Group-theoretic analysis of long-wavelength vibrations of polar crystals*

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A group-theoretic method is described for analyzing the long-wavelength lattice vibrations of polar crystals made up of deformable and polarizable ions. A set of $3r$-dimensional matrices is constructed (where r is the number of ions in a primitive unit cell of the crystal), each of which commutes with the dynamical matrix for such crystals, and which also provides a representation of the point group $G_0(\hat{k}; -\hat{k})$, which is the subgroup of the point group of the space group of the crystal whose elements $\{R\}$ have the property that $\underline{R}\hat{k} = \pm\hat{k}$. Here $\underline{R}$ is a 3×3 real, orthogonal matrix representative of the symmetry operation R, while $\hat{k}$ is a unit vector in the direction of the wave vector $\vec{k}$ of the long-wavelength lattice vibrations being studied. Reduction of this matrix representation yields the symmetries of the long-wavelength normal modes of the crystal, and the forms of the corresponding eigenvectors can be obtained by projection-operator techniques. Additional degeneracies imposed by time-reversal symmetry are automatically taken into account in this treatment, which is illustrated by applying it to an analysis of the long-wavelength vibration modes of graphite.

I. INTRODUCTION

The use of group-theoretic methods for the determination of the symmetry properties of the normal vibration modes of perfect[1-4] and imperfect[5-7] crystals is now a well-established tool in theoretical and experimental studies of the dynamical properties of crystals. In the case of perfect crystals, with which we will be exclusively concerned in this paper, the classification of the symmetry properties of the normal modes is according to the irreducible multiplier representations of the point group of the wave vector of the modes, i.e., the subgroup of the point group of the space group of the crystal which leaves the wave-vector invariant modulo a translation vector of the reciprocal lattice.

However, all of the group-theoretic methods developed to date for this purpose are deficient in their application to the classification of the symmetry properties of the long-wavelength vibration modes of polar crystals. This is because by being based on the point group of the wave vector, which is $\vec{k}=0$ for such modes, they neglect the lowering of the symmetry of the crystal by the macroscopic electric field associated with the long-wavelength longitudinal-optical modes in polar crystals (in the electrostatic approximation). This lowering of symmetry can result in the splitting of degeneracies among the long-wavelength optical modes predicted on the basis of the geometrical symmetry of the crystal alone. A well-known example of this is the Lyddane-Sachs-Teller splitting between the frequencies of the transverse- and longitudinal-optical modes in diatomic cubic crystals with two ions in a primitive unit cell.[8] According to an analysis based on the point group of the wave vector $\vec{k}=0$, which is O_h for crystals of the rocksalt structure, the three optical modes for such crystals should transform as the basis functions for the three-dimensional irreducible representation Γ_4^- (Ref. 9); these modes should therefore be triply degenerate. In fact, it is well known that two of the three optical modes (the transverse modes) are degenerate, while the third (the longitudinal mode) is higher in frequency than the degenerate pair, and that this difference is due to the macroscopic electric field associated with the longitudinal mode, which stiffens the effective force constant determining its frequency.

In this paper we present a group-theoretic analysis of the long-wavelength vibrations in polar crystals, which takes proper account of the presence of the macroscopic electric field in such crystals. It is not limited to point-ion models of such crystals, but incorporates the deformability and polarizability of the ions. There are no results here that cannot be obtained by combining the analyses in Refs. 4 and 7, for example. However, because the lack of a group-theoretic discussion of the long-wavelength vibrations in polar crystals in the literature on the subject is noted from time to time,[10,11] it was thought to be useful to present in one place the results necessary for carrying out such an analysis. The results obtained here are illustrated by applying them to the long-wavelength vibrations of graphite. A brief account of some of the latter results has appeared elsewhere.[12]

II. GENERAL THEORY

The equations of motion for an arbitrary crystal made up of deformable and polarizable atoms takes the following form in the long-wavelength limit[13]:

$$\omega_j^2 w_\alpha(\kappa|j) = \sum_{\kappa'\beta} \mathcal{C}_{\alpha\beta}(\kappa\kappa'|\hat{k}) w_\beta(\kappa'|j)\ , \qquad (2.1)$$

where the elements of the dynamical matrix $\mathcal{C}_{\alpha\beta}(\kappa\kappa'|\hat{k})$ are given by

$$\mathcal{C}_{\alpha\beta}(\kappa\kappa'|\hat{k}) = \frac{f_{\alpha\beta}(\kappa\kappa')}{(M_\kappa M_{\kappa'})^{1/2}} + \frac{4\pi}{v_a \epsilon_L^\infty} \frac{1}{(M_\kappa M_{\kappa'})^{1/2}} \times \left(\sum_\mu \hat{k}_\mu z_{\mu\alpha}(\kappa)\right)\left(\sum_\nu \hat{k}_\nu z_{\nu\beta}(\kappa')\right) . \quad (2.2)$$

In this expression $f_{\alpha\beta}(\kappa\kappa')$ are the force constants between the sublattices κ and κ' corresponding to all the short-range forces acting between the atoms, including the force associated with the Lorentz field, M_κ is the mass of the κth kind of ion, v_a is the volume of a primitive unit cell, $z_{\mu\alpha}(\kappa)$ is the transverse effective charge tensor for the κth kind of ion, $\hat{k}$ is a unit vector in the direction of the wave vector $\vec{k}$, and ϵ_L^∞ is the longitudinal-optical frequency dielectric constant, which is defined in terms of the optical-frequency dielectric tensor $\epsilon_{\mu\nu}^\infty$ by

$$\epsilon_L^\infty = \sum_{\mu\nu} \hat{k}_\mu \epsilon_{\mu\nu}^\infty \hat{k}_\nu . \quad (2.3)$$

The second term on the right-hand side of Eq. (2.2) represents the α Cartesian component of the force on the sublattice κ owing to the macroscopic electric field set up by the long-wavelength longitudinal-optical vibration modes.

