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Symmetry and Reststrahlen in Elemental Crystals

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Lattice vibrations in elemental crystals can possess a first-order electric moment, and thus exhibit reststrahlen (symmetry-allowed one-phonon infrared absorption), by the mechanism of displacement-induced charge redistribution (dynamic charge). By a group-theoretical investigation of the relation between symmetry and reststrahlen, we show that *a necessary and sufficient condition for the existence of reststrahlen in an elemental crystal is a structure with at least three atoms in the primitive unit cell*, $s\geq 3$. Using n_ν^{ir} for the number of infrared-active phonon frequencies (reststrahlen bands), this minimum-complexity condition states: (a) $n_\nu^{\mathrm{ir}}=0\leftrightarrow s=1$ or 2; (b) $n_\nu^{\mathrm{ir}}\geq 1\leftrightarrow s\geq 3$. To derive (a) and (b), group-theoretical arguments are used to determine the number of infrared-active phonons and phonon frequencies, and thereby the form of the effective charge tensor $(\partial\mathbf{p}/\partial\mathbf{u})$, in terms of crystal symmetry (group characters) and unit-cell structural complexity (structure factors specifying the number of sublattices invariant under factor-group symmetry operations). The proof of (a), $s\geq 3$ as a structural requirement for a reststrahlen-displaying elemental crystal, follows from these results and the observation that all $s=2$ elemental crystals possess an inversion operation which interchanges the two sublattices; (a) is equivalent to a generalization of the Lax-Burstein argument for the vanishing first-order moment in Ge. The demonstration of (b), $s\geq 3$ as a sufficient condition for a first-order moment, is obtained by developing an inequality relating n_ν^{ir}, s, and g (the order of the factor group), and by considering the highest-symmetry crystal classes in some detail. Other applications of his approach, to compounds as well as elemental crystals, are discussed.

1. INTRODUCTION

THE highly successful application of the rigid-ion model to lattice vibrations in ionic crystals,[1] taken together with the absence of ionic charge in a crystal composed of identical atoms, has sometimes led to the assumption[2] that elemental nonmetallic crystals cannot exhibit reststrahlen—allowed one-phonon infrared absorption. This widespread impression has been reenforced by the circumstance that for the familiar group-IV semiconductors (C,Si,Ge) the zone-center optical phonons are indeed infrared-inactive. As a general statement, however, this idea is incorrect. Lattice vibrations in elemental crystals can possess a first-order electric moment, and thus exhibit reststrahlen, by the mechanism of displacement-induced charge redistribution (dynamic charge).[3,4] The following paper[4] discusses a shell-model analysis of effective charges in two important examples, the reststrahlen-displaying elemental semiconductors Se and Te.

The purpose of this paper is to present a group-theoretical investigation of the relation between symmetry and reststrahlen in elemental crystals. The principal result obtained is the derivation of the following dependence on structural complexity: An elemental crystal displays symmetry-allowed one-phonon absorption if and only if the primitive cell contains three or more atoms. Letting s denote the number of primitive-cell atoms and n_ν^{ir} the number of infrared (ir) active eigenfrequencies (number of reststrahlen bands), we may express this as

$$n_\nu^{\mathrm{ir}}=0\leftrightarrow s=1 \text{ or } 2\,, \tag{1.1}$$

$$n_\nu^{\mathrm{ir}}\geq 1\leftrightarrow s\geq 3\,. \tag{1.2}$$

Here (1.1) states that $s\geq 3$ is a necessary minimum-complexity condition for the occurrence of reststrahlen in an elemental crystal, and (1.2) indicates that this condition is sufficient as well as necessary. Hence, the absence of reststrahlen for Ge (for which $s=2$), and its presence for Se ($s=3$).

In order to demonstrate both (1.1) and (1.2), we develop expressions for n_ν^{ir} in terms of crystal symmetry (group characters) and unit-cell structure (structure factors to be introduced). We can also obtain (1.1) by means of a straightforward generalization of the Lax-Burstein argument for the vanishing first-order moment in Ge, and begin with this simple proof in Sec. 2. In Sec. 3 we discuss the relation between the eigenvibration symmetries and the effective charge tensor, $\partial\mathbf{p}/\partial\mathbf{u}$. The group-theoretical formulation is presented in Sec. 4 and is applied to some simple situations for illustration. The results of this section are then used to derive (1.1) in Sec. 5 and (1.2) in Sec. 6, the latter requiring somewhat more work in that a detailed treatment of the highest-symmetry crystal classes is necessary. Further applications, to compounds and to a discussion of the maximum unit-cell complexity compatible with a single reststrahlen band, are given in Sec. 7.

2. STRUCTURAL REQUIREMENT FOR RESTSTRAHLEN-DISPLAYING ELEMENTAL CRYSTALS

We shall use s to denote the number of atoms in the primitive cell. (Henceforth we will frequently use "unit

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

[2] D. H. Martin, Advan. Phys. **14**, 39 (1965), especially p. 50, and Ref. 1, p. 87, lines 12 and 13.

[3] E. Burstein, M. H. Brodsky, and G. Lucovsky, in Proceedings of the Symposium on Atomic, Molecular, and Solid State Theory, Sanibel Island, 1967 (unpublished); Intern. J. Quantum Chem. **1S**, 759 (1967); W. Cochran, Nature **191**, 60 (1961).

[4] I. Chen and R. Zallen, following paper, Phys. Rev. **173**, 833 (1968).

cell" as an abbreviation for "primitive unit cell," the smallest translational unit of the crystal.) For crystals with $s=1$, of course, there are no optical branches and hence no reststrahlen. We will now show that for elemental crystals with $s=2$, the optical modes are necessarily infrared-inactive.

In 1955, Lax and Burstein (LB) demonstrated that the vanishing first-order electric moment (absence of reststrahlen) for Ge was a consequence of the following symmetry property of diamond-structure crystals[5]: an inversion center located midway between the two atoms of the unit cell. With the aid of unit-cell charge neutrality, LB showed the first-order moment to be invariant under this symmetry operation. Since a vector must reverse under inversion, the first-order moment must vanish for Ge.[6,7]

It does not seem to have been previously pointed out that the crucial symmetry property mentioned above is one which is possessed not only by the diamond structure but by every elemental crystal with $s=2$. This is easily seen by taking the origin of coordinates midway between the two atoms in a unit cell. The location of any atom is then given by $\mathbf{x}(l)\pm\boldsymbol{\varrho}$, where $\mathbf{x}(l)$ is a lattice vector and $\pm\boldsymbol{\varrho}$ are the positions of the two atoms in the cell containing the origin. Since $-[\mathbf{x}(l)\pm\boldsymbol{\varrho}]=\mathbf{x}(-l)\mp\boldsymbol{\varrho}$ is clearly also an atomic location, the chosen origin is a center of symmetry.

Thus $s=2$ elemental crystals cannot exhibit reststrahlen; the first-order moment is suppressed by symmetry. The following theorem, equivalent to (1.1), therefore follows as a simple extension of the LB proof:

Theorem. A necessary condition for the occurrence of reststrahlen in an elemental crystal is $s\geq 3$.

