FACTOR GROUP ANALYSIS OF THE VIBRATIONAL SPECTRA OF CRYSTALS: A REVIEW AND CONSOLIDATION

BERNARDO A. DEANGELIS,[1] ROBERT E. NEWNHAM,[2] AND WILLIAM B. WHITE,[2] *Materials Research Laboratory*
The Pennsylvania State University
University Park, Pennsylvania 16802

ABSTRACT

The factor group method for calculation of the symmetry properties, and selection rules for vibrational modes of crystals with known structures is reviewed. A systematic procedure is presented which permits routine calculations for structures belonging to both symmorphic and non-symmorphic space groups.

INTRODUCTION

The interpretation of vibrational spectra of crystalline solids has been limited largely to empirical approaches. The reason for this state of affairs is that there has been no readily applicable way of predicting the number and selection rules for the vibrational modes of an arbitrary structure. Considerable work has been done on molecular crystals and on simple crystals of high symmetry. Actually the factor group method developed long ago is applicable to the general case, but it has been little used. It is the purpose of this paper to review the calculation of vibrational behavior for crystals from their symmetry properties and to outline an easily applicable procedure which requires only a pre-knowledge of the space group and the population of the equipoints.[3]

The factor group method, whose introduction is credited to Bhagavantam and Venkatarayudu (1939), allows the analysis of the vibrations at $\mathbf{k} = 0$, the center of the Brillouin zone for the entire crystal. The site group method of Halford (1946) consists in deriving the number of allowed modes of specified molecular entities on the basis of the symmetry of the site on which the molecule or coordinated group lies. It is obviously an approximation that is acceptable only to molecular crystals such as carbonates, sulfates, phosphates, and the like, where the forces between molecules are considerably weaker than those

---

[1] Present address SNAM PROGETTI SpA, Centro di Richerche di Monterotondo, Rome, Italy.

[2] Also affiliated with the Department of Geochemistry and Mineralogy.

[3] An equipoint is a set of positions in the crystal which are related by symmetry operations. The more common term "site" is sometimes used interchangeably for both "equipoint" and "position."

between atoms inside the molecule. Hornig (1948) and Winston and Halford (1949) discussed the relationship of the factor group method to the site group method. Following a long gap in the literature, a number of recent papers have appeared that discuss factor and site group analysis (Kopelman, 1967; Adams and Newton, 1970; Bertie and Bell, 1971). A specific application to the spinel structure also uses both methods (White and DeAngelis, 1967).

The main interest in the physics literature concerns the full dispersion curves. Therefore, the approach is more strictly connected with the irreducible representations of the full space groups and the factorization of the dynamical matrix. Recent discussions include Chen (1967), Streitwolf (1964), Warren (1968), and the extensive review of Maradudin and Vosko (1968).

Most crystallographic and mineralogic application of infrared and Raman spectroscopy requires only an interpretation of the first order spectrum and only selection rules for the zone center, $\mathbf{k} = 0$, are required. Thus the analytical treatment can be a great deal simpler than that required for treatment of the dispersion curves for the entire Brillouin zone. It is still required, however, to take account of the entire unit cell and not merely molecular groupings within the cell.

Factor Group Analysis

A crystal may be considered to be composed of N primitive unit cells, each of which contains r atoms. The total number of vibrational degrees of freedom is $3rN$. These are distributed in $3r$ branches (some of which may be degenerate) throughout the first Brillouin zone. The individual vibrations along the branches are labeled with a linear momentum vector, $\mathbf{k}$. Complete information about the vibrational displacements of all atoms in the crystal is contained in the dynamical matrix, $D(\mathbf{k})$. (See Maradudin and Vosko, 1968). A central problem in lattice dynamics is the factorization and diagonalization of the dynamical matrix for some choice of interatomic forces. $D(\mathbf{k})$ is invariant under the primitive translations of the lattice, due to cyclic boundary conditions and thus can be constructed from a single unit cell. $D(\mathbf{k})$ is of dimension $3r \times 3r$.

