moment, a tensor, as in Raman scattering, etc. Alternatively, one may absorb any external perturbation, such as an electromagnetic field, in H and may assume (5.1) to be the energy of the interaction, in which case it always represents a scalar.

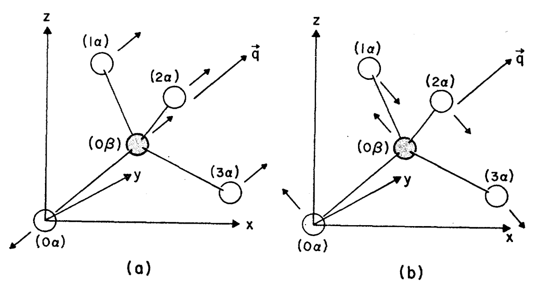

FIG. 1. Oscillations of the particle (0β) and its nearest neighbors $(l\alpha)$. The particles are shown in their equilibrium positions. The small arrows indicate the displacements for a mode (a) LO, and (b) TO, with $\mathbf{q}$ at L.

To investigate the interaction between phonons of modes $(\mathbf{q}j)$, $(\mathbf{q}'j')$, and $(\mathbf{q}''j'')$, we put

$$u_i(l\kappa)=u_i(l\kappa|\mathbf{q}j)+u_i(l\kappa|\mathbf{q}'j')+u_i(l\kappa|\mathbf{q}''j'').\quad(5.2)$$

Substituting in (5.1) and expanding, we retain only those terms which involve all three of the modes. Employing the invariance of the crystal with respect to arbitrary translations,[10] we can replace all but one of the displacements by displacement differences. The considerations of this section will be confined to nearest-neighbor two-particle interactions. The contribution to (5.1) of the interaction of a particle (0β) with its nearest neighbors $(l\alpha)$ may then be written

$$H(0\beta)=\sum_{ii'i''}\sum_{l}H_{ii'i''}(l\alpha,l\alpha,0\beta)u_i(l\alpha,0\beta|\mathbf{q}j)\times u_{i'}(l\alpha,0\beta|\mathbf{q}'j')u_{i''}(0\beta|\mathbf{q}''j''),\quad(5.3)$$

where

$$u_i(l\alpha,0\beta|\mathbf{q}j)=u_i(l\alpha|\mathbf{q}j)-u_i(0\beta|\mathbf{q}j).\quad(5.4)$$

We are interested in the condition under which the difference (5.4) will vanish. Obviously, this condition requires that the two displacement vectors agree in direction, phase, and magnitude. For the modes under consideration, the agreement with respect to the directions is guaranteed according to (4.1). The agreement in phase (for a normal crystal) is satisfied whenever the phase factor in Table II is equal to one. Equality of the displacement magnitudes requires that the magnitudes w of the polarization vectors at α and β have to be equal,

$$w(\alpha|\mathbf{q}j)=w(\beta|\mathbf{q}j).\quad(5.5)$$

In lattices of the diamond structure this condition is always satisfied; in zinc-blende structures the ratio of the magnitudes of the displacement amplitudes depends on the harmonic force constants and will be discussed in Sec. 8.

Let us consider a multiple-phonon process in a normal crystal involving, among others, the pair of phonons $(\mathbf{q}j)$ and $(\pm\mathbf{q}j')$, each of which may be either absorbed or emitted. Table II shows that for LA or TO at L the particle (0α) is in phase with (0β), while for LO or TA at L the particles (1α), (2α), and (3α) are in phase with (0β). If (5.5) is satisfied for each of the two modes, then for LALO, LATA, LOTO, or TATO, all at L, one of the displacement-difference factors in (5.3) will always vanish. Consequently, if the magnitudes of the relevant displacements at α and β are equal, nearest neighbors will give no contribution to any two-phonon (or higher) process containing one of these combinations. The situation occurring for LOTO at L has been illustrated in Fig. 1. It is easy to show that the combinations that vanish for L at $(\pi/a,\ \pi/a,\ \pi/a)$ will also vanish at any other L point in wave-vector space; the interaction will not vanish, however, if the two phonons belong to L points with different reduced wave vectors.

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[10] G. Leibfried and W. Ludwig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1961) Vol. 12, p. 275.

Further selection rules can be derived for interactions which are central, i.e., which involve only the components of the displacements along the vector connecting the two interacting particles. In this case, by again employing the translational invariance of the crystal, one can combine all of the displacements in the form of differences. The interaction (5.3) may then be written

$$H(0\beta)=-\tfrac{1}{2}\sum_l H(l\alpha,l\alpha,0\beta)[\mathbf{r}(l\alpha,0\beta)\cdot\mathbf{u}(l\alpha,0\beta|\mathbf{q}j)]$$
$$\times[\mathbf{r}(l\alpha,0\beta)\cdot\mathbf{u}(l\alpha,0\beta|\mathbf{q}'j')]$$
$$\times[\mathbf{r}(l\alpha,0\beta)\cdot\mathbf{u}(l\alpha,0\beta|\mathbf{q}''j'')],\quad(5.6)$$

where the **u** are the displacement vector differences and the sum extends over the nearest neighbors of (0β).

The transverse branches 1 at X are polarized along $[0,1,1]$; hence the corresponding dot products in (5.6) with $\mathbf{r}(2\alpha,0\beta)$ and $\mathbf{r}(3\alpha,0\beta)$ will vanish. Similarly, the transverse branches 2 at X, polarized along $[0,1,-1]$, give vanishing dot products with $\mathbf{r}(0\alpha,0\beta)$ and $\mathbf{r}(1\alpha,0\beta)$, as do the transverse branches at L with $\mathbf{r}(0\alpha,0\beta)$. When these properties are combined with Table II, it is found that every interaction of the form (5.6) which contains TA at X or L will vanish, assuming that (5.5) is satisfied for this mode. Also, if (5.5) holds for LO at L, then every central nearest-neighbor interaction containing LOTA or LOTO at L vanishes.

Collecting our results, we present in Table III the NSRB for multiple-phonon processes which couple the modes $(\mathbf{q}j)$, $(\mathbf{q}'j')$, and any further phonons in arbitrary modes through an anharmonic interaction H. The conditions in Table III partly overlap, each set of conditions being sufficient, however. If a crystal behaves anomalously for a certain wave vector and polarization, then the roles of the corresponding acoustical and optical branches must be interchanged. In diamond, e.g., rule (b) of Table III refers to LATA and LATO; rule (c) to LALO, LOTA, LATO, and TATO.