This condition sets a lower limit on the crystal-structure complexity which is compatible with the existence of a first-order moment in an elemental crystal. While even the simplest diatomic crystal, with a monomolecular unit cell ($s=2$), exhibits reststrahlen (See Secs. 4B and 7A), a monatomic crystal requires a unit cell containing at least three atoms in order to display one-phonon absorption.

3. EFFECTIVE CHARGE TENSOR

The linear relation between the unit-cell first-order moment $\mathbf{p}$ and the atomic displacements $\mathbf{u}$ may be expressed as[5]

$$\mathbf{p}=\mathbf{B}\mathbf{u}. \tag{3.1}$$

(Throughout this paper we will use boldface lower case letters for vectors, boldface capitals for matrices.) As $\mathbf{p}$ is a 3-vector and $\mathbf{u}$ a $3s$-vector, the coefficients joining them form a $3\times 3s$ rectangular matrix, $\mathbf{B}=\partial\mathbf{p}/\partial\mathbf{u}$. ($\mathbf{B}$ corresponds to b coefficient b_{21} in Huang's elegant macroscopic theory for diatomic ionic crystals.[1,8]) We shall refer to $\mathbf{B}$, the first-order electric-moment tensor, as the effective charge tensor.

The simplest nonvanishing $\mathbf{B}$ occurs for an ionic crystal with $s=2$. For NaCl in the rigid-ion approximation, the effective charge tensor has the following appearance in Cartesian coordinates (only nonvanishing matrix elements are shown),

$$\mathbf{B}=e\begin{bmatrix} 1 & \cdot & \cdot & -1 & \cdot & \cdot \\ \cdot & 1 & \cdot & \cdot & -1 & \cdot \\ \cdot & \cdot & 1 & \cdot & \cdot & -1 \end{bmatrix}. \tag{3.2}$$

This can be simplified to a form containing but three nonzero entries by transforming to symmetrized coordinates, $\mathbf{e}_{i\pm}=(1/\sqrt{2})(\mathbf{e}_i^{\mathrm{Na}}\pm\mathbf{e}_i^{\mathrm{Cl}})$, where $\mathbf{e}_i$ denotes a unit displacement in direction i:

$$\mathbf{B}=\sqrt{2}e\begin{bmatrix} \cdot & \cdot & \cdot & 1 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & 1 \end{bmatrix}. \tag{3.3}$$

The three nonvanishing elements correspond to the three polarizations of the optical phonons ($\mathbf{e}_{i-}$), all ir-active and equivalent by cubic symmetry. Since $B_{14}=B_{25}=B_{36}$, a single independent element specifies the full tensor.

For elemental crystals with $s=2$ (diamond structure, arsenic structure, hcp, etc.), the 3×6 effective charge tensor, by virtue of (1.1), contains only zeros.

The size ($3\times 3s$) of the smallest nonvanishing $\mathbf{B}$ for elemental crystals, in which the first-order moment is due entirely to charge-deformation effects, therefore occurs for $s=3$. A group-theoretical shell-model derivation of the effective charge tensor for Se and Te, for which $s=3$ and which are the simplest known reststrahlen-displaying elemental crystals, is given in the following article.[4] The form of the tensor for these trigonal crystals in the appropriate symmetrized coordinates, is as follows:

$$\mathbf{B}=\begin{bmatrix} \cdot & \cdot & \cdot & \cdot & B_{15} & B_{16} & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & B_{15} & B_{16} \\ \cdot & B_{32} & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{bmatrix}. \tag{3.4}$$

The five nonvanishing matrix elements correspond to the five ir-active optical modes; since symmetry requires four of these to occur as two pairs of degenerate vibrations, there are only three independent elements.

The two examples of (3.3) and (3.4) illustrate the connection between the symmetrized effective charge tensor and the symmetry of the unit cell normal modes: the number of nonvanishing matrix elements equals the number of ir-active eigenvibrations (n^{ir}), while the number of independent elements corresponds to the number of ir-active eigenfrequencies (n_ν^{ir}). For NaCl:

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

[6] M. Lax, Phys. Rev. Letters **1**, 131 (1958); **1**, 133 (1958).

[7] As Lax points out in Ref. 6, the one-dimensional proof of Ref. 5 carries over directly to the diamond structure. The analogous three-dimensional proof is explicitly given by M. Lax, Symmetry Principles in Solid State Physics (to be published).

[8] K. Huang, Proc. Roy. Soc. (London) **A208**, 352 (1951).

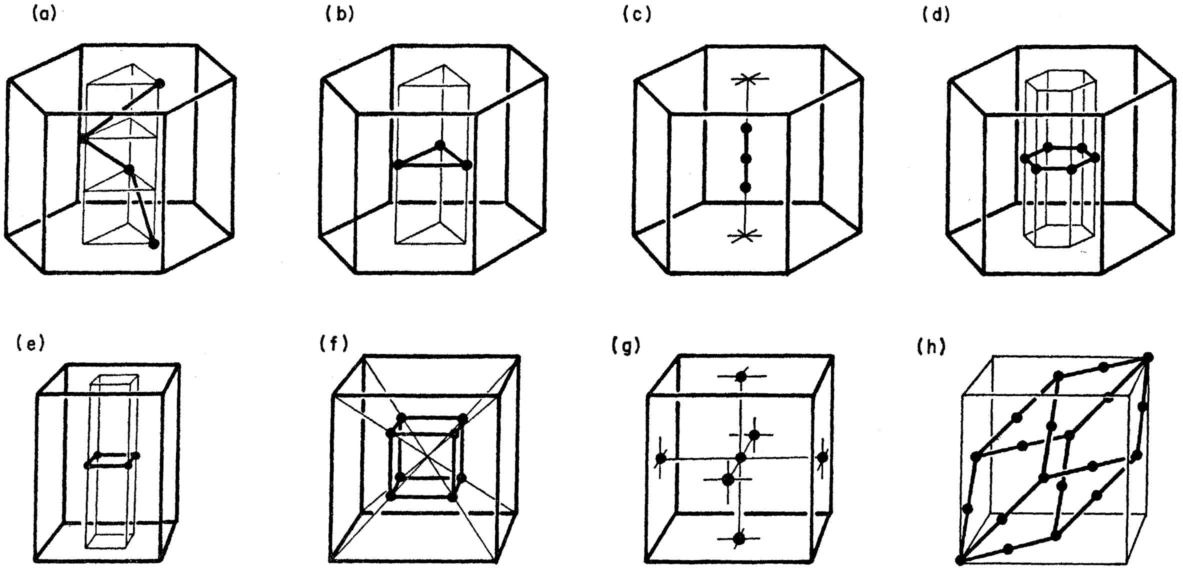

FIG. 1. Primitive cells for crystal structures discussed in the text. Table II lists the crystal symmetries and values of s, n_ν^{ir}, and n^{ir} for these structures.