The coefficients $f_{\alpha\beta}(\kappa\kappa')$, $z_{\mu\alpha}(\kappa)$, and $\epsilon_{\mu\nu}^\infty$, appearing in Eqs. (2.2) and (2.3) satisfy several invariance conditions which simplify Eqs. (2.1)–(2.3) for a given crystal.

The first kind of condition on these coefficients are simple symmetry conditions which can be stated

$$f_{\alpha\beta}(\kappa\kappa') = f_{\beta\alpha}(\kappa'\kappa) \quad (2.4)$$

$$\epsilon_{\mu\nu}^\infty = \epsilon_{\nu\mu}^\infty . \quad (2.5)$$

The second type of condition on these coefficients follows from considerations of infinitesimal translational invariance, and can be expressed as

$$\sum_\kappa f_{\alpha\beta}(\kappa\kappa') = 0 = \sum_{\kappa'} f_{\alpha\beta}(\kappa\kappa') \quad (2.6)$$

$$\sum_\kappa z_{\mu\alpha}(\kappa) = 0 . \quad (2.7)$$

The final conditions on these coefficients follow from the symmetry and structure of the crystal. Let us denote an operation of the space group of the crystal in the Seitz[14] notation as $\{\underline{S}|\vec{v}(S)+\vec{x}(m)\}$. Here $\underline{S}$ is a 3×3, real symmetric matrix representative of a proper or improper rotation belonging to the point group of the space group, $\vec{v}(S)$ is a displacement vector which is smaller than any of the primitive translation vectors of the crystal, and $\vec{x}(m)$ is a translation vector of the crystal.

The effect of a space-group operation on the equilibrium position vector of the κth atom in the lth primitive unit cell, $\vec{x}(l\kappa)$, is expressed by

$$\{\underline{S}|\vec{v}(S)+\vec{x}(m)\}\vec{x}(l\kappa) = \underline{S}\vec{x}(l\kappa) + \vec{v}(S) + \vec{x}(m) = \vec{x}(LK) . \quad (2.8)$$

In what follows we will use capital letters to express the indices of the site into which a given site, denoted by lower case letters, is sent by a space-group operation.

When an operation from its space group is applied to a crystal, the coefficients $f_{\alpha\beta}(\kappa\kappa')$, $z_{\mu\alpha}(\kappa)$, and $\epsilon_{\mu\nu}^\infty$ transform according to

$$f_{\alpha\beta}(KK') = \sum_{\gamma\delta} S_{\alpha\gamma} S_{\beta\delta} f_{\gamma\delta}(\kappa\kappa') , \quad (2.9)$$

$$z_{\mu\alpha}(K) = \sum_{\rho\gamma} S_{\mu\rho} S_{\alpha\gamma} z_{\rho\gamma}(\kappa) , \quad (2.10)$$

$$\epsilon_{\mu\nu}^\infty = \sum_{\rho\sigma} S_{\mu\rho} S_{\nu\sigma} \epsilon_{\rho\sigma}^\infty . \quad (2.11)$$

When we combine Eq. (2.2) with Eqs. (2.9)–(2.11) we find that the dynamical matrix $\mathcal{C}_{\alpha\beta}(\kappa\kappa'|\hat{k})$ transforms according to

$$\mathcal{C}_{\alpha\beta}(KK'|\underline{S}\hat{k}) = \sum_{\gamma\delta} S_{\alpha\gamma} S_{\beta\delta} \mathcal{C}_{\gamma\delta}(\kappa\kappa'|\hat{k}) , \quad (2.12)$$

when the crystal is subjected to a space-group operation.

With every operation $\{\underline{S}|\vec{v}(S)+\vec{x}(m)\}$ of the space group of the crystal, we associate a $3r\times3r$ matrix (where r is the number of atoms in a primitive unit cell), $\mathcal{S}_{\alpha\beta}(\kappa\kappa'|S)$ defined by

$$\mathcal{S}_{\alpha\beta}(\kappa\kappa'|S) = S_{\alpha\beta}\delta(\kappa, F_0(\kappa';S)) = \mathcal{S}_{\beta\alpha}^{-1}(\kappa'\kappa|S) . \quad (2.13)$$

We denote by $F_0(\kappa';S)=K'$ the sublattice into which the sublattice κ' is sent by the space-group operation $\{\underline{S}|\vec{v}(S)+\vec{x}(m)\}$. This correspondence is unique despite the fact that with each matrix $\mathcal{S}_{\alpha\beta}(\kappa\kappa'|S)$ there is associated an infinity of space-group operations described by different choices of the lattice translation vectors $\{\vec{x}(m)\}$. The number of matrices $\{\mathcal{S}_{\alpha\beta}(\kappa\kappa'|S)\}$ is equal to the number of proper and improper rotation $\{\underline{S}\}$ in the space group of the crystal, i.e., to the order of the point group G_0 of the space group, or to the order of the crystal class.