The momenta of phonons excited by first order infrared absorption and Raman scattering are very small. We are therefore concerned with the special case of $\mathbf{k} = 0$, the vibrational behavior of the crystal at the center of the Brillouin zone—the so-called Γ-point. The energy of three of the $3r$ phonon branches goes to zero as $\mathbf{k} \rightarrow 0$. These are called the acoustic modes and are equivalent to pure translations of free molecules. There remain $3r - 3$ optical branches with finite energy at $\mathbf{k} = 0$; some are possibly degenerate.

The Factor Group

There has been some confusion in the chemical literature over the various groups which describe the symmetry of crystals and sites within crystals. The factor group must be derived properly to lead to an exact definition of the invariance properties of a unit cell.

A space group, G, is a set of operators of the type[1]

$$\{R \mid T + t\}$$

where R represents a rotation (proper or improper), T is a lattice translation, and t is a fractional lattice translation.

Operators of the type $\{R|0\}$ represent rotations (proper or improper) and form one of the thirty-two crystallographic point groups. $\{E \mid 0\}$ is the identity element. Operators of the type $\{E \mid T\}$ represent pure lattice translations and form an invariant (or normal) subgroup of the space group, called the translation group.

A subgroup is invariant if its left and right cosets, with respect to an element of the group, are equal:

$$\{R \mid T + t\} \{E \mid T\} = \{E \mid T\} \{R \mid T + t\}$$

or of it is formed from whole classes of the group.

For 73 of the 230 space groups $t = 0$ for all elements (that is, there are no fractional translations) and they are called symmorphic. The remaining 157 space groups have some elements with $t \neq 0$ (i.e., contain glide planes or screw axes) and are called non-symmorphic.

Given an invariant subgroup T, we can define a factor group G/T whose elements are the cosets of the invariant subgroup. In the case of the space groups, the factor group of the invariant subgroup of translations is formed by the elements

$$\{E \mid 0\} \{E \mid T\}, \qquad \{R_2 \mid t\} \{E \mid T\}, \cdots \{R_g \mid t\} \{E \mid T\}.$$

The identity element of the factor group is the translation group itself. The elements of the space group

$$\{E \mid 0\}, \qquad \{R_2 \mid t\}, \qquad \{R_3 \mid t\}, \cdots \{R_g \mid t\}$$

are called coset representatives. The coset representatives can be defined also as the symmetry elements of a unit cell. There are as many coset representatives as there are elements in the crystallographic point group. Each element of the factor group, therefore, contains an infinite number of components. The geometric reality of

---

[1] Brillouin zones for all 14 Bravais lattices and the operator notation used above are described in detail by Koster (1957).

these can be seen by sketching the symmetry elements onto a model of the crystal. Each element of rotational symmetry is duplicated many times by the lattice translations. It is this property that gives all unit cells the same rotational symmetry regardless of their selection from an arbitrary position in the crystal.

The most important properties of the factor group are its isomorphism (one-to-one correspondence) with the crystallographic point group and the fact that its irreducible representations are also irreducible representations of the space group. The irreducible representations of the translation group $\{E \mid T\}$ are all one-dimensional, and are given by $e^{i\mathbf{k}\cdot\mathbf{T}}$, where $\mathbf{k}$ is the wave vector and $\mathbf{T}$ is a lattice translation, here considered as a vector.

In symmorphic space groups $(t = 0)$ the coset representatives are all of the type $\{R \mid 0\}$ and they form a group which is the point group. In non-symmorphic space groups the coset representatives do not form a group and this is due to the presence of glide planes and screw axes (successive application of a glide or a screw operation is equivalent to a lattice translation, which does not belong to the factor group). Some authors have defined a "unit cell group." Hornig (1948) identifies it with the factor group. Kopelman (1967), however, considers it as distinct from the point group and the factor group. This cannot be considered correct, because for non-symmorphic space groups the coset representatives do not form a group (therefore a "unit cell group" cannot be defined), and for symmorphic space groups they form a group which is identical with the point group.

If the coset representatives act on a function which has translational symmetry a representation of the factor group is obtained (Jones, 1960). In other words, the coset representatives of a non-symmorphic space group do not form a group, but the matrices obtained by acting with them on a function with translational symmetry do form a group, which is a representation of the factor group. This property permits us to use simple factor group analysis for all structures regardless of whether their space groups are symmorphic or nonsymmorphic.