6. NSR IN KEATING'S FORMALISM (NSRK)

The building blocks of Keating's formalism[5,6] are the $\lambda_{mn}(l\kappa)$ involving the equilibrium positions and the displacements of the particle $(l\kappa)$ and its nearest neighbors. We shall decompose λ in the form

$$\lambda_{mn}(l\kappa)=\lambda_{mn}'(l\kappa)+\lambda_{mn}''(l\kappa),\quad(6.1)$$

and it will suffice to write down the definition of these quantities for $l=0$ and $\kappa=\beta$:

$$\lambda_{mn}'(0\beta)=(2/a)[\mathbf{r}(m\alpha,0\beta)\cdot\mathbf{u}(n\alpha,0\beta)+\mathbf{r}(n\alpha,0\beta)\cdot\mathbf{u}(m\alpha,0\beta)],\quad(6.2)$$
$$\lambda_{mn}''(0\beta)=(2/a)\mathbf{u}(m\alpha,0\beta)\cdot\mathbf{u}(n\alpha,0\beta),$$

where a is the lattice constant and m, $n=0$, 1, 2, 3 run over the nearest neighbors of (0β) as in Fig. 1. The corresponding quantities $\lambda_{mn}(0\alpha)$ are defined similarly.

TABLE III. NSRB for anharmonic nearest-neighbor interaction H in a normal crystal of zinc-blende or diamond structure.

(a) H central in **u** vanishes for $j=$TA with **q** at X or L, if $w(\alpha|\mathbf{q}j)=w(\beta|\mathbf{q}j)$;
(b) H central in **u** vanishes for $jj'=$LOTA or LOTO with $\mathbf{q}=\pm\mathbf{q}'$ at L, if $w(\alpha|\mathbf{q},\text{LO})=w(\beta|\mathbf{q},\text{LO})$;
(c) H vanishes for $jj'=$LALO, LATA, LOTO, or TATO with $\mathbf{q}=\pm\mathbf{q}'$ at L, if $w(\alpha|\mathbf{q}j)=w(\beta|\mathbf{q}j)$ and $w(\alpha|\mathbf{q}'j')=w(\beta|\mathbf{q}'j')$.

For $m=n$ the quantity λ connects two particles and we shall designate such as λ as "central." For $m\neq n$ three particles are being connected and the λ is "noncentral."

By restricting the anharmonic interactions to those between one particle and its nearest neighbors, a typical contribution to an interaction of, say, third degree in λ will be written

$$H(0\beta)=\frac{1}{3!}\sum H_{mnm'n'm''n''}(0\beta)\lambda_{mn}(0\beta)\times\lambda_{m'n'}(0\beta)\lambda_{m''n''}(0\beta),\quad(6.3)$$

where the summation refers to $m,\ldots,n''$ and runs over the nearest-neighbor sites of (0β). We may say that the interaction term (6.3) is "centered at (0β)" and corresponding contributions will be centered at each other lattice site.

Depending upon the relations among the subscripts $m,\ldots,n''$, we can distinguish four classes of terms in (6.3), which we designate as follows:

(i) $m=n=m'=n'=m''=n''$: diagonal central in λ;
(ii) $m=m'=m''\neq n=n'=n''$: diagonal noncentral in λ;
(iii) $m=n$, $m'=n'$, $m''=n''$, but not all equal to each other: nondiagonal central in λ;
(iv) all other terms: nondiagonal noncentral in λ.

The generalization to an interaction of arbitrary degree in λ is obvious. Case (i) represents a nearest-neighbor two-particle interaction. The other cases actually involve first and second neighbors because, for $m\neq n$, $(m\alpha)$ and $(n\alpha)$ are second neighbors of each other. Nevertheless, since the interaction always occurs via a common nearest neighbor, we shall keep referring to all four cases as nearest-neighbor interactions.

Due to the fact that λ' is linear and λ'' quadratic in **u**, an interaction of given degree in λ will contain terms of various degrees in **u**. An important special case of (6.3) is obtained by replacing each λ by λ'; the resulting interaction will be designated as H'. An interaction H' of given degree in λ' is then of the same degree in **u**, and if the interaction is diagonal central in λ', then it is of the two-particle central type in **u**, as defined in (5.6).

By providing each displacement difference with a mode label and combining the definitions of this section

TABLE IV. NSRK for anharmonic nearest-neighbor interaction H in a normal crystal of zinc-blende or diamond structure.

(a)	H'	(diagonal or nondiagonal) central in λ' vanishes for $j=\text{TA}$ with $\mathbf{q}$ at X or L, if $w(\alpha\|\mathbf{q}j)=w(\beta\|\mathbf{q}j)$;
(b)	H'	diagonal central in λ' vanishes for $jj'=\text{LOTA}$ or LOTO with $\mathbf{q}=\pm\mathbf{q}'$ at L, if $w(\alpha\|\mathbf{q},\text{LO})=w(\beta\|\mathbf{q},\text{LO})$;
(c)	H	diagonal central in λ vanishes for $jj'=\text{LALO}$, LATA, LOTO, or TATO with $\mathbf{q}=\pm\mathbf{q}'$ at L, if $w(\alpha\|\mathbf{q}j)=w(\beta\|\mathbf{q}j)$ and $w(\alpha\|\mathbf{q}'j')=w(\beta\|\mathbf{q}'j')$;
(d)	H'	diagonal noncentral in λ' vanishes for $jj'=\text{LOTO}$ or TATO with $\mathbf{q}=\pm\mathbf{q}'$ at L, if $w(\alpha\|\mathbf{q}j)=w(\beta\|\mathbf{q}j)$ and $w(\alpha\|\mathbf{q}'j')=w(\beta\|\mathbf{q}'j')$.

with the phase relations given in Table II, we obtain the NSR in Keating's formalism. For a normal crystal, we give in Table IV the NSRK for an anharmonic interaction H of the phonons $(\mathbf{q}j)$, $(\mathbf{q}'j')$, and any further phonons of arbitrary modes. If the crystal is anomalous, the modifications required are the same as those discussed in connection with the NSRB.