It is readily verified that Eq. (2.12) can be rewritten in terms of the matrices $\{\mathcal{S}_{\alpha\beta}(\kappa\kappa'|S\}$ as

$$\mathcal{C}_{\alpha\beta}(\kappa\kappa'|\underline{S}\hat{k}) = \sum_{\gamma\kappa_1}\sum_{\delta\kappa_2} \mathcal{S}_{\alpha\gamma}(\kappa\kappa_1|S)\mathcal{C}_{\gamma\delta}(\kappa_1\kappa_2|\hat{k}) \times \mathcal{S}_{\delta\beta}^{-1}(\kappa_2\kappa'|S) . \quad (2.14)$$

Let us denote by $G_0(\hat{k};-\hat{k})$ the point group (a subgroup of G_0) whose elements $\{R\}$ have the prop-

erty that

$$\underline{R}\,\hat{k} = \pm\hat{k} \ . \tag{2.15}$$

Then, because $\mathcal{C}_{\alpha\beta}(\kappa\kappa'|\hat{k})$ is even in $\hat{k}$,

$$\mathcal{C}_{\alpha\beta}(\kappa\kappa'|-\hat{k}) = \mathcal{C}_{\alpha\beta}(\kappa\kappa'|\hat{k}) \ , \tag{2.16}$$

we see from Eq. (2.14) that if we restrict our attention to the subgroup of the point group of the space group of the crystal, which we have denoted by $G_0(\hat{k}; -\hat{k})$, the transformation law for the dynamical matrix becomes

$$\mathcal{C}_{\alpha\beta}(\kappa\kappa'|\hat{k}) = \sum_{\gamma\kappa_1}\sum_{\delta\kappa_2} S_{\alpha\gamma}(\kappa\kappa_1|R) \times \mathcal{C}_{\gamma\delta}(\kappa_1\kappa_2|\hat{k}) S^{-1}_{\delta\beta}(\kappa_2\kappa'|R) \ . \tag{2.17}$$

Thus the set of matrices $\{S_{\alpha\beta}(\kappa\kappa'|R)\}$ commutes with the dynamical matrix $\mathcal{C}_{\alpha\beta}(\kappa\kappa'|\hat{k})$.

The matrices $\{S_{\alpha\beta}(\kappa\kappa'|R)\}$ also provide a representation of the group $G_0(\hat{k}; -\hat{k})$,

$$\sum_{\kappa_1\gamma} S_{\alpha\gamma}(\kappa\kappa_1|R_1) S_{\gamma\beta}(\kappa_1\kappa'|R_2) = S_{\alpha\beta}(\kappa\kappa'|R_1R_2) \ . \tag{2.18}$$

Consequently, the reduction of the representation of $G_0(\hat{k}; -\hat{k})$ provided by the $\{S_{\alpha\beta}(\kappa\kappa'|R)\}$ yields the symmetries of the long-wavelength vibrations of a crystal, which correspond to the wave vector $\hat{k}$.

The number of times the sth irreducible representation of $G_0(\hat{k}; -\hat{k})$ is contained in the representation by the $\{S_{\alpha\beta}(\kappa\kappa'|R)\}$ is given by

$$N_s = \frac{1}{h}\sum_{R\subset G_0(\hat{k};-\hat{k})} \chi(R)\chi^{(s)*}(R) \ , \tag{2.19}$$

where h is the order of the group $G_0(\hat{k}; -\hat{k})$, $\chi^{(s)}(R)$ is the character of the rotation R in the sth irreducible representation, and

$$\chi(R) = \sum_{\kappa\alpha} S_{\alpha\alpha}(\kappa\kappa|R) = \sum_{\alpha} S_{\alpha\alpha}\sum_{\kappa}\delta(\kappa, F_0(\kappa;R)) \ . = (\pm 1 + 2\cos\varphi_R)\, n_R \ . \tag{2.20}$$

In this expression φ_R is the angle through which the crystal is rotated by the operation R, the + sign obtains if the rotation is a proper rotation and the − sign obtains if R is a rotation reflection. n_R is the number of sublattices which are left invariant by the space-group operation corresponding to the rotation R.

It should be pointed out that in view of the definition of the group $G_0(\hat{k}; -\hat{k})$ provided by Eq. (2.15), and the results expressed by Eqs. (2.14), (2.16), and (2.17), the present treatment incorporates any degeneracies among the long-wavelength vibration modes of polar crystals which have their origin in time-reversal symmetry.[4] Degeneracies imposed by spatial symmetry alone would be obtained by restricting attention to the point group $G_0(\hat{k})$, whose elements $\{R\}$ have the property that $\underline{R}\,\hat{k} = \hat{k}$.