$n_\nu^{\text{ir}}=1$, $n^{\text{ir}}=3$; for Se and Te: $n_\nu^{\text{ir}}=3$, $n^{\text{ir}}=5$. [The symmetrized **B**'s of (3.3) and (3.4) are obtained by expressing **u** in symmetrized coordinates and **p** in cartesian coordinates determined by symmetry axes. Thus in (3.4) for Se, p_3 is the dipole component parallel to the triad axis, p_1 the component parallel to a diad axis. When Cartesian bases are not defined by symmetry elements, as for triclinic and monoclinic crystals, the connection between **B** and n^{ir}, n_ν^{ir} is less simple than stated above.]

The unit-cell structure of trigonal Se is shown in Fig. 1(a). There are $s=3$ elemental crystal structures which would give rise to simpler one-phonon spectra, such as the hexagonal crystal of Fig. 1(b) discussed in the following section. For this structure $n_\nu^{\text{ir}}=1$ and $n^{\text{ir}}=2$, so that the 3×9 effective charge tensor contains just two equal, nonvanishing elements, and is much simpler than (3.4).

4. GROUP-THEORETICAL FORMULATION

In order for a displacement eigenvector $\mathbf{e}_j$ to induce a polarization with component $\mathbf{p}_i$ (i.e., $B_{ij}\neq0$), it must transform as does the x_i component of a vector. We introduce the following definitions and notation:

$G\equiv$ the crystal factor group, of order g;

α is an operation belonging to G;

$P\equiv$ the 3-dimensional polar-vector representation of G;

$\Gamma\equiv$ the $3s$-dimensional representation of G generated by the unit-cell atomic coordinates (the displacements of the s atoms in the primitive cell);

$\Gamma_i\equiv$ an irreducible representation (I.R.) of G;

$\Gamma_p\equiv$ a Γ_i occurring in the reduction of P (a vector I.R.), $\{\Gamma_p\}\subset\{\Gamma_i\}$.

The Γ_p's appearing in the reduction of Γ correspond to eigenvibrations which transform as vector components, and which thus may induce first-order moments. However, one P set of Γ_p's contained in Γ corresponds to the acoustical modes which, by unit-cell charge neutrality, induce no macroscopic polarization. Thus the number and type of ir-active modes are determined by the Γ_p's occurring in $\Gamma-P$. Group-theoretical analyses are outlined in Table I for NaCl, Ge, Se, and the structure of Fig. 1(b).

TABLE I. Group-theoretical analyses for reststrahlen in some simple crystals.

Crystal structure	Class[a]	s	Γ[b]	P	Γ-P	n_ν^{ir}	n^{ir}
NaCl, ZnS	$m3m$, $\bar{4}3m$	2	$2\Gamma_{15}$	Γ_{15}	Γ_{15}	1	3
Ge	$m3m$	2	$\Gamma_{15}+\Gamma_{25'}$	Γ_{15}	$\Gamma_{25'}$	0	0
Se	32	3	A_1+2A_2+3E	A_2+E	A_1+A_2+2E	3	5
Fig. 1(b)	$\bar{6}m2$	3	$A_1'+A_2'+A_2''+2E'+E''$	$A_2''+E'$	$A_1'+A_2'+E'+E''$	1	2

[a] The international short symbol (Ref. 13) is used for point-group symmetry.

[b] The notation for tne irreducible representations follows Ref. 12 for groups 32 and $\bar{6}m2$, while the familiar BSW notation is used for cubic symmetry [L. P. Bouckaert, R. Smoluchowski, and E. P. Wigner, Phys. Rev. **50**, 58 (1936)].

In order to develop expressions for n^{ir} and n_ν^{ir}, the number of ir-active vibrations and frequencies, we need to consider both the crystal symmetry (contained in Γ_i and P) and the unit-cell structure (contained in Γ). In the $3s$-dimensional representation Γ, the atomic displacements $\mathbf{u}_1, \mathbf{u}_2, \cdots, \mathbf{u}_s$ comprise a $3s$-vector $\mathbf{u}$, and each factor-group operator α is represented by a $3s\times 3s$ matrix $\mathbf{S}^\Gamma(\alpha)$.[9] Using the individual atomic displacement-vectors $\mathbf{u}_j$ as bases, we can write (showing a specific $\mathbf{S}^\Gamma$ for concreteness)

$$\mathbf{u}=\begin{bmatrix}\mathbf{u}_1\\ \mathbf{u}_2\\ \cdot\\ \cdot\\ \mathbf{u}_{s-1}\\ \mathbf{u}_s\end{bmatrix},\quad \mathbf{S}^\Gamma(\alpha)=\begin{bmatrix}\mathbf{S}^P(\alpha) & & & & & & \\ & \mathbf{S}^P(\alpha) & & & & & \\ & & \cdot & & & & \\ & & & \cdot & & & \\ & & & & 0 & \mathbf{S}^P(\alpha) & \cdot \\ & & & & \cdot & 0 & \mathbf{S}^P(\alpha) \\ & & & & \mathbf{S}^P(\alpha) & \cdot & 0\end{bmatrix}, \tag{4.1}$$

where the submatrix $\mathbf{S}^P(\alpha)$ is the 3-dimensional polar-vector representation of operator α. $\mathbf{S}^P(\alpha)$ appears s times in $\mathbf{S}^\Gamma(\alpha)$, all other elements vanishing. For each sublattice (unit-cell atomic site) which does not go over to another sublattice under α, $\mathbf{S}^P(\alpha)$ occurs on the diagonal of $\mathbf{S}^\Gamma(\alpha)$. Off-diagonal submatrices correspond to an interchange of sublattices under α; for example, the threefold permutation among sites $s-2$, $s-1$, and s which is illustrated in (4.1) corresponds to $\alpha=3$ (C_3), a threefold rotation.

Let $s(\alpha)$ be the number of sublattices not converted to other sublattices under symmetry operation α, i.e., the number of sublattices invariant under α. Then $\mathbf{S}^P(\alpha)$ appears $s(\alpha)$ times on the diagonal of $\mathbf{S}^\Gamma(\alpha)$, so that the characters of Γ, $\chi^\Gamma(\alpha)\equiv Tr\mathbf{S}^\Gamma(\alpha)$, are simply related to those of P by

$$\chi^\Gamma(\alpha)=s(\alpha)\chi^P(\alpha). \tag{4.2}$$

The g quantities $s(\alpha)$ contain all of the essential information about the primitive-cell structure which is needed in addition to the crystal symmetry G.