7. COMPARISON OF SELECTION RULES

We shall first compare the NSRB with the NSRK and then the NSR with the group-theoretical selection rules (GSR).

The NSRB of Table III and the NSRK of Table IV involve the same modes but, in part, different forms of the interaction. Every interaction which is expressed in Keating's formalism can also be described in Born's formalism, but Keating's formalism will be found as more convenient for certain of our applications.

The NSRB and those of the NSRK referring to diagonal central interactions are "two-particle NSR," while the remaining NSRK, referring to nondiagonal or noncentral interactions, involve three or more particles. A detailed comparison shows that NRSK (a), if restricted to diagonal H', becomes identical with NSRB (a), and that the cases NSRB (b) and NSRK (b) are identical to each other. NSRB (c) contains NSRK (c) insofar as the anharmonic forces in NSRB (c) are not restricted to any particular directions; however, for the modes LOTO and TATO at L, NSRK (c) plus (d) go beyond NSRB (c).

While the NSR depend on the form, the GSR depend on the type of the interaction. By "type" we mean a physical characterization of the process, such as infrared two-phonon absorption, three-phonon Raman scattering, etc.; more specifically, it is the group-theoretical representations which determine the GSR. The "form," on the other hand, characterizes the way in which the displacements of the lattice particles contribute to the anharmonic interaction, such as central or noncentral, diagonal or nondiagonal, and a specification of the order of neighbors involved. However, the type and form of an interaction are not independent of each other, since the type of an interaction will impose symmetry conditions on its form.

While the GSR require a complete specification of all the modes involved in a process, the NSR refer to only one or two of the participating modes. For instance, if NSRB (a) is satisfied for a given two-phonon process in a certain material, then for this process all two-phonon combinations and overtones involving TA at L or X will be forbidden. No such correlation between different combinations exists for the GSR.

Certain processes, such as the overtones for two-phonon absorption in diamond structures, are forbidden according to the GSR, but do not follow as forbidden from the NSR. The reason for this discrepancy is connected with the fact that the total interaction consists of a sum of terms, each term involving a certain set of particles. The NSR designate an interaction as forbidden if each term vanishes separately. The GSR, however, refer to the total interaction, i.e., the sum of terms, which may vanish due to cancellations. It is the restriction to individual terms which makes the NSR independent of the type of the interaction. Of course, if the type of the interaction is specified in addition to its form, then a wider set of selection rules can be obtained which contains both the NSR and the GSR.

8. MAGNITUDES OF AMPLITUDES

Our NSR have been found to depend on the harmonic lattice properties through the normality of the crystal, and—in the case of zinc-blende structure—on the magnitude w of the displacement amplitudes for the relevant modes. If the w's at the lattice positions α and β are equal, and if the necessary conditions on the anharmonicity are satisfied, then the anharmonic interaction will vanish; if the ratio for the w's is close to unity, we shall expect the anharmonic interaction to be small.

For a given mode at X or L, the ratio of the magnitudes of the displacement amplitudes may be found, from Sec. 2, to be

$$w(\alpha|\mathbf{q}j)/w(\beta|\mathbf{q}j)=[B(\mathbf{q}j)/A(\mathbf{q}j)]^{1/2}, \qquad (8.1)$$

where the quantities A and B are obtained from (2.5) by substitution of the appropriate eigenfrequencies. Let us introduce the abbreviations

$$\begin{aligned} x(\mathbf{q}P)&=(m_\beta/m_\alpha)a(\mathbf{q}\mathrm{P})/b(\mathbf{q}\mathrm{P}),\\ y(\mathbf{q}P)&=[\omega(\mathbf{q},\mathrm{PO})/\omega(\mathbf{q},\mathrm{PA})]^2, \end{aligned} \qquad (8.2)$$

where a and b are given in Sec. 2, P stands for the polarization (L or T), and the labels A and O refer to the acoustical and the optical branch, respectively. Then, from Eq. (8.1), it follows that

$$\begin{aligned} w(\alpha|\mathbf{q},\mathrm{PA})/w(\beta|\mathbf{q},\mathrm{PA})&=[b(\mathbf{q}\mathrm{P})/a(\mathbf{q}\mathrm{P})]^{1/2}\\ &\quad\times\{[y(\mathbf{q}\mathrm{P})-x(\mathbf{q}\mathrm{P})]/[y(\mathbf{q}\mathrm{P})-1/x(\mathbf{q}\mathrm{P})]\}^{1/2}, \end{aligned} \qquad (8.3)$$

$$\begin{aligned} w(\alpha|\mathbf{q},\mathrm{PO})&/w(\beta|\mathbf{q},\mathrm{PO})\\ &=(m_\beta/m_\alpha)w(\beta|\mathbf{q},\mathrm{PA})/w(\alpha|\mathbf{q},\mathrm{PA}). \end{aligned} \qquad (8.4)$$

Equation (8.4) relates the optical and acoustical amplitude ratios through the known mass ratio. Equation (8.3) depends, in addition, on the ratio of optical to acoustical eigenfrequencies, and on a/b. Little information exists on a/b, because a complete description of a crystal requires information on both the lattice frequencies and the polarization vectors, while most of the present epxerimental data refer to the lattice frequencies only. Even a complete knowledge of the frequency spectrum is not sufficient to determine all the force constants. This particular problem already occurs for primitive lattices,[11] but becomes much more serious for complex structures. A ratio $a/b=1$ may be interpreted as the equivalence of the total forces acting on particles of the type α and β; for rigid particles with nearest-neighbor interaction only, this is trivially satisfied; more sophisticated models will allow deviations from unity.