The forms of the eigenvectors corresponding to a mode of particular symmetry can be obtained by projection operator techniques. If we introduce an arbitrary $3r$ component vector $\vec{\psi}$ whose components are $\{\psi_\alpha(\kappa)\}$ where $\alpha = x, y, z$ and $\kappa = 1, 2, \ldots, r$, then the vector

$$W_\alpha(\kappa|s\lambda) = \sum_{R\subset G_0(\hat{k};-\hat{k})} \Gamma^{(s)}_{\lambda\lambda'}(R)^* \times \sum_{\beta\kappa'} S_{\alpha\beta}(\kappa\kappa'|R)\psi_\beta(\kappa') \tag{2.21}$$

for any fixed λ' transforms according to the λth row of the sth irreducible representation of $G_0(\hat{k}; -\hat{k})$, where $\Gamma^{(s)}(R)$ is the matrix representation of the operation R in the irreducible representation s. In case the sth irreducible representation occurs N_s times in the reduction of the representation of $G_0(\hat{k}; -\hat{k})$ provided by the matrices $S_{\alpha\beta}(\kappa\kappa'|R)$, the vector $W_\alpha(\kappa|s\lambda)$ generated by Eq. (2.21) is a function of N_s parameters. In general, the values of these parameters can be determined only by substituting the vector into the eigenvalue equation [Eq. (2.1)].

III. APPLICATION TO THE LONG-WAVELENGTH VIBRATIONS OF GRAPHITE

We now apply the preceding results to the case of the long-wavelength vibrations of graphite. Graphite belongs to the nonsymmorphic space group D^4_{6h}.[15] The primitive translation vectors of this crystal are

$$\vec{t}_1 = \tfrac{1}{2}a(\sqrt{3}\,\hat{i}_1 - \hat{i}_2), \quad \vec{t}_2 = a\hat{i}_2 \ , \quad \vec{t}_3 = c\hat{i}_3 \ , \tag{3.1}$$

where $\hat{i}_1$, $\hat{i}_2$, and $\hat{i}_3$ are three unit vectors along the Cartesian x, y, and z axes, respectively. We pick the origin of coordinates midway between two nearest neighbors along the z axis (at the center of inversion for the crystal). There are four atoms in a primitive unit cell. The basis vectors $\{\vec{x}(\kappa)\}$, which give the positions of these four atoms with respect to an origin which in the lth primitive unit cell is given by $\vec{x}(l) = l_1\vec{t}_1 + l_2\vec{t}_2 + l_3\vec{t}_3$, where l_1, l_2, and l_3 are any three integers to which we refer collectively as l, are

$$\begin{aligned} \vec{x}(1) &= (0, 0, -\tfrac{1}{4}c) \\ \vec{x}(2) &= (\tfrac{1}{6}\sqrt{3}a, \tfrac{1}{2}a, -\tfrac{1}{4}c) \\ \vec{x}(3) &= (\tfrac{1}{3}\sqrt{3}a, 0, \tfrac{1}{4}c) \\ \vec{x}(4) &= (0, 0, \tfrac{1}{4}c) \ . \end{aligned} \tag{3.2}$$

We can use the conditions expressed by Eqs. (2.4)–(2.7) and Eqs. (2.9)–(2.11) to determine the independent nonzero components of the tensors $\epsilon^{\infty}_{\mu\nu}$, $z_{\mu\alpha}(\kappa)$, and $f_{\alpha\beta}(\kappa\kappa')$ for graphite.

From Eq. (2.11) and the fact that the point group of the crystal is D_{6h}, we find that $\epsilon^{\infty}_{\mu\nu}$ is diagonal and has only two independent elements

$$\underline{\epsilon}^{\infty} = \begin{pmatrix} \epsilon^{\infty}_{xx} & 0 & 0 \\ 0 & \epsilon^{\infty}_{xx} & 0 \\ 0 & 0 & \epsilon^{\infty}_{zz} \end{pmatrix} . \tag{3.3}$$

From Eq. (2.10) we find that if we use the operations of D_{6h} which are not associated with an interchange of sublattices, viz., the operations E, $2C_3$, $3C_2'$, σ_h, $2S_3$, and $3\sigma_d$, the tensor $z_{\mu\alpha}(\kappa)$ is diagonal for every κ,

$$\underline{z}(\kappa) = \begin{pmatrix} z_{xx}(\kappa) & 0 & 0 \\ 0 & z_{xx}(\kappa) & 0 \\ 0 & 0 & z_{zz}(\kappa) \end{pmatrix} . \tag{3.4}$$

When we use the remaining operations of D_{6h}, which are associated with interchanges of the sublattices, we find that

$$z_{\mu\alpha}(1) = z_{\mu\alpha}(4), \quad z_{\mu\alpha}(2) = z_{\mu\alpha}(3) . \tag{3.5}$$

From the infinitesimal translational invariance condition, Eq. (2.7), we find in addition that

$$z_{\mu\alpha}(1) = -z_{\mu\alpha}(2) . \tag{3.6}$$

Combining the results expressed by Eqs. (3.4)–(3.6), we find for the effective charge tensors of graphite

$$\underline{z}(1) = \underline{z}(4) = -\underline{z}(2) = -\underline{z}(3) = \begin{pmatrix} e_1^* & 0 & 0 \\ 0 & e_1^* & 0 \\ 0 & 0 & e_3^* \end{pmatrix} . \tag{3.7}$$