Reducible Representations

The classification of the degrees of freedom of the vibrating crystal among the irreducible representations of the factor group can be approached in several ways. The most general would be to construct a set of g (one for each element of the factor group) $3r \times 3r$ matrices which transform the structure into itself. This set of matrices forms a reducible representation of the factor group. The traces of these

matrices are the reducible characters which can then be analyzed by standard methods.

Such a procedure is unnecessary if one needs only the classification of the normal modes. The symmetry operators acting on individual atoms in the structure are all matrices of the form

$$\begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & \pm1 \end{bmatrix} \tag{1}$$

where θ is the angle of rotation about the particular symmetry axis. The full $3r \times 3r$ matrices are constructed of these 3×3 blocks, one for each atom. Only those blocks which lie on the diagonal of the $3r \times 3r$ matrices will contribute to the reducible character and these will be the blocks assigned to atoms which remain fixed during the symmetry operation. We can construct a generalized character for each class of symmetry operations as

$$\chi_\rho = \omega_\rho(\pm1 + 2\cos\theta) \tag{2}$$

where ω_ρ is the number of atoms which remain fixed during the operations of class ρ. This is indeed the formula used by Bhagavantam and Venkatarayudu (1939) in their original paper, and which has since been widely used by others. The problem of analyzing the symmetry properties is simplified to the problem of determining the invariance conditions of the unit cell.

The operations of screw axes and glide planes, which are proper elements of the factor group, cannot, in general, contribute to the reducible character, because the fractional translation will not leave any atoms invariant.

The equation takes the positive sign for proper rotations and the negative sign for improper rotations. The identities

$$E = C_1$$
$$\sigma = S_1$$
$$i = S_2$$

permit all symmetry operations to be treated as rotations.

When a complete set of reducible characters has been calculated, the distribution of normal modes is made by the group theory theorem

$$n_i = \frac{1}{g} \sum_\rho \chi_\rho g_\rho \chi_\rho{}^i \tag{3}$$

n_i is the number of times the i th irreducible representation is contained in the reducible representation, g is the order of the factor group; χ_ρ is the reducible character calculated above for each class, ρ; g_ρ is the order of the classes, and $\chi_\rho{}^i$ is the character of class ρ in the i th irreducible representation. The summation is over all classes of the factor group. The isomorphism between the factor group and the crystallographic point group permits the use of standard character tables for the irreducible representations such as published in Wilson, Decius, and Cross (1955), Koster (1957), or in many other books on spectroscopy.

The selection rules for each irreducible representation of the factor group are determined by noting the transformation properties for the dipole moment operator (for *IR* activity) and the polarizability tensor (for Raman activity). The distribution of these functions is given in many of the standard tables and the method for their derivation, or for the derivation of other operators is given by Mitra and Gielisse (1964). The polarization dependence of the vibrational spectra of noncubic crystals is likewise given by the selection rules.

CHOICE OF UNIT CELL

There are several choices for the unit cell on which to perform the factor group calculation: the crystallographic cell, the primitive cell, and the Wigner-Seitz cell. Those space groups with primitive unit cells pose no problems, since the normal crystallographic cell can be used directly. If the crystallographic cell is nonprimitive, the factor group calculation will introduce redundant modes.

The usual construction of the primitive cell for a nonprimitive lattice is not very useful, since it does not reflect directly the full symmetry of the structure.

The Wigner-Seitz cell has maximum possible symmetry, and it is primitive. It reflects the full factor group symmetry for symmorphic space groups. The Wigner-Seitz cell is constructed for each Bravais lattice by first locating all of the lattice points. Using an arbitrary lattice point as an origin, vectors are drawn to each of the neighboring lattice points. This done, perpendicular bisectors to these vectors are constructed. These planes will intersect to form a closed volume which is the Wigner-Seitz cell. This cell is the one commonly used for analytical calculations of band properties. It has the advantage that the origin is in the center of the cell and that there is a close relationship between the Wigner-Seitz cell drawn in real space and the Brillouin zone drawn in reciprocal (**k**) space. Koster (1957) illustrates these cells for all Bravais lattices.