A special situation occurs for the longitudinal modes at X. In this case, according to (2.4) and (2.7), the product $A\cdot B$ vanishes for both the acoustical and the optical modes, and we can calculate $a(X\mathrm{L})$ and $b(X\mathrm{L})$ from (2.5). A certain ambiguity remains, since a given particle mass, say m_α, may be connected with either $\omega(X,\mathrm{LA})$ or $\omega(X,\mathrm{LO})$. For GaAs, for instance, which consists of atoms that are very close in the Periodic Table ($m_\beta/m_\alpha=1.075$), we can take the eigenfrequencies at X from neutron scattering data,[12] and if we relate the lighter mass m_α to $\omega(X,\mathrm{LO})$ we obtain $a/b=1.05$; the alternate case yields $a/b=0.83$. As another example, let us take AlSb, which shows a mass ratio of 4.51. Associating the light mass with $\omega(X,\mathrm{LO})$ and accepting Kaplan and Sullivan's frequency assignments[13] for the infrared lattice bands measured by Turner and Reese,[14] we get $a/b=1.12$. This indicates that even strongly different masses are not incompatible with a ratio $a/b\approx 1$.

If we assume the ratio a/b to be independent of wave vector and polarization, we can calculate a/b from the longitudinal eigenfrequencies at X, and then obtain the amplitude ratios for the other modes of interest from Eqs. (8.2)–(8.4).

In GaAs, under the assumption of a constant $a/b=1.05$, the ratios (8.3) and (8.4) for the transverse modes at X and L have values close to unity. For the longitudinal modes we obtain ratios (8.3) and (8.4) of 0.63 and 1.70, respectively; these values deviate from unity by more than those for the transverse modes, but still may lead to weak interactions.

In AlSb, with $a/b=1.12$, we obtain for TA at X an amplitude ratio of 0.81 or 0.71, depending upon whether we use the frequency assignments of Kaplan and Sullivan[13] or Johnson[15]; for TA at L, with Johnson's frequency assignments, the amplitude ratio becomes 0.83; all other modes yield amplitude ratios strongly deviating from unity. This result may be generalized by stating that for zinc-blende structures built up of elements from different rows of the periodic system, a ratio of the magnitudes of the displacement amplitudes close to unity would have to be considered accidental for the modes under consideration, with the exception of TA at X or L.

9. THIRD-ORDER POTENTIAL

The energy per unit cell connected with an elastic strain of the diamond structure may be written as

$$H=H(0\alpha)+H(0\beta), \tag{9.1}$$

where[5]

$$\begin{aligned} H(0\beta)=a^{-3}\Big\{&2\alpha\sum_{m}[\lambda_{mm}(0\beta)]^2+2\beta\sum_{m,n}{}'[\lambda_{mn}(0\beta)]^2\\ &+\frac{8}{3}\gamma\sum_{m}[\lambda_{mm}(0\beta)]^3+\frac{8}{3}\delta\sum_{m,n}{}'[\lambda_{mn}(0\beta)]^3\\ &+8\epsilon\sum_{m,n}{}'\lambda_{mm}(0\beta)[\lambda_{mn}(0\beta)]^2\Big\}, \end{aligned} \tag{9.2}$$

with a the lattice constant. The sums extend over the nearest neighbors $(m\alpha)$ of (0β), and the primes at the double sums indicate omission of the terms with $m=n$. The expression for $H(0\alpha)$ is analogous. When expanded according to (6.1) and (6.2), each of the five terms in (9.2) contains expressions of third degree in the particle displacements $\mathbf{u}$; the collection of these expressions yields the cubic anharmonic interaction of a particle with its neighbors. We shall use the same decomposition for zinc-blende structures. In N4[2] we discussed the effect of the α and γ terms on the third-order potential; here we shall retain the cubic contributions of all five terms.

To investigate the interaction of a fundamental phonon $(0f)$, that is, a transverse-optical phonon at $\mathbf{q}=0$, with the pair of phonons $(\mathbf{q}j)$ and $(-\mathbf{q}j')$, we substitute these three phonons in (5.2) and retain only those products of $\mathbf{u}$'s in (9.2) which contain each phonon exactly once. It will be convenient to introduce normalization factors

$$[N(\mathbf{q}j)]^2=\{m_\alpha[w(\alpha|\mathbf{q}j)]^2+m_\beta[w(\beta|\mathbf{q}j)]^2\}/m^*, \tag{9.3}$$

with

$$1/m^*=1/m_\alpha+1/m_\beta. \tag{9.4}$$

From the normalization of the polarization vectors[16] it follows that

$$N(\mathbf{q}j)=[h/2m^*\omega(\mathbf{q}j)]^{1/2}. \tag{9.5}$$

Using the phase factors of Table II, we can calculate the contributions of the modes $(\mathbf{q}j)$ and $(-\mathbf{q}j')$ to λ. For the

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[11] A. J. E. Foreman and W. M. Lomer, Proc. Phys. Soc. (London) **B70**, 1143 (1957).

[12] J. L. T. Waugh and G. Dolling, Phys. Rev. **132**, 2410 (1963); G. Dolling and J. L. T. Waugh, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon Press, Ltd., London, 1965), p. 19.

[13] H. Kaplan and J. J. Sullivan, Phys. Rev. **130**, 120 (1963).

[14] W. J. Turner and W. E. Reese, Phys. Rev. **127**, 126 (1962).

[15] F. A. Johnson, in *Progress in Semiconductors*, edited by A. F. Gibson and R. E. Burgess (Heywood Books, London, 1965), Vol. 9, p. 179.

[16] D. A. Kleinman, Phys. Rev. **118**, 118 (1960).

fundamental mode we employ the relation[16]

$$w(\alpha|0f)-w(\beta|0f)=N(0f)\hat{\mathbf{\mu}}, \qquad (9.6)$$

where the direction $\hat{\mathbf{\mu}}$ of the polarization of the fundamental mode may be chosen arbitrarily. The cubic interaction energy H is then written in the form

$$H(0f,\mathbf{q}j,-\mathbf{q}j')=(\tfrac{1}{4}a)^3N(0f) \times N(\mathbf{q}j)N(-\mathbf{q}j')V(0f,\mathbf{q}j,-\mathbf{q}j'). \qquad (9.7)$$