Turning now to the elements of the force-constant matrix $\{f_{\alpha\beta}(\kappa\kappa')\}$, we find from Eq. (2.9) by the use of the operations of D_{6h} which are not associated with an interchange of sublattices that $f_{\alpha\beta}(\kappa\kappa')$ is diagonal in α and β,

$$f_{\alpha\beta}(\kappa\kappa') = \delta_{\alpha\beta} f_{\alpha}(\kappa\kappa') = \delta_{\alpha\beta} f_{\alpha}(\kappa'\kappa) , \tag{3.8a}$$

where

$$f_{xx}(\kappa\kappa') = f_{yy}(\kappa\kappa') \neq f_{zz}(\kappa\kappa') , \tag{3.8b}$$

and where we have also used Eq. (2.4). From the operations of D_{6h} which are associated with the interchange of sublattices we find with the aid of Eq. (2.9) that

$$\begin{aligned} &f_{\alpha}(11) = f_{\alpha}(44), \quad f_{\alpha}(22) = f_{\alpha}(33), \\ &f_{\alpha}(12) = f_{\alpha}(43), \quad f_{\alpha}(13) = f_{\alpha}(42) . \end{aligned} \tag{3.9}$$

Finally, the condition expressed by Eq. (2.6) yields for the diagonal elements

TABLE I. Atomic-force-constant matrix for the short-range forces (only the nonzero elements are displayed).

κ/κ'	1	2	3	4
1	$a(11)$ $a(11)$ $b(11)$	$a(12)$ $a(12)$ $b(12)$	$a(13)$ $a(13)$ $b(13)$	$a(14)$ $a(14)$ $b(14)$
2	$a(12)$ $a(12)$ $b(12)$	$a(22)$ $a(22)$ $b(22)$	$a(23)$ $a(23)$ $b(23)$	$a(13)$ $a(13)$ $b(13)$
3	$a(13)$ $a(13)$ $b(13)$	$a(23)$ $a(23)$ $b(23)$	$a(22)$ $a(22)$ $b(22)$	$a(12)$ $a(12)$ $b(12)$
4	$a(14)$ $a(14)$ $b(14)$	$a(13)$ $a(13)$ $b(13)$	$a(12)$ $a(12)$ $b(12)$	$a(11)$ $a(11)$ $b(11)$

$a(11) = -[a(12) + a(13) + a(14)]$
$b(11) = -[b(12) + b(13) + b(14)]$
$a(22) = -[a(12) + a(13) + a(23)]$
$b(22) = -[b(12) + b(13) + b(23)]$

$$\begin{aligned} f_x(11) &= -[f_x(12) + f_x(13) + f_x(14)] , \\ f_z(11) &= -[f_z(12) + f_z(13) + f_z(14)] , \\ f_x(22) &= -[f_x(12) + f_x(13) + f_x(23)] , \\ f_z(22) &= -[f_z(12) + f_z(13) + f_z(23)] . \end{aligned} \tag{3.10}$$

The form of the force-constant matrix is shown in Table I.

If the phonon wave vector $\vec{k}$ tends to zero along the z axis, so that $\hat{k} = (0, 0, 1)$, the point group $G_0(\hat{k}; -\hat{k})$ is D_{6h}. The 24 operations of the point group and the corresponding characters calculated from Eq. (2.20) are

R	E	C_2	$2C_3$	$2C_6$	$3C_2'$	$3C_2''$	I	σ_h	$2S_6$	$2S_3$	$3\sigma_d$	$3\sigma_v$
$\chi(R)$	12	0	0	0	0	−4	0	4	0	−8	4	0

(3.11)

Here C_2' is a twofold rotation about the y axis and about two other axes in the xy plane, rotated from it by $\pm 60°$, C_2'' is a twofold rotation about the x axis and about two other axes in the xy plane rotated from it by $\pm 60°$, σ_d is a reflection in the plane containing the z axis and one of the C_2'' axes, and σ_v is a reflection in a plane containing the z axis and one of the C_2' axes. The 12 operations E, $2C_3$, $3C_2'$, I, $2S_6$, and $3\sigma_d$, comprising the point group D_{3d} have no nonprimitive translation associated with them; the remaining 12 operations are accompanied by a displacement through the vector $\vec{v}(R) = +\frac{1}{2}c$.

The reduction of the representation of D_{6h} provided by the matrices $\{S_{\alpha\beta}(\kappa\kappa'|R)\}$ by the use of Eqs. (2.19), (2.20), and (3.11) yields

$$\Gamma = 2\Gamma_3^+ \oplus 2\Gamma_6^+ \oplus 2\Gamma_2^- \oplus 2\Gamma_5^- \tag{3.12}$$

in the notation of Koster *et al.*[9] The polar vector irreducible representations are Γ_2^- (basis function z) and Γ_5^- [basis functions $(x - iy)$, $-(x + iy)$]. Consequently,

we can write for the representations according to which the acoustic and optical modes transform

$$\Gamma_{ac} = \Gamma_2^- \oplus \Gamma_5^- \tag{3.13a}$$

$$\Gamma_{opt} = 2\Gamma_3^+ \oplus 2\Gamma_6^+ \oplus \Gamma_2^- \oplus \Gamma_5^- . \tag{3.13b}$$

The modes of Γ_6^+ symmetry are Raman active, those of Γ_2^- and Γ_5^- symmetry are infrared active, and the modes of Γ_3^+ symmetry are silent. Thus, with $\hat{k}$ along the z axis graphite possesses two doubly degenerate Raman-active optical modes of Γ_6^+ symmetry, one nondegenerate infrared-active optical mode of Γ_2^- symmetry, and one doubly degenerate infrared-active optical mode of Γ_5^- symmetry.