In general, Γ and P are reducible representations. $C(\Gamma,\Gamma_i)$ will be our notation for the number of times Γ_i is contained in Γ; similarly $C(P,\Gamma_p)$ will denote the number of times Γ_p is contained in P. From familiar representation theory[10,11] we can write

$$\begin{aligned}\chi^\Gamma(\alpha)&=\sum_{\Gamma_i} C(\Gamma,\Gamma_i)\chi^{\Gamma_i}(\alpha),\\ C(\Gamma,\Gamma_i)&=\left(\frac{1}{g}\right)\sum_\alpha \chi^\Gamma(\alpha)\chi^{\Gamma_i}(\alpha)^*;\end{aligned} \tag{4.3}$$

$$\begin{aligned}\chi^P(\alpha)&=\sum_{\Gamma_p} C(P,\Gamma_p)\chi^{\Gamma_p}(\alpha),\\ C(P,\Gamma_p)&=\left(\frac{1}{g}\right)\sum_\alpha \chi^P(\alpha)\chi^{\Gamma_p}(\alpha)^*.\end{aligned} \tag{4.4}$$

From the opening discussion of this section, it follows directly that the sets of integers $C(\Gamma,\Gamma_p)$ and $C(P,\Gamma_p)$ determine n_ν^{ir} and n^{ir}:

$$n_\nu^{\mathrm{ir}}=\sum\nolimits_{\Gamma_p}[C(\Gamma,\Gamma_p)-C(P,\Gamma_p)], \tag{4.5}$$

$$n^{\mathrm{ir}}=\sum\nolimits_p[C(\Gamma,\Gamma_p)-C(P,\Gamma_p)]\chi^{\Gamma_p}(1). \tag{4.6}$$

The negative second term within each sum avoids including the acoustical modes. The factor $\chi^{\Gamma_p}(1)$ appearing inside the sum for n^{ir}, the number of ir-active vibrations, is just the degeneracy of each of the ir-active eigenfrequencies counted in the expression for n_ν^{ir} ($\alpha=1$ denotes the identity operation, so that $\chi^{\Gamma_p}(1)$ is the dimensionality of Γ_p). In (4.3)–(4.6), $\sum_{\Gamma_i}$ indicates a sum over all of the I.R.'s of G, while $\sum_{\Gamma_p}$ indicates a sum taken only over the vector I.R.'s.

Substituting (4.2)–(4.4) into (4.5)–(4.6) yields expressions for n_ν^{ir} and n^{ir} which we will make extensive use of:

$$n_\nu^{\mathrm{ir}}=(1/g)\sum_{\alpha,\,\Gamma_p}[s(\alpha)-1]\chi^P(\alpha)\chi^{\Gamma_p}(\alpha)^*, \tag{4.7}$$

$$n^{\mathrm{ir}}=(1/g)\sum_{\alpha,\,\Gamma_p}[s(\alpha)-1]\chi^P(\alpha)\chi^{\Gamma_p}(\alpha)^*\chi^{\Gamma_p}(1). \tag{4.8}$$

These results determine the number of symmetry-allowed ir-active optical phonons (n^{ir}) and phonon frequencies (n_ν^{ir}) for a crystal of given symmetry and unit-cell structure. Equivalently, n^{ir} and n_ν^{ir} fix the number of nonvanishing elements and independent elements, respectively, in the symmetrized effective charge tensor **B** discussed in Sec. 3. The crystal symmetry appears in these expressions through the characters $\chi(\alpha)$ of the crystal point group isomorphic to G.[12] In addition, the complexity of the atomic structure of the primitive cell makes itself felt by means of the structure factors $s(\alpha)$. In Table I, both NaCl and Ge belong to the same crystal class (point group $m3m$, or O_h) so that their character systems are equivalent, yet their infrared behavior is markedly different. As will be shown in Secs. 4B and 5, the appearance of reststrahlen in one and not the other reflects their different $s(\alpha)$'s.

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[9] Examples of representation Γ, demonstrating its applicability to nonsymmorphic as well as symmorphic crystals, are given in Ref. 4 and in S. H. Chen, Phys. Rev. **163**, 532 (1967).

[10] G. F. Koster, MIT Solid State and Molecular Theory Group, Technical Report No. 8, 1956 (unpublished).

[11] V. Heine, *Group Theory in Quantum Mechanics* (Pergamon Press, Ltd., London, 1960).

[12] A convenient listing of the character tables for the crystal point groups is given in Appendix K of Ref. 11.

Before proceeding we note, for later use, a simplification which obtains for all crystal symmetries higher than triclinic and monoclinic. Expression (4.7) for the number of reststrahlen bands can be written as

$$n_v^{\text{ir}}=(1/g)\sum_\alpha\{[s(\alpha)-1]\chi^P(\alpha)\sum_{\Gamma_p}\chi^{\Gamma_p}(\alpha)^*\}.$$

Except for the five low-symmetry classes discussed below in Sec. 4C, each vector I.R. appears just once in the reduction of P (each $C(P,\Gamma_p)=1$) so that, by (4.4), $\chi^P(\alpha)^*=\sum_{\Gamma_p}\chi^{\Gamma_p}(\alpha)^*$ and the above expression becomes

$$n_v^{\text{ir}}=(1/g)\sum_\alpha[s(\alpha)-1]|\chi^P(\alpha)|^2. \tag{4.9}$$

In the Secs. 4A, 4B, 4C, and 4D below, we apply (4.7) and (4.8) to some simple cases (including obvious ones) in order to illustrate the approach developed above.

A. Elemental Crystals with $s=1$

With a single sublattice $s(\alpha)=1$ for all α, so that $n_v^{\text{ir}}=n^{\text{ir}}=0$, as must be the case since a space-lattice crystal has no optical modes.

B. Diatomic Compounds with $s=2$

Since the two atoms in the primitive cell are not identical no symmetry operation interchanges the two sublattices, so that $s(\alpha)=2$ for all α. Therefore (4.7) and (4.8) yield

$$n_v^{\text{ir}}=(1/g)\sum_{\alpha,\,\Gamma_p}\chi^P(\alpha)\chi^{\Gamma_p}(\alpha)^*=\sum_{\Gamma_p}C(P,\Gamma_p), \tag{4.10}$$

$$\begin{aligned}n^{\text{ir}}&=(1/g)\sum_{\alpha,\,\Gamma_p}\chi^P(\alpha)\chi^{\Gamma_p}(\alpha)^*\chi^{\Gamma_p}(1)\\&=\sum_{\Gamma_p}C(P,\Gamma_p)\chi^{\Gamma_p}(1)=\chi^P(1)=3.\end{aligned} \tag{4.11}$$

Thus for such crystals, of which rocksalt and zinc blende are examples, the three zone-center optical phonons are all infrared active.

C. Low-Symmetry Crystals: Crystals Classes 1, 2, m, $\bar{1}$, and $2/m$

In this section we dispose of the exceptions to (4.9), the triclinic and monoclinic crystal classes. (We shall use international "short" notation for the crystal classes.[13] For the point-group operations, n will denote an n-fold rotation and $\bar{n}$ an n-fold rotation inversion.) Since these five point groups possess only one-dimensional representations, $n_v^{\text{ir}}=n^{\text{ir}}$ in what follows.