We shall call V the reduced third-order potential. The information obtained from Table II and the resulting V refer to $\mathbf{q}$ at $X=(2\pi/a,0,0)$ and $L=(\pi/a,\pi/a,\pi/a)$. Corresponding V's can be derived at the two other X points and the three other L points of the first Brillouin zone. Averaging $|V|^2$ over symmetrically equivalent wave vectors and averaging over the degenerate transverse branches, one finally obtains $\langle|V|^2\rangle$, which is independent of the choice of $\hat{\mathbf{\mu}}$. For Ge, Keating[5,6] gives the values $\alpha=0.38$, $\beta=0.12$ (in 10^5 dyn/cm), and $\gamma=-2.72$, $\delta=0.34$, $\epsilon=0.48$ (in 10^{12} dyn/cm^2). For GaAs, we have assumed a constant ratio of $a/b=1.05$, as discussed in Sec. 8, and, using the measured frequency values,[12] we have calculated the amplitude ratios from Eqs. (8.3) and (8.4). The coefficients α through ϵ can be derived from the elasticity measurements by Drabble and Brammer[17] and are given in the Appendix. The lattice constants[18] are $a=5.658\times10^{-8}$ cm for Ge and 5.646×10^{-8} cm for GaAs. Table V lists the resulting values for $\langle|V|^2\rangle$ and compares them with the contribution of the γ term in Ge.[19] Table V shows a number of features which deserve discussion:

(i) In Ge, the longitudinal acoustical and optical modes at X degenerate into L(X). To facilitate comparison with GaAs, we have defined LA(X) and LO(X) in Ge as the limits of $\mathbf{q}\rightarrow X$ along Δ and have listed their contributions separately.

(ii) Let us consider the vanishing interactions. The γ term for Ge is diagonal central in λ' and therefore obeys all of our NSRK. Furthermore, the longitudinal overtones at X are forbidden for all cases because of the GSR for infrared two-phonon absorption in zinc-blende structures, for which effect the third-order potential is instrumental. There remains to be explained the vanishing of the γ term and the total interaction for TA+TO at X in Ge, as well as the vanishing of the total third-order potential for a number of combinations in Ge with $\mathbf{q}$ at L. These features turn out to be forbidden according to the GSR for a third-order potential. A scalar potential transforms as $\Gamma^{(1+)}$, and the GSR are then identical with the GSR for three-phonon Raman processes in samples of diamond structure in powdered form, if depolarized Raman scattering is excluded. Such GSR are given by Birman,[1] and all three-phonon combinations in Birman's Table III which are either $R(dp)$ or not Raman active at all lead to a vanishing third-order potential.[20] In application to our Table III, where one phonon is in the mode O(Γ), the group-theoretically forbidden combinations $j+j'$ for a normal crystal of diamond structure are

$$\begin{aligned}&\text{TA+TO at } X;\\ &\text{LA+LO,}\quad \text{LA+TA,}\quad \text{LO+TO,}\quad \text{TA+TO at } L.\end{aligned} \qquad (9.8)$$

For an anomalous crystal the roles of LA and LO must be interchanged. Notice that the combinations at L in (9.8) are the same as those in case (c) of our NSRB and NSRK, but the GSR (9.8) hold, of course, for an arbitrary form of the third-order potential. All of the zeros in our Table V have, therefore, been traced back to selection rules.

TABLE V. Reduced third-order potential, magnitude squared and averaged, for interaction of the phonons ($0f$), ($\mathbf{q}j$), and ($-\mathbf{q}j'$), in units of 10^{24} dyn^2/ cm^4.

	$\mathbf{q}$ at X point			$\mathbf{q}$ at L point		
Branches $j+j'$	Ge γ term	Ge total	GaAs total	Ge γ term	Ge total	GaAs total
2 LA	0	0	0	0.206	0.137	0.229
LA+LO	2.47	0.85	0.73	0	0	0.274
2 LO	0	0	0	16.6	8.7	7.84
LA+TA	0	0.018	0.030	0	0	0.002
LA+TO	4.93	3.07	2.94	3.29	2.41	2.21
LO+TA	0	0.018	0.013	0	0.004	0.007
LO+TO	4.93	3.07	3.22	0	0	0.151
2 TA	0	0.130	0.125	0	0.043	0.048
TA+TO	0	0	0.0002	0	0	0.001
2 TO	4.93	3.46	3.49	8.22	6.65	6.74

(iii) For 2LA at L, the γ term in Ge does not vanish but is rather small. It is shown analytically in $N3$ that for a normal crystal with amplitudes of equal magnitudes at the two lattice sites, the γ term for 2LA at L is smaller by a factor of 81 than for 2LO at L; in a crystal anomalous at L, the situation is reversed.

(iv) A comparison of the values of the γ term with the total interaction in Ge shows that the differences are by no means negligible. Nevertheless, those modes which lead to vanishing γ terms give but small values for the total interaction. A more detailed analysis shows that for all the nonvanishing combinations and overtones in Table V, the dominant term comes either from γ or α. Analytical expressions for the contributions of α plus γ terms at L in crystals of the diamond structure are given in N4.

(v) The coefficients α through ϵ of the third-order potential have rather similar values in Ge and GaAs. The differences in the values of $\langle|V|^2\rangle$ in Ge and GaAs are, therefore, primarily due to the fact that the ratio of the magnitudes of the amplitudes in GaAs deviates from unity. Again, while the relative differences be-

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[17] J. R. Drabble and A. J. Brammer, Solid State Commun. 4, 467 (1966).

[18] J. D. H. Donnay and W. Nowacki, *Crystal Data* (Geological Society of America, New York, 1954).

[19] Analytical expressions for the contribution of the γ term to the matrix elements of two-phonon absorption are given in $N3$.

[20] We are indebted to Professor J. L. Birman who confirmed in private communication that the single combination TO(X)+TA(X)+O(Γ) in Table III of Ref. 1 should be $R(dp)$ instead of R.

tween Ge and GaAs are not necessarily small, it remains true that small or vanishing values in Ge correspond to small values in GaAs.

10. MODELS OF TWO-PHONON ABSORPTION

The anharmonic interaction energies responsible for infrared two-phonon absorption are the third-order potential[16] and the second-order dipole moment.[21] For zinc-blende structures, both mechanisms are active[22]; for diamond structures, only the last one.