In Table II we list the components of the vectors $\{W_\alpha(\kappa|s\alpha\lambda)\}$ defined by Eq. (2.21) for $\hat{k} = (0, 0, 1)$. Because graphite is monatomic, the components of the exact eigenvectors $\{w_\alpha(\kappa|j)\}$ of the matrix obey two conditions which enable us to determine completely the eigenvectors which correspond to the infrared-active modes, even though they occur twice in the reduction [Eq. (3.12)]. As a consequence of infinitesimal translation invariance, the eigenvectors of the three $\vec{k} = 0$ acoustic modes possess the property that $w_\alpha(\kappa|j)/(M_\kappa)^{1/2}$ is independent of κ.[16] Consequently, for graphite we have that

$$w_\alpha(1|j) = w_\alpha(2|j) = w_\alpha(3|j) = w_\alpha(4|j) ,$$
$$\alpha = x, y, z, \quad j = \text{acoustic}. \tag{3.14}$$

From the orthonormality condition

$$\sum_{\kappa\alpha} w_\alpha^*(\kappa|j) w_\alpha(\kappa|j') = \delta_{jj'} \tag{3.15}$$

obeyed by the eigenvectors, we find that when j' refers to an acoustic branch, while j refers to an optical branch, in view of Eq. (3.14),

$$w_\alpha(1|j) + w_\alpha(2|j) + w_\alpha(3|j) + \omega_\alpha(4|j) = 0,$$
$$\alpha = x, y, z, \quad j = \text{optical}. \tag{3.16}$$

TABLE II. (un-normalized) eigenvectors for the Raman- and infrared-active modes for $\hat{k} = (0, 0, 1)$.

	Γ_{61}^+	Γ_{62}^+	Γ_2^-	Γ_{51}^-	Γ_{52}^-
$W_x(1)$	A	A^*	0	A	A^*
$W_y(1)$	$-iA$	iA^*	0	$-iA$	iA^*
$W_z(1)$	0	0	a	0	0
$W_x(2)$	B	B^*	0	B	B^*
$W_y(2)$	$-iB$	iB^*	0	$-iB$	iB^*
$W_z(2)$	0	0	b	0	0
$W_x(3)$	$-B$	$-B^*$	0	B	B^*
$W_y(3)$	iB	$-iB^*$	0	$-iB^*$	iB^*
$W_z(3)$	0	0	b	0	0
$W_x(4)$	$-A$	$-A^*$	0	A	A^*
$W_z(4)$	iA	$-iA^*$	0	$-iA$	iA^*
$W_y(4)$	0	0	a	0	0

$a = b$ for acoustic modes
$a = -b$ for optical modes
$A = B$ for acoustic modes
$A = -B$ for optical modes

TABLE III. (un-normalized) eigenvectors for the Raman- and infrared-active modes for $\hat{k} = (1, 0, 0)$.

	Γ_1^+	Γ_2^+	Γ_3^+	Γ_2^-	Γ_3^-	Γ_4^-
$W_x(1)$	a	0	0	0	0	a
$W_y(1)$	0	0	a	a	0	0
$W_z(1)$	0	a	0	0	a	0
$W_x(2)$	b	0	0	0	0	b
$W_y(2)$	0	0	b	b	0	0
$W_z(2)$	0	b	0	0	b	0
$W_x(3)$	$-b$	0	0	0	0	b
$W_y(3)$	0	0	$-b$	b	0	0
$W_z(3)$	0	$-b$	0	0	b	0
$W_x(4)$	$-a$	0	0	0	0	a
$W_y(4)$	0	0	a	a	0	0
$W_z(4)$	0	$-a$	0	0	a	0

$a = b$ for acoustic modes
$a = -b$ for optical modes

This condition states that the center of mass of a primitive unit cell is stationary in any optical mode of graphite. The consequences of Eqs. (3.14) (3.14) and (3.16) are incorporated into the results for the eigenvectors $\{W_\alpha(\kappa|s\alpha\lambda)\}$ displayed in Tables II and III.

If the phonon wave vector $\vec{k}$ tends to zero along the x axis so that $\hat{k} = (1, 0, 0)$, the point group $G_0(\hat{k}; -\hat{k})$ is D_{2h}. The eight operations of this group and the corresponding characters calculated from Eq. (2.20) are

R	E	C_2	C_2'	C_2''	I	σ_h	σ_d	σ_v
$\chi(R)$	12	0	0	−4	0	4	4	0

. (3.17)

Here C_2, C_2', and C_2'' are rotations by 180° about the z, y, and x axes, respectively; and σ_h, σ_d, and σ_v are reflections in the xy, zx, and yz planes, respectively.