For classes 1, 2, and m, the set of vector I.R.'s coincides with the full set of I.R.'s, $\{\Gamma_p\}=\{\Gamma_i\}$, so that in (4.8) we can exploit an orthogonality relation for group characters[10,11]:

$$\begin{aligned}n^{\text{ir}}&=(1/g)\sum_\alpha\{[s(\alpha)-1]\chi^P(\alpha)\sum_{\Gamma_i}[\chi^{\Gamma_i}(\alpha)^*\chi^{\Gamma_i}(1)]\}\\&=(1/g)\sum_\alpha[s(\alpha)-1]\chi^P(\alpha)g\delta_{\alpha 1}\\&=[s(1)-1]\chi^P(1)\\&=3s-3.\end{aligned} \tag{4.12}$$

This result means that all optical modes are allowed by symmetry to be ir-active in these crystals. We note that an elemental crystal must satisfy $s\geq 3$ in order to belong to one of these three classes; in Sec. 2 we have seen that with $s=1$ or 2 it automatically possesses inversion symmetry.

Crystal class $\bar{1}$, with only the inversion operation $\alpha=\bar{1}$ in addition to the identity $\alpha=1$, is the simplest ($g=2$) for which ir-inactive optical modes are present. Since $\chi^P(\alpha)\sum_{\Gamma_p}\chi^{\Gamma_p}(\alpha)^*=3$ for both $\alpha=1$ and $\alpha=\bar{1}$, (4.7) yields

$$\begin{aligned}n_v^{\text{ir}}&=\tfrac{3}{2}\{[s(1)-1]+[s(\bar{1})-1]\}\\&=\tfrac{3}{2}[s+s(\bar{1})-2].\end{aligned} \tag{4.13}$$

For class $2/m$, $\chi^P(\alpha)\sum_{\Gamma_p}\chi^{\Gamma_p}(\alpha)^*=6$ for $\alpha=1$ and $\alpha=\bar{1}$, 0 for $\alpha=2$ and $\alpha=\bar{2}$. Since $g=4$ in this case, substituting into (4.7) yields a result identical to (4.13). For an elemental crystal with $s=2$ belonging to one of these two classes, $s(\bar{1})=0$ so that n_v^{ir} vanishes. These are then special cases of (1.1) and of the discussion to follow in Sec. 5. For $s\geq 3$, (4.13) reveals that n_v^{ir} cannot vanish since $s(\bar{1})$ is nonnegative. This result, along with (4.12) for classes 1, 2, and m, is generalized in Sec. 6 to include all crystal classes, yielding (1.2).

D. Cubic Crystals: Crystal Classes 23, $m3$, 432, $\bar{4}3m$, and $m3m$

For each of the five cubic point groups, $P=\Gamma_p$; there is a single 3-dimensional vector I.R. In (4.7) and (4.8), $\sum_{\Gamma_p}$ collapses to a single term:

$$\begin{aligned}n_v^{\text{ir}}&=(1/g)\sum_\alpha[s(\alpha)-1]|\chi^{\Gamma_p}(\alpha)|^2,\\n^{\text{ir}}&=3n_v^{\text{ir}}.\end{aligned} \tag{4.14}$$

5. ELEMENTAL CRYSTALS WITH $s=2$: ABSENCE OF RESTSTRAHLEN

We will now use the results of the previous section to derive the vanishing first-order moment for any elemental crystal with a two-atom primitive cell. As shown in Sec. 2, all crystals of this type have a center of symmetry midway between the two unit-cell atoms. Because G contains the inversion operation it must have the form of a direct product group, $G_0\times\{1,\bar{1}\}$, where G_0 is a group of order $g/2$ and $\{1,\bar{1}\}$ is the group of order 2 containing the identity and the inversion. Thus the operators $\alpha\subset G$ occur in pairs; for every $\alpha_0\subset G_0$, G has two α's: α_0 and $\alpha_0\bar{1}$. We can therefore rewrite (4.7) so as to replace the sum over α by a sum over α_0:

$$\begin{aligned}n_v^{\text{ir}}&=(1/g)\sum_{\alpha_0,\,\Gamma_p}\{[s(\alpha_0)-1]\chi^P(\alpha_0)\chi^{\Gamma_p}(\alpha_0)^*\\&\qquad+[s(\alpha_0\bar{1})-1]\chi^P(\alpha_0\bar{1})\chi^{\Gamma_p}(\alpha_0\bar{1})^*\}\\&=(1/g)\sum_{\alpha_0,\,\Gamma_p}[s(\alpha_0)+s(\alpha_0\bar{1})-2]\chi^P(\alpha_0)\chi^{\Gamma_p}(\alpha_0)^*,\end{aligned} \tag{5.1}$$

where we have made use of the fact that $\chi^{\Gamma_p}(\alpha_0\bar{1})=-\chi^{\Gamma_p}(\alpha_0)$ and $\chi^P(\alpha_0\bar{1})=-\chi^P(\alpha_0)$. The inversion oper-

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[13] *International Tables for X-Ray Crystallography, Symmetry Groups* (Kynoch Press, Birmingham, England, 1952), Vol. I.

ation for this type of crystal interchanges the two sublattices $[s(\bar{1})=0]$, so that if $s(\alpha_0)=2$ then $s(\alpha_0\bar{1})=0$, if $s(\alpha_0)=0$ then $s(\alpha_0\bar{1})=2$. Thus

$$s(\alpha_0)+s(\alpha_0\bar{1})=2 \tag{5.2}$$

and $n_\nu{}^{\text{ir}}$ vanishes. Elemental crystals with $s=2$ cannot exhibit reststrahlen, as stated in (1.1).

6. ELEMENTAL CRYSTALS WITH $s\geq 3$: PRESENCE OF RESTSTRAHLEN

Sections 2 and 5 establish that $s\geq 3$ is a structural requirement which must be satisfied in order for an elemental crystal to display a first-order electric moment. In this section we demonstrate that this condition is sufficient, as well as necessary, for the occurrence of reststrahlen. Sufficiency, in this context, means that reststrahlen is not suppressed *by symmetry* in any elemental crystal with $s\geq 3$. (Of course, the detailed dynamics for a particular crystal, such as very tightly-bound shells—nearly "rigid" atoms—may cause a symmetry-allowed first-order moment to be quite small in a specific instance.) We will then have established connection (1.2) between the number of reststrahlen bands and the primitive-cell complexity: $n_\nu{}^{\text{ir}}\geq 1 \leftrightarrow s\geq 3$.

A demonstration of (1.2) in one dimension is given in Sec. 6A. The proof in three dimensions is presented in two parts. A simple equality is derived in Sec. 6B which enables us to establish sufficiency for all but four crystal classes. These high-symmetry classes are treated separately in Sec. 6C, which completes the derivation of (1.2). Information about specific $s\geq 3$ structures discussed in this paper is collected in Sec. 6D.