The matrix element for absorption of a photon of frequency ω and creation of two phonons, due to a third-order potential of the form of the γ term in the previous section, has been given by Kleinman.[16] This matrix element, magnitude squared and averaged over symmetrically equivalent directions and over degenerate modes, is related to the interaction H in (9.7) according to

$$\langle |M|^2\rangle \propto \omega(\omega^2-\omega^2{}_f)^{-2}\langle |H|^2\rangle, \qquad (10.1)$$

where ω_f is the frequency of the fundamental phonon. The relation (10.1) is independent of the form of the third-order potential. By taking the entries for GaAs in Table V and multiplying them by $1/\omega(\mathbf{q}j)\omega(-\mathbf{q}j')$ and the frequency factors in (10.1), we obtain a measure for the strength of two-phonon absorption at the X and L points in this material, with an anharmonic interaction due to a five-parameter third-order potential. The division by the eigenfrequencies will boost the relative strength of those features involving TA, but the combinations involving this mode will still be weak.

The NSR refer to interactions at X and L. How do the interactions change in the vicinity of these symmetry points? The answer depends upon how the conditions on which the NSR are based are satisfied by (a) the phases and directions of the harmonic amplitudes, and (b) the magnitudes of the harmonic amplitudes and the form of the anharmonicities. At a symmetry point, for a "forbidden" feature, (a) strictly satisfies the NSR, while (b) is responsible for any deviations of the matrix element from zero. Moving away from the symmetry points, the contribution due to (a) increases rapidly, while that of (b) stays approximately constant. The total behavior depends upon whether (a) or (b) is dominant. An example is provided by the matrix elements of two-phonon absorption along Δ and Λ for a zinc-blende model with noncentral harmonic and central anharmonic nearest-neighbor interaction, as calculated in N2. For strongly different masses, as in AlSb, the contributions of (b) are dominant; the forbidden matrix elements at X and L are moderately small and (after removal of the resonance denominator) stay approximately constant through nearly half of the the Brillouin zone along Δ and Λ. For a mass ratio close to unity, as in GaAs, the "forbidden" matrix elements at X and L are much smaller than those in AlSb; they increase rapidly due to (a) when leaving the symmetry points, and then level off at about the values obtained for AlSb. A more realistic model, containing noncentral anharmonic contributions, would give a stronger contribution by (b). This would tend to fill the minima at X and L in GaAs, while —if the noncentral portion of the anharmonicity is not too large—it will have little effect in AlSb.

To show the effect of the matrix elements on absorption, if only in the simplest possible case, we have calculated and compared in N1 the two-phonon density of states and two-phonon absorption for a zinc-blende model with central (harmonic plus cubic anharmonic) nearest-neighbor interaction. The result agrees with the discussion in the preceding paragraph; in particular, for a mass ratio such as in GaAs, the strong P_2 type singularity[23] in the joint density of states for LO+TO at L is cut off in absorption and replaced by a smooth and much weaker maximum at a somewhat lower frequency.

The results of our model calculations involving the third-order potential are well in agreement with the NSR. It would be of interest to perform a similar calculation for the second-order dipole moments in zinc-blende structures, but no numerical data for these dipole moments are available.

A special situation arises for the second-order dipole moment in diamond structures. Symmetry and invariance considerations show[24] that for pure nearest-neighbor interaction the coefficients of the second-order dipole moment in diamond structures vanish. Our two-particle NSR are then trivially satisfied. If second-neighbor interactions are taken into account, then nonvanishing first-neighbor contributions will occur, but the first- and second-neighbor matrix elements will be of the same order of magnitude. The two-particle NSR can then provide no help in distinguishing the intensities of the various combinations. To see if those of the NSRK which include the effects of second neighbors via three-particle interactions are applicable, we performed a numerical calculation of the second-order dipole moment in diamond, based on the values of the parameters for second-neighbor interaction given by Wehner *et al.*[25] The analysis shows, however, a considerable contribution by the nondiagonal noncentral terms for which no NSRK exist.

11. COMPARISON WITH EXPERIMENT

The size of an observed multiple-phonon feature may depend on, among others, the following factors: the densities of states, occupation probabilities, frequency

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[21] M. Lax and E. Burstein, Phys. Rev. **97**, 39 (1955).

[22] B. Szigeti, Proc. Roy. Soc. (London) **A258**, 377 (1960); P. N. Keating, Phys. Rev. **140**, A369 (1965).

[23] For the general shape of the contribution of such a singularity to the density of states see, e.g., F. A. Johnson and R. Loudon, Proc. Roy. Soc. (London) **A281**, 274 (1964).

[24] R. Szigeti, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon Press, Ltd., Oxford, 1965), p. 405; R. Wehner, Phys. Status Solidi **17**, K179 (1966).

[25] R. Wehner, H. Borik, W. Kress, A. R. Goodwin, and S. D. Smith, Solid State Commun. **5**, 307 (1967).

factors, and the specific anharmonic interaction which couples the phonons in the process under consideration. By dividing the anharmonic interaction by the magnitudes (9.5) of the (six-component) polarization vectors of the participating phonons, we obtain the "reduced" interaction; this is the quantity with which we shall be concerned.

The simplest example of a coupling of phonons is presented by the harmonic potential Φ. The eigenvalue problem may formally be written

$$\omega^2 = \sum_{ll'} u(l)^*\Phi(l,l')u(l')/\sum_{l''} m(l'')u(l'')^*u(l''), \quad (11.1)$$

where the summations extend over all particles of the lattice and over all components. Here we consider Φ as an "anharmonicity" which couples two phonons of the same mode; the denominator serves as a normalization factor similar to (9.3). If the conditions of NSRB (a) were strictly satisfied, then ω^2 for TA at X and L should vanish. Actually, $\omega_{\mathrm{TA}}{}^2$ at L and X in Si, Ge, and GaAs is found from neutron scattering data[26] to be an order of magnitude smaller than $\omega_\nu{}^2$ for the other branches ν at the zone boundary. This suggests that the central nearest-neighbor interaction dominates the harmonic potential and that the amplitudes of the transverse acoustical mode at the two lattice sites of GaAs are of approximately equal magnitude. The latter conclusion on the amplitudes in GaAs is in agreement with our findings in Sec. 8, which are based on a different kind of reasoning.