Reducing the representation of the group D_{2h} provided by the matrices $\{s_{\alpha\beta}(\kappa\kappa'|R)\}$ yields

$$\Gamma = 2\Gamma_1^+ \oplus 2\Gamma_2^+ \oplus 2\Gamma_3^+ \oplus 2\Gamma_2^- \oplus 2\Gamma_3^- \oplus 2\Gamma_4^- . \tag{3.18}$$

The polar vector irreducible representations of the group D_{2h} are Γ_2^-, Γ_3^-, and Γ_4^-, for which the basis functions are y, z, and x, respectively. Consequently, the irreducible representations of D_{2h} according to which the acoustic and optical modes transform are

$$\Gamma_{ac} = \Gamma_2^- \oplus \Gamma_3^- \oplus \Gamma_4^- \tag{3.19}$$

$$\Gamma_{opt} = 2\Gamma_1^+ \oplus 2\Gamma_2^+ \oplus 2\Gamma_3^+ \oplus \Gamma_2^- \oplus \Gamma_3^- \oplus \Gamma_4^- . \tag{3.20}$$

The modes of Γ_1^+, Γ_2^+, and Γ_3^+ symmetry are Raman active and the modes of Γ_2^-, Γ_3^-, and Γ_4^- symmetry are infrared active. In Table III we have tabulated the vectors $\{W_\alpha(\kappa|s\alpha\lambda\}$ defined by Eq. (2.21) for $\hat{k} = (1, 0, 0)$.

Finally, in Table IV we list the squares of the frequencies of the Raman- and infrared-active modes of graphite for $\hat{k} = (0, 0, 1)$ and $\hat{k} = (1, 0, 0)$.

TABLE IV. Squared frequencies of the Raman- and infrared-active optical modes of graphite for $\hat{k}=(1,0,0)$ and $\hat{k}=(1,0,0)$.

$$\hat{k}=(0,0,1)$$

$$M\omega^2_{\Gamma_6^+}=\begin{cases}\frac{1}{2}\{a_{11}-a_{14}+a_{22}-a_{23}+[(a_{11}-a_{14}-a_{22}+a_{23})^2+4(a_{12}-a_{13})^2]^{1/2}\}\\ \frac{1}{2}\{a_{11}-a_{14}+a_{22}-a_{23}-[(a_{11}-a_{14}-a_{22}+a_{23})^2+4(a_{12}-a_{13})^2]^{1/2}\}\end{cases}$$

$$M\omega^2_{\Gamma_2^-}=\begin{cases}2(b_{11}+b_{14})+16\pi(e_3^*)^2/v_a\epsilon^\infty_{zz}\\ 0\end{cases}$$

$$M\omega^2_{\Gamma_5^-}=\begin{cases}2(a_{11}+a_{14})\\ 0\end{cases}$$

$$\hat{k}=(1,0,0)$$

$$M\omega^2_{\Gamma_1^+}=\begin{cases}\frac{1}{2}\{a_{11}-a_{14}+a_{22}-a_{23}+[(a_{11}-a_{14}-a_{22}+a_{23})^2+4(a_{12}-a_{13})^2]^{1/2}\}\\ \frac{1}{2}\{a_{11}-a_{14}+a_{22}-a_{23}-[(a_{11}-a_{14}-a_{22}+a_{23})^2+4(a_{12}-a_{13})^2]^{1/2}\}\end{cases}$$

$$M\omega^2_{\Gamma_2^+}=\begin{cases}\frac{1}{2}\{b_{11}-b_{14}+b_{22}-b_{23}+[(b_{11}-b_{14}-b_{22}+b_{23})^2+4(b_{12}-b_{13})^2]^{1/2}\}\\ \frac{1}{2}\{b_{11}-b_{14}+b_{22}-b_{23}-[(b_{11}-b_{14}-b_{22}+b_{23})^2+4(b_{12}-b_{13})^2]^{1/2}\}\end{cases}$$

$$M\omega^2_{\Gamma_3^+}=\begin{cases}\frac{1}{2}\{a_{11}-a_{14}+a_{22}-a_{23}+[(a_{11}-a_{14}-a_{22}+a_{23})^2+4(a_{12}-a_{13})^2]^{1/2}\}\\ \frac{1}{2}\{a_{11}-a_{14}+a_{22}-a_{23}-[(a_{11}-a_{14}-a_{22}+a_{23})^2+4(a_{12}-a_{13})^2]^{1/2}\}\end{cases}$$

$$M\omega^2_{\Gamma_2^-}=\begin{cases}2(a_{11}+a_{14})\\ 0\end{cases}$$

$$M\omega^2_{\Gamma_3^-}=\begin{cases}2(b_{11}+b_{14})\\ 0\end{cases}$$

$$M\omega^2_{\Gamma_4^-}=2(a_{11}+a_{14})\quad 16\pi(e_1^*)^2/v_a\epsilon^\infty_{xx}$$

They are obtained by substituting the vectors listed in Tables II and III into the eigenvalue equation [Eq. (2.1)] and making use of the results given by Eqs. (3.3) and (3.7) and Table I.