A. Proof of Sufficiency in One Dimension

The one-dimensional proof is quite simple since there are only two crystal classes, 1 and $\bar{1}$, corresponding to the absence or presence of inversion symmetry. The number of ir-active modes for the two one-dimensional classes are already contained in the results of Sec. 4C, and are obtained by removing a factor of 3 from the right-hand side of (4.12) and (4.13):

$$\text{class } 1\text{:}\quad n_\nu{}^{\text{ir}}=s-1; \tag{6.1}$$

$$\text{class } \bar{1}\text{:}\quad n_\nu{}^{\text{ir}}=\tfrac{1}{2}[s+s(\bar{1})-2]. \tag{6.2}$$

Elemental crystals with $s=1$ and $s=2$ belong to class $\bar{1}$, with (6.2) yielding $n_\nu{}^{\text{ir}}=0$. For $s\geq 3$ both symmetries are possible, and both (6.1) and (6.2) show that $n_\nu{}^{\text{ir}}$ does not vanish. This completes the proof. Note that for class 1, all optical modes are ir-active. For class $\bar{1}$, $s\geq 3$, $n_\nu{}^{\text{ir}}$ depends on the number of atoms located at centers of symmetry (there are two in each one-dimensional unit cell). For odd s, one atom is at a symmetry center so that $s(\bar{1})=1$ and $n_\nu{}^{\text{ir}}=\frac{1}{2}(s-1)$. For even s, there are either zero or two atoms at symmetry centers so that $s(\bar{1})=0$ or 2 and $n_\nu{}^{\text{ir}}=\frac{1}{2}(s-2)$ or $\frac{1}{2}s$. Thus, for class $\bar{1}$, $\approx$ half of the optical modes are ir-active (to within $\pm\frac{1}{2}$).

B. Proof of Sufficiency in Three Dimensions: Most Crystal Classes

In three dimensions we must contend with 32 crystal classes. Our discussion of Sec. 4C constitutes a proof for the 5 triclinic and monoclinic classes; in this and the following section we address ourselves to the remaining 27. The approach taken here will be to proceed considering the minimum number of details needed at each stage: For most classes only the group characters are required; at higher symmetry we consider limitations on symmetry operations satisfying $s(\alpha)=0$; finally, for full cubic symmetry, we must investigate the 10 $m3m$ (O_h) space groups. Most of the proof is provided by means of a simple inequality, derived below, connecting $n_\nu{}^{\text{ir}}$, s, and g.

For the 27 crystal classes of concern here, (4.9) is valid:

$$gn_\nu{}^{\text{ir}}=\textstyle\sum_\alpha [s(\alpha)-1]|\chi^P(\alpha)|^2.$$

Negative terms within the sum can arise only through the presence of symmetry operations under which no primitive-cell sublattice is transformed into itself, $s(\alpha)=0$. [The proof of vanishing $n_\nu{}^{\text{ir}}$ for $s=2$ elemental crystals given in Sec. 5 depends upon the fact that for such crystals precisely *half* of the factor-group symmetry operations satisfy $s(\alpha)=0$.] The total negative contribution to (4.9) is

$$gn_\nu{}^{\text{ir}}(-)=-\sum_{\alpha\subset s(\alpha)=0}|\chi^P(\alpha)|^2. \tag{6.3}$$

Since $s(1)=s$ and $|\chi^P(1)|^2=g$, the identity operation always makes a positive contribution to $gn_\nu{}^{\text{ir}}$ given by $9(s-1)$. Thus a lower limit to $gn_\nu{}^{\text{ir}}(-)$ is obtained by including all α's, other than the identity, in the sum of (6.3):

$$gn_\nu{}^{\text{ir}}(-)\geq -\sum_{\alpha\neq 1}|\chi^P(\alpha)|^2. \tag{6.4}$$

Since a lower limit on the positive contribution to $gn_\nu{}^{\text{ir}}$ is $9(s-1)$, it follows that

$$\begin{aligned} gn_\nu{}^{\text{ir}} &\geq 9(s-1)-\sum_{\alpha\neq 1}|\chi^P(\alpha)|^2 \\ &\geq 9s-\textstyle\sum_\alpha|\chi^P(\alpha)|^2. \end{aligned} \tag{6.5}$$

Since each Γ_p occurs just once in the reduction of P for each of these 27 classes, it follows directly from the orthogonality relations for group characters[10,11] that

$$\textstyle\sum_\alpha|\chi^P(\alpha)|^2=gh, \tag{6.6}$$

where h is the number of Γ_p's, $h=\sum\Gamma_p(1)$. (h is 1 for the cubic, 3 for the orthorhombic, and 2 or 3 for the tetragonal, trigonal, and hexagonal groups.) Substituting (6.6) into (6.5) puts the inequality into a very simple form:

$$gn_\nu{}^{\text{ir}}\geq 9s-gh. \tag{6.7}$$

The first term on the rhs of (6.7) equals the size of **B**, the effective charge tensor; the second term may be interpreted as the number of constraints imposed by symmetry. The former increases with the unit-cell degrees of freedom; the latter is fixed for each crystal point group. Thus this inequality indicates the manner in which the constraints of symmetry are outstripped by unit-cell complexity with increasing s.

For 23 of the 27 classes the inequality immediately establishes sufficiency, since for these classes $gh \leq 24$ and (6.7) requires that $n_\nu^{\rm ir} > 0$ if $s \geq 3$. For the remaining four high-symmetry classes, the highest-order cubic, hexagonal, and tetragonal point groups (*m*3*m*, 6/*mmm*, and 4/*mmm*) plus an additional hexagonal group (6/*m*), gh takes on values from 32 to 48:

class	g	h	gh
*m*3*m*	48	1	48
6/*mmm*	24	2	48
4/*mmm*	16	2	32
6/*m*	12	3	36.

(6.8)

For these cases (6.7) is not strong enough, as it stands, to demand that $s \geq 3 \rightarrow n_\nu^{\rm ir} > 0$, although it does immediately establish that

$$\begin{aligned} &s \geq 6 \rightarrow n_\nu^{\rm ir} > 0 \text{ for } m3m,\ 6/mmm;\\ &s \geq 5 \rightarrow n_\nu^{\rm ir} > 0 \text{ for } 6/m; \qquad (6.9)\\ &s \geq 4 \rightarrow n_\nu^{\rm ir} > 0 \text{ for } 4/mmm. \end{aligned}$$

We need to look at $s = 3$, 4, 5 in somewhat more detail for these classes, in order to show that $n_\nu^{\rm ir} > 0$.

C. Proof of Sufficiency in Three Dimensions: Crystal Classes *m*3*m*, 6/*mmm*, 4/*mmm*, and 6/*m*

The lower limit expressed in (6.7) corresponds to the situation in which the equal sign obtains in (6.4), $s(\alpha) = 0$ for all α other than the identity. In order for this condition to be satisfied, every atom must be at a general point—no atom on any element of symmetry. Since general positions within the primitive cell occur in sets of g equivalent points, s must be an integral multiple of g for such a crystal. For the crystals remaining to be treated here $3 \leq s \leq 5$ and $12 \leq g \leq 48$, so that this condition cannot be fulfilled and, in fact, is missed by a wide margin.