While the use of the Wigner-Seitz cell seems advantageous when deriving symmetry coordinates, the crystallographic cell is by far the most convenient to use in mode classification, since most available crystal structure data are referred to this cell and the tables to be used later are based on this cell. The redundancy of the nonprimitive cells is easily removed. There are, however, numerous instances in the literature of failure to account for the redundancy with the result of predicting more modes than were observed.

A primitive cell is defined by Koster (1957) as the smallest volume from which the entire crystal can be reproduced by translation through the primitive translations. It follows that the primitive cell contains a single lattice point which is invariant under all rotational operations of the space group. The usual crystallographic cell is made up of a small integral number of primitive cells obtained by translating the primitive cell lattice point in a prescribed manner, and then redefining the translation vectors to correspond to the expanded cell. Since the redefinition of the cell affects only the elements of the translation group, by definition the identity element of the factor group, the distribution of degrees of freedom among the factor group irreducible representations does not change. The redundancy is introduced, because each set of equipoints in the primitive cell is duplicated for each additional lattice point in the enlarged cell.

When an analysis is made of the invariance conditions of atoms in the full crystallographic cell, each invariant atom will, in fact, have been counted too many times. Since the redefinition of unit cell does not affect the rotational symmetry, the redundancy is contained equally in the characters of all symmetry classes and can be simply divided out.

$$\chi_{\text{prim. cell}} = \frac{\chi_{\text{full cell}}}{\ell} \tag{4}$$

where ℓ is the number of lattice points (primitive cells) in the full crystallographic cell.

$\ell = 4$ for face-centered cells
$= 3$ for hexagonal forms of rhombohedral cells
$= 2$ for body-centered and base-centered cells

This analysis also applies to any larger cell which it might be convenient to construct for some special purpose.

DETERMINATIONS OF THE INVARIANCE CONDITIONS FOR CRYSTALS

It seems clear that the main stumbling block in the path of widespread application of factor group analysis to complex crystals is the

determination of the invariance conditions. Once these are known the remainder of the analysis is mechanical. It is easy to determine which atoms of a molecule are invariant under the various symmetry operations by simple inspection. Analysis of a complex structure, particularly one belonging to a non-symmorphic space group is much less obvious. One can, of course, construct a model of the crystal, locate all elements of factor group symmetry, and inspect for invariance and use equation 4 to eliminate redundancy. This approach works well for simple crystals but is tedious for complex ones. Likewise, the chances for error increase with complexity.

The information inputs that one normally has available are the International Tables of Crystallography (Henry and Lonsdale, 1965) and the crystal structure of the material. The International Tables list all equipoints for each space group with the point symmetry and published structure analyses give the distribution of atoms among the equipoints. We have developed a method to calculate the number of atoms invariant under each factor group symmetry class directly from this crystallographic information.

The formula to be justified is

$$\omega_\rho(\text{cryst. cell}) = \omega_S \frac{h_\rho}{g_\rho} \tag{5}$$

or

$$\omega_\rho(\text{prim. cell}) = \frac{g}{h} \frac{h_\rho}{g_\rho} \tag{6}$$

where g is the order of the factor group, h is the order of H, the point symmetry of the equipoint (or site group), g_ρ the number of elements in the class ρ in G, h_ρ the number of elements in the same class ρ in H. ω_ρ is the number of atoms left unshifted by the operations of class ρ in the factor group and ω_S is the number of atoms on the equipoint.

As first step, let us justify

$$\frac{g}{h} = m,$$

m being the number of crystallographically equivalent sites having symmetry H. Buerger (1960) calls m the "rank of the equipoint." He shows that the rank of the general position is equal to g (p. 249). He also shows that when a point lies on a symmetry element of order n ($n = 3$ for C_3, $n = 2$ for σ, etc.) its rank is reduced by a factor $1/n$ and when it lies on two symmetry elements of order n_1 and n_2 its rank is reduced by a factor $(1/n_1 n_2)$. If we take $n = h$ (we can think of

the order h of H as being made up of the product of the orders n_1, n_2, $n_3 \cdots$ of the generating elements of H) $m = g/h$ follows immediately.

Consider m points (the m positions of symmetry H). There are g_ρ symmetry elements of class ρ. These symmetry elements pass (h_ρ at a time) through the m points. One needs $m \times h_\rho$ elements to cover all the points, but only g_ρ are