The preceding results can be used to obtain the dielectric constants of graphite. Quite generally, the dielectric constant of any crystal in the absence of spatial dispersion and damping can be written in the form[17]

$$\epsilon_{\mu\nu}(\omega)=\epsilon^\infty_{\mu\nu}+\frac{4\pi}{v_a}\sum_{j=4}^{3r}\frac{f_\mu(j)f_\nu^*(j)}{\lambda_j^2-\omega^2}\ , \tag{3.21}$$

where

$$f_\mu(j)=\sum_{\kappa\alpha}\frac{z_{\mu\alpha}(\kappa)\xi_\alpha(\kappa|j)}{\sqrt{M_\kappa}}\ . \tag{3.22}$$

In these expressions $\{\lambda_j^2\}$ and $\{\xi_\alpha(\kappa|j)\}$ are the $3r$ eigenvalues and the corresponding unit eigenvectors of the matrix $f_{\alpha\beta}(\kappa\kappa')/(M_\kappa M_{\kappa'})^{1/2}$:

$$\sum_{\kappa'\beta}\frac{f_{\alpha\beta}(\kappa\kappa')}{(M_\kappa M_{\kappa'})^{1/2}}\xi_\beta(\kappa'|j)=\lambda_j^2\,\xi_\alpha(\kappa|j)\ . \tag{3.23}$$

According to Eq. (2.14) the matrix $s_{\alpha\beta}(\kappa\kappa'|S)$ commutes with the matrix $f_{\alpha\beta}(\kappa\kappa')/(M_\kappa M_{\kappa'})^{1/2}$ for each operation S of the point group G_0 of the space group of the crystal. Consequently, the eigenvalues $\{\lambda_j^2\}$ and the eigenvectors $\{\xi_\alpha(\kappa|j)\}$ can be obtained from the results of Tables II and IV, respectively, where in the latter table we must restrict our attention to the results quoted for $\hat{k}\equiv(0,0,1)$, and must set $e_3^*=0$. In this way we obtain the results

$$f_x(\Gamma_2^-)=f_y(\Gamma_2^-)=0,\quad f_z(\Gamma_2^-)=(e_3^*/\sqrt{M})(4a), \tag{3.24a}$$

$$\lambda^2_{\Gamma_2^-}=(2/M)(b_{11}+b_{14})\ , \tag{3.24b}$$

$$f_x(\Gamma_{51}^-)=\frac{e_1^*}{\sqrt{M}}(4A),\quad f_y(\Gamma_{51}^-)=\frac{e_1^*}{\sqrt{M}}(-4iA),$$

$$f_z(\Gamma_{51}^-)=0\ , \tag{3.25a}$$

$$f_x(\Gamma_{52}^-)=\frac{e_1^*}{\sqrt{M}}(4A^*),\quad f_y(\Gamma_{52}^-)=\frac{e_1^*}{\sqrt{M}}(4iA^*)\ ,$$

$$f_z(\Gamma_{52}^-)=0\ , \tag{3.25b}$$

$$\lambda^2_{\Gamma_5^-}=(2/M)(a_{11}+a_{14})\ . \tag{3.25c}$$

Only the contributions from the infrared-active optical modes have been included in obtaining the results expressed by Eqs. (3.24) and (3.25). This is because, by the definition of infrared-active modes, it is only these modes which give rise to nonzero coefficients $\{f_\mu(j)\}$.

From the orthonormality condition satisfied by the eigenvectors $\{\xi_\alpha(\kappa|j)\}$,

$$\sum_{\kappa\alpha}\xi_\alpha(\kappa|j)\,\xi_\alpha^*(\kappa|j')=\delta_{jj'}\ . \tag{3.26}$$

we find that

$$a^2=\tfrac{1}{4},\quad |A|^2=\tfrac{1}{8}. \tag{3.27}$$

Substituting Eqs. (3.24), (3.25), and (3.27) into Eq. (3.21) we obtain as the only nonzero elements of the dielectric tensor $\epsilon_{\mu\nu}(\omega)$

$$\epsilon_{xx}(\omega)=\epsilon^\infty_{xx}+\frac{4\pi}{v_a}\frac{4(e_1^*)^2}{M}\frac{1}{(2/M)(a_{11}+a_{14})-\omega^2}$$

$$=\epsilon_{yy}(\omega) \tag{3.28}$$

$$\epsilon_{zz}(\omega)=\epsilon^\infty_{zz}+\frac{4\pi}{v_a}\frac{4(e_3^*)^2}{M}\frac{1}{(2/M)(b_{11}+b_{14})-\omega^2}\ . \tag{3.29}$$

It should be noted that the frequency for which $\epsilon_{zz}(\omega)=0$ is just the frequency of the longitudinal-optical mode of Γ_2^- symmetry for $\hat{k}=(0,0,1)$ is as it should be. Similarly, the frequency at which $\epsilon_{xx}(\omega)=0$ is the frequency of the longitudinal-optical mode of Γ_4^- symmetry for $\hat{k}=(1,0,0)$ is as it should be.

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[8]See, for example, Ref. 7, p. 255.
[9]Here and elsewhere in this paper we use the notation and results of G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz [*Properties of the Thirty-Two Point Groups* (MIT, Cambridge, Mass., 1963)].
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