Gallium arsenide is the only III-V compound for which neutron scattering data are available. Another source for the determination of the phonon spectrum are two-phonon absorption[27] and emittance[28] bands. If we allow for certain ambiguities in the assignments of the critical point frequencies, the ratios $\omega_{\mathrm{TA}}/\omega_{\mathrm{TO}}$ at X and L for AlSb, GaP, GaAs, InP, InAs, and InSb probably lie between about $\frac{1}{3}$ and $\frac{1}{6}$. For GaSb the "characteristic" phonon frequencies[27] give a similar ratio. No data are available for AlP and AlAs, but we expect frequency ratios in the same range. For AlP this assumption finds support in the fact that the ratio c_{12}/c_{11} of the elastic constants[9] is almost identical with that for Si and Ge. We conclude that for each of the III-V compounds the amplitude ratio of the transverse acoustical modes at the two lattice sites is close enough to unity to approximately satisfy the NSR.

An example for the coupling of two phonons of the same mode through the third-order potential is represented by the Grüneisen constants.[3,29] The measurement[30] of the Grüneisen constants in Ge at the L point yields a value for the transverse acoustical mode slightly smaller than that for the other branches. To obtain the reduced interaction for mode ν, we divide by a frequency factor $1/\omega_\nu$ which is inherent to the definition of the Grüneisen constant, and by another factor $1/\omega_\nu$, which originates from the magnitudes (9.5) of the polarization vectors. The resulting reduced interaction is smaller by a factor of 15–60 for TA than for the other branches.

In Secs. 9 and 10 the NSR have been found to be in satisfactory agreement with the results for certain models of two-phonon absorption. A more direct check of the applicability of the NSR can be obtained from observed multiple-phonon bands,[27,28] provided that we have enough information on the density of states. For GaAs, part of this information can be obtained from neutron scattering data.[12] To reduce the interaction, we have to divide by the frequency factors in (10.1), the squares of (9.5) for each participating mode, and the appropriate combinations of occupation probabilities. This reduction is particularly important for processes involving TA. A case where the weakness of the interaction can be seen even without previous reduction is that of LO+TO at L. We expect the joint density of states to exhibit there a reasonably strong singularity, probably of type P_2[23]; in comparison, the measured absorption spectrum[15,31] in that region shows a flat maximum with very weak singularities superimposed. The flat maximum is essentially similar to what we have obtained from our simple GaAs model in N1, and the weakness of the singularity suggests that the relevant conditions of the NSR are approximately satisfied.

Finally, let us take a look at Geick's[32] comparison of multiple-phonon absorption in Ge and GaAs. After removal of the resonance denominator, it is found that in the regions $1.2 \leq \Omega \leq 1.5$ and $2 \leq \Omega \leq 3$, with $\Omega = \omega/\omega_f$ the reduced frequency, the effect of the nonlinear dipole moment is of the same order of magnitude as that of the anharmonic potential. This makes the absorption (or, more accurately, the damping functions) of Ge and GaAs agree in those regions. The situation is different for $1.5 \leq \Omega \leq 2$, where the damping function of Ge is noticeably weaker than that of GaAs. Geick suggests this is due partly to the difference in the selection rules and partly to the fact that two-phonon absorption in GaAs originates from two-particle interactions, whereas the second-order dipole moment in Ge ensues from three-particle interactions. In agreement with our previous considerations, three-particle interactions are expected to be weak compared to two-particle interactions, which explains the weakness of the second-order dipole moment in diamond structures. But why, then, do the damping functions of Ge and GaAs agree for $1.2 \leq \Omega \leq 1.5$? The reason for this can be related to the NSR for GaAs. The two-phonon summation bands in this region mainly consist of combinations involving the

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[26] A collection of data is contained in Ref. 15.

[27] W. G. Spitzer, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic Press Inc., New York, 1967), Vol. 3, p. 17.

[28] D. L. Stierwalt and R. F. Potter, in Ref. 27, Vol. 3, p. 71.

[29] A. A. Maradudin, Phys. Status Solidi **2**, 1493 (1962).

[30] R. T. Payne, Phys. Rev. Letters **13**, 53 (1964).

[31] W. Cochran, S. J. Fray, F. A. Johnson, J. E. Quarrington, and N. Williams, J. Appl. Phys. Suppl. **32**, 2102 (1961).

[32] R. Geick, Phys. Rev. **138**, A1495 (1965).

mode TA. According to the NSR, these combinations are forbidden for **q** at X and L, and, according to Sec. 10, these combinations are expected to stay rather weak, even away from X and L. Consequently, the damping function of GaAs in that region is depressed to the level of Ge.

12. CONCLUSIONS

The utility of the NSR lies in predicting, explaining, and correlating certain anharmonic processes which are unexpectedly weak. We shall summarize the assumptions underlying the NSR and the extent to which these assumptions seem to be satisfied, and shall make some tentative predictions.

(a) Normality: Si and Ge are normal, whereas diamond is anomalous for the longitudinal modes at the L point. The III-V compounds are expected to be normal (see Sec. 3).

(b) Harmonic amplitudes: The NSR assume, for certain of the modes, an harmonic amplitude ratio (8.1) of magnitude one. For diamond structures this is trivially satisfied. For zinc-blende structures, for lack of any better model, the amplitude ratios can be calculated from frequency ratios under the assumption of constant a/b, according to Sec. 8. For the transverse modes at X or L in GaAs, we obtain deviations of the amplitude ratio from unity of the order of 10%; for the longitudinal modes at L the deviation is stronger, but not so strong as to render the NSR inapplicable. We expect InSb to behave similarly. For AlP (which, like GaAs and InSb, has a mass ratio close to unity) there exist no frequency data, but—barring any proof to the contrary—we shall assume it to exhibit amplitude ratios similar to GaAs. The remaining III-V compounds are made up of atoms with distinctly dissimilar masses, and the only modes of interest with an expected amplitude ratio in the vicinity of unity are TA at X and L (see Secs. 8 and 11).

(c) Existence of anharmonic two-particle interactions: Before applying the NSR, it must be determined if pure nearest-neighbor two-particle interactions can exist for the process in question, or if such interactions are prohibited altogether by symmetry and invariance conditions. Such an investigation involves no data other than the symmetries of the interaction and of the crystal, and lies outside the realm of the NSR or the usual GSR. In the example of two-phonon absorption, genuine two-particle interactions exist for zinc-blende structure, but not for diamond structures.