We now, in effect, strengthen (6.7) by considering the restrictions on the symmetry operations which may satisfy $s(\alpha) = 0$ for these low s, high-symmetry crystals. For $s = 3$, the only possible candidates for $s(\alpha) = 0$ are $\alpha = 3$ and $\alpha = \bar{6}$. For $s = 4$, $s(\alpha) = 0$ is possible for $\alpha = \bar{1}$, 2, $\bar{2}$, 4, $\bar{4}$. For $s = 5$, no operation can satisfy $s(\alpha) = 0$. Bearing these restrictions on $\alpha \subset s(\alpha) = 0$ in mind, we evaluate a new lower limit for $gn_\nu^{\rm ir}$ using

$$gn_\nu^{\rm ir} \geq 9(s-1) - \sum_{\alpha \subset s(\alpha)=0} |\chi^P(\alpha)|^2. \qquad (6.10)$$

4/*mmm* $s = 3$: no group operators qualify for $s(\alpha) = 0$ so that (6.10) becomes $16\, n_\nu^{\rm ir} \geq 18 - 0$ so that $n_\nu^{\rm ir} > 0$;

$s \geq 4$: (6.7) requires $n_\nu^{\rm ir} > 0$.

6/*m* $s = 3$: (6.10) becomes $12\, n_\nu^{\rm ir} \geq 18 - 8$ so that $n_\nu^{\rm ir} > 0$;

$s = 4$: (6.10) becomes $12\, n_\nu^{\rm ir} \geq 27 - 11$ so that $n_\nu^{\rm ir} > 0$;

$s \geq 5$: (6.7) requires $n_\nu^{\rm ir} > 0$.

6/*mmm* $s = 3$: (6.10) becomes $24\, n_\nu^{\rm ir} \geq 18 - 2$ so that $n_\nu^{\rm ir} > 0$;

$s = 4$: (6.10) becomes $24\, n_\nu^{\rm ir} \geq 27 - 23$ so that $n_\nu^{\rm ir} > 0$;

$s = 5$: (6.10) becomes $24\, n_\nu^{\rm ir} \geq 36 - 0$ so that $n_\nu^{\rm ir} > 0$;

$s \geq 6$: (6.7) requires $n_\nu^{\rm ir} > 0$.

*m*3*m* $s = 3$: (6.10) becomes $48\, n_\nu^{\rm ir} \geq 18 - 0$ so that $n_\nu^{\rm ir} > 0$;

$s = 4$: (6.10) becomes $48\, n_\nu^{\rm ir} \geq 27 - 39 = -12$ so that $n_\nu^{\rm ir} > 0$ is *not* proved;

$s = 5$: (6.10) becomes $48\, n_\nu^{\rm ir} \geq 36 - 0$ so that $n_\nu^{\rm ir} > 0$;

$s \geq 6$: (6.7) requires $n_\nu^{\rm ir} > 0$.

One case thus remains outstanding, elemental crystals of full cubic symmetry (*m*3*m*, or O_h) with four atoms in the primitive cell. For this situation, the new lower limit for $n_\nu^{\rm ir}$ provided by (6.10) is 0, not 1. Rather than considering the inequality in more detail, it is simpler now to use (4.14) to evaluate $n_\nu^{\rm ir}$ directly for these crystals, showing it to be nonzero in each case. An investigation of the 10 space groups belonging to this highest-symmetry crystal class reveals that there are only two possible structures for an *m*3*m* elemental crystal with $s = 4$[13]:

(1) space group *Pm*3*m* (O_h^1), with one atom at a site of *m*3*m* symmetry and three atoms at equivalent sites of 4/*mmm* symmetry;

(2) space group *Fd*3*m* (O_h^7), with four atoms at equivalent sites of $\bar{3}m$ symmetry.

Structures (1) and (2) are shown in Figs. 1(g) and 1(h), respectively. They are obtained by placing atoms at the corners and edge centers (or, equivalently, at the body and face centers) of the primitive cells for simple cubic and face-centered cubic Bravais lattices. [Structure (1) would be obtained by replacing cation and anion with identical atoms in several cubic AB_3 compounds: MoF_3, ReO_3, Cu_3N.[14]] For both structures the atoms lie on

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[14] R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1963), Vol. I, p. 36.

many symmetry elements, e.g., for both, every atomic site is a center of symmetry. In fact for (1), one sublattice occupies a site of full cubic symmetry so that no operation interchanges it with another; $s(\alpha)\geq 1$ for all α and no negative terms appear in the sum. Using (4.14), we obtain

$$\text{for (1)},\quad n_\nu{}^{\text{ir}}=2;$$

$$\text{for (2)},\quad n_\nu{}^{\text{ir}}=1.$$

We have now covered every case for $s\geq 3$, demonstrating for all of them that $n_\nu{}^{\text{ir}}>0$. This completes the proof that the structural condition $s\geq 3$ is sufficient for the existence of a symmetry-allowed first-order moment.

D. Examples

Figure 1 displays primitive cells, shown in solid outline, for some of the $s\geq 3$ crystal structures discussed in this paper. Table II lists the corresponding crystal symmetries and values of s, $n_\nu{}^{\text{ir}}$, and n^{ir}. The structure of Fig. 1(a), that of trigonal Se and Te,[4,14] corresponds to the **B** shown in (3.4). This has the lowest symmetry of those shown in Fig. 1, and is the only one of these structures which is known to occur for an elemental crystal. Structures (b) and (c) are higher-symmetry $s=3$ crystals, the former having the smallest number of ir-active vibrations, $n^{\text{ir}}=2$, possible for crystals with $s\geq 3$. The group-theoretical decomposition of the eigenvibration symmetries for (a) and (b) has been given in Table I. The two cubic $s=4$ crystals of the preceding section are shown in Fig. 1(g), (h), while Fig. 1(d)-(f) show three high-symmetry $n_\nu{}^{\text{ir}}=1$ structures to be discussed in Sec. 7B.

7. FURTHER APPLICATIONS

A. Polyatomic Crystals, Inequivalent Sites

For a polyatomic crystal, the symmetry operations can only permute sublattices among one another which are occupied by the same atomic species; nonidentical atoms cannot occupy sites equivalent by symmetry. With two atomic species we can write

$$s(\alpha)=s_1(\alpha)+s_2(\alpha)\,, \tag{7.1}$$

where each $s_i(\alpha)$ describes the interchanges within each set of identical atoms. Let us consider a diatomic crystal belonging to one of the two most symmetric crystals classes, $m3m$ or $6/mmm$, so that the compound has the same symmetry as does each of the two elemental crystals formed by either atomic species alone. Then

$$\begin{aligned} n_\nu{}^{\text{ir}} &= (1/g)\textstyle\sum_\alpha [s(\alpha)-1]|\chi^P(\alpha)|^2 \\ &= (1/g)\textstyle\sum_\alpha [s_1(\alpha)+s_2(\alpha)-1]|\chi^P(\alpha)|^2 \\ &= (1/g)\textstyle\sum_\alpha [s_1(\alpha)-1]|\chi^P(\alpha)|^2 \\ &\qquad +(1/g)\textstyle\sum_\alpha [s_2(\alpha)-1]|\chi^P(\alpha)|^2 \\ &\qquad\qquad +(1/g)\textstyle\sum_\alpha|\chi^P(\alpha)|^2 \\ &= n_\nu{}^{\text{ir}}(1)+n_\nu{}^{\text{ir}}(2)+h\,, \end{aligned} \tag{7.2}$$

TABLE II. Symmetries and reststrahlen properties for the structures of Fig. 1.