(d) Higher-order neighbors: The NSR refer to anharmonic nearest-neighbor interactions but neglect the contributions of higher-order neighbors. Are such rules of practical relevance? For the two-particle NSR, according to the examples of Sec. 11, the answer is yes. For the utility of NSR which involve three or more particles, we have no positive evidence; such NSR can become important only where two-particle interactions are ineffective (Sec. 10), and will depend on the formalism employed. Examples for many-particle rules are the nondiagonal or noncentral NSRK of Table IV; other formalisms are available,[33,34] but have not been investigated in this connection.

(e) Reduced interactions: The quantities to be compared in an application of the NSR to experiment are the reduced interactions (Sec. 11). The factors involved in this reduction depend on occupation probabilities, eigenfrequencies, etc., which are usually known.

The NSR have been formulated rigorously in Secs. 5 and 6. For a practical application, at least at our present state of knowledge, the fine distinctions drawn there between the various cases are perhaps confusing rather than helpful. To obtain rules which can readily be compared with experiment, we combine the above propositions with the NSR in Tables III and IV. If genuine anharmonic two-particle interactions exist, we propose the following rules:

(i) Reduced interactions in Si, Ge, and the III-V compounds are expected to be weak for TA at X or L and for all overtones, combinations, and general combinations involving these modes.

(ii) Reduced interactions in Si, Ge, AlP, GaAs, and InSb are furthermore expected to be weak for all combinations and general combinations involving LALO or LOTO at L.

Examples of processes where these rules should be applicable are the two- and more-phonon summation and difference bands in zinc-blende structures. A reduced interaction proposed as weak is expected to have an intensity of $\frac{1}{10}$ or less than the dominating intensities of the allowed modes. Let us emphasize that the conditions for such an intensity ratio are not stringent at all. Where allowed, a predominance of the two-particle over the more-particle interactions by a factor of at least 3 seems perfectly reasonable, and because of the dependence of absorption on the squares of the matrix elements, this will give the desired effect. As far as the amplitudes are concerned, the ratio of "allowed" to "forbidden" interactions is essentially that of the sum over the difference of the amplitudes. For an amplitude ratio deviating from unity as much as 2 to 1, this leads to a ratio of $(2+1)/(2-1)$, the square of which again yields the desired magnitude.

For diamond, which is anomalous, the modes of rule (i) remain unchanged, whereas in rule (ii) the combination LOTO has to be replaced by LATO. However, connected with the anomaly—or better, the source of the anomaly—are unusually large three-particle contributions to the harmonic forces. This fact suggests strong three-particle contributions also for the anharmonic

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

[34] M. J. P. Musgrave and J. A. Pople, Proc. Roy. Soc. (London) **A268**, 474 (1962); H. L. McMurry, A. W. Solbrig, J. K. Boyter, and C. Noble, J. Phys. Chem. Solids **28**, 2359 (1967).

interactions, which may make two-particle rules for diamond rather ineffective.

If no genuine two-particle interactions exist, the process is expected to be weak throughout (see the comparison of two-phonon absorption in Ge and GaAs in Sec. 11).

Rules (i) and (ii) are formulated for symmetry points but, clearly, they also affect a certain vicinity of these points. A discussion of the sources which determine the behavior of interactions in the vicinity of X and L has been given in Sec. 10. We distinguish three cases: First, the interactions of rule (i) for AlAs, AlSb, GaP, GaSb, InP, and InAs are expected to change but little in the vicinity of X and L. Second, the interactions referred to in rule (ii) are expected to grow strongly when leaving L. The third case comprises the interactions of rule (i) for Si, Ge, AlP, GaAs, and InSb. In this case the outcome is undecided: The interactions are expected to be weak along Δ and Λ, and therefore at X and L, but they may or may not exhibit minima at these points.

With an increasing body of experimental information, it will become progressively easier to establish the exact range and degree of applicability of our rules and to answer those questions which we have had to leave undecided. Within this range, rules of the type of our NSR will be useful for a semiquantitative classification of interaction features as "weak" or "strong," and for a correlation of the weak features.

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APPENDIX

We sketch here a calculation of the coefficients of the second- and third-order potential in GaAs. The second- and third-order elastic constants of GaAs have been measured by Drabble and Brammer.[17] Ignoring the complications introduced by the fact that the two kinds of lattice positions are occupied by particles of opposite charges, we analyze the elastic constants according to Keating's equation (10) of Ref. 5 and Eq. (5) of Ref. 6, established there for crystals of diamond structure. An unweighted nonlinear least-squares approximation of the second-order elastic constants of GaAs leads to $\alpha=0.391$, $\beta=0.098$ (in 10^5 dyn/cm). Employing these values for α and β, we then obtain from an unweighted least-squares analysis of the third-order elastic constants the coefficients $\gamma=-2.72$, $\delta=0.34$, and $\epsilon=-0.45$ (in 10^{12} dyn/cm^2). The measured values of the elastic constants and the values calculated from the above coefficients are given in Table VI; for comparison we also show the values measured by McSkimin and Andreatch.[35]

TABLE VI. Calculated and measured values of second- and third-order elastic constants for GaAs in units of 10^5 dyn/cm and 10^{12} dyn/cm^2, respectively.

Elastic constants	Calculated	Measured[a]	Measured[b]
C_{11}	1.22	1.19	1.19
C_{12}	0.52	0.54	0.54
C_{44}	0.56	0.60	0.59
C_{111}	−7.16	−6.75	−6.22
C_{112}	−3.52	−4.02	−3.87
C_{123}	−0.34	−0.04	−0.57
C_{144}	0.03	−0.70	0.02
C_{166}	−2.86	−3.20	−2.69
C_{456}	−0.18	−0.69	−0.39

[a] Reference 17.
[b] Reference 35.

The agreement between theory and experiment is reasonably good, particularly in view of the discrepancies between the two sets of measured values for the third-order elastic constants. A better agreement between calculated and measured values can be achieved by relaxing the theoretical connection between second- and third-order elastic constants, as has been done by Singh and Verma,[36] but such an independent treatment of second- and third-order constants is unsuitable for our specific purpose.

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[35] H. J. McSkimin and J. R. Andreatch, J. Appl. Phys. **38**, 2610 (1967).

[36] R. P. Singh and G. S. Verma, J. Appl. Phys. **39**, 4032 (1968).