Crystal structure	Class	Space group[a]	s	$n_\nu{}^{\text{ir}}$	n^{ir}
Fig. 1(a)	32	$P3_121$ $(D_3{}^4)$	3	3	5
Fig. 1(b)	$\bar{6}m2$	$P6m2$ $(D_{3h}{}^1)$	3	1	2
Fig. 1(c)	$6/mmm$	$P6/mmm$ $(D_{6h}{}^1)$	3	2	3
Fig. 1(d)	$6/mmm$	$P6/mmm$ $(D_{6h}{}^1)$	6	1	2
Fig. 1(e)	$4/mmm$	$P4/mmm$ $(D_{4h}{}^1)$	4	1	2
Fig. 1(f)	$m3m$	$Pm3m$ $(O_h{}^1)$	8	1	3
Fig. 1(g)	$m3m$	$Pm3m$ $(O_h{}^1)$	4	2	6
Fig. 1(h)	$m3m$	$Fd3m$ $(O_h{}^7)$	4	1	3

[a] The international short symbol of Ref. 13 (with Schoenflies notation in parentheses).

where $n_\nu{}^{\text{ir}}(i)$ is the number of reststrahlen bands for the elemental crystal which atomic species i forms by itself, and where $h=1$ for $m3m$, 2 for $6/mmm$. Similarly, for polyatomic crystals of these symmetries containing k distinct atomic species,

$$n_\nu{}^{\text{ir}}=\sum_{i=1}^{k} n_\nu{}^{\text{ir}}(i)+(k-1)h\,. \tag{7.3}$$

Thus, for a crystal composed of k different atomic species

$$n_\nu{}^{\text{ir}}\geq k-1\,, \tag{7.4}$$

so that one-phonon absorption is symmetry-allowed for all crystalline compounds. Exactly the same argument applies to an elemental crystal with atoms located at k sets of equivalent sites [e.g., structure (1) of the preceding section] since such a crystal has the identical symmetry as one with different atoms at the inequivalent sites.

B. Crystal Complexity Compatible with a Single Reststrahlen Band

We have seen that the only crystals for which $n_\nu{}^{\text{ir}}=0$ are elemental crystals with $s=1$ or 2; elemental crystals with $s\geq 3$ must display at least one reststrahlen band. (Of course, as discussed above, all compounds display one or more reststrahlen bands.) Let us now ask what is the largest number of primitive-cell atoms consistent with a single reststrahlen band, max s such that $n_\nu{}^{\text{ir}}=1$ (max s such that $n_\nu{}^{\text{ir}}=0$ is 2). Since this must occur for a highly-symmetric structure we can use (6.7). Solving for s, we find

$$s\leq\tfrac{1}{9}(gn_\nu{}^{\text{ir}}+gh)\,. \tag{7.5}$$

We are interested in $n_\nu{}^{\text{ir}}=1$:

$$s\leq\tfrac{1}{9}(g+gh)\,. \tag{7.6}$$

From (6.8) we see that $g+gh$ is 96 for class $m3m$, 72 for class $6/mmm$, and ≤ 48 for all other classes; so that $s\leq 10$ for $m3m$, ≤ 8 for $6/mmm$, and ≤ 5 for the rest.

Thus far the maximum possibility is $s=10$, for full cubic symmetry. Now we note the fact that the discussion of the preceding subsection rules out the possibility, for such large s, of the occupation of more than one set of equivalent sites, since this would require $n_\nu^{\text{ir}} \geq 2$. With $k \geq 3$, (7.4) shows that $n_\nu^{\text{ir}} \geq 2$. With $k=2$ and $s \geq 5$, at least one set, say $i=1$, contains 3 or more atoms. Then $n_\nu^{\text{ir}}(1) \geq 1$ so that, from (7.2), $n_\nu^{\text{ir}} \geq 2$. Therefore we must have $k=1$ in order for $n_\nu^{\text{ir}}=1$ to be possible with $s \geq 5$. This argument also shows that for a *compound* the largest s compatible with $n_\nu^{\text{ir}}=1$ is $s=4$, and that this occurs for a cubic ($m3m$), diatomic ($k=2$) crystal with $s_1=s_2=2$. For this case $n_\nu^{\text{ir}}(1)=n_\nu^{\text{ir}}(2)=0$, $h=1$, yielding $n_\nu^{\text{ir}}=1$ in (7.2).

For crystal class $m3m$, the largest number of equivalent sites which is consistent with $s \leq 10$ is $s=8$,[13] which thereby provides the answer to the question placed above:

$$8 = \max s \text{ such that } n_\nu^{\text{ir}}=1. \tag{7.7}$$

For class $6/mmm$, the corresponding value is $s=6$. For the most symmetric classes among the other 30, $s=4$ is the largest number of primitive-cell atoms which can give rise to only one reststrahlen band. Figures 1(f), 1(d), and 1(e) display primitive cells containing 8, 6, and 4 atoms, for $n_\nu^{\text{ir}}=1$ crystal structures of highest cubic, hexagonal, and tetragonal symmetry, respectively. Statements analogous to (7.7) can similarly be obtained for larger values of n_ν^{ir}.

8. SUMMARY

We have shown that a necessary and sufficient condition for the existence of symmetry-allowed, one-phonon, infrared absorption in an elemental crystal is a crystal structure in which the primitive unit cell contains three or more atoms, $s \geq 3$. This minimum-complexity condition, more succinctly stated in (1.1)–(1.2), has been demonstrated by developing expressions (4.7)–(4.9) which count the number of infrared-active phonons and phonon frequencies, and which determine the form of the effective charge tensor, for a crystal of given symmetry and unit-cell structure. Crystal symmetry enters (4.7)–(4.9) through the factor-group characters, while the structural complexity of the primitive cell enters in the form of structure factors, $s(\alpha)$, specifying the number of sublattices invariant under the symmetry operations α.

The proof of (1.1), $s \geq 3$ as a necessary condition for reststrahlen, follows from (4.7) and the observation that all $s=2$ elemental crystals possess an inversion operation which interchanges the two sublattices; this is equivalent to a generalization of the Lax-Burstein argument for the vanishing first-order moment in Ge. The proof of (1.2), $s \geq 3$ as a sufficient condition, has been obtained by generating a simple inequality, (6.7), which illustrates how the constraints of symmetry are outstripped by unit-cell complexity with increasing s, and by a detailed treatment of the highest-symmetry crystal classes.

In other applications, the present approach provides a simple means for showing that a compound composed of k atomic species possesses at least k-1 reststrahlen bands, and that the largest s compatible with a single reststrahlen band is 8 for elemental crystals and 4 for diatomic compounds, both obtaining for full cubic symmetry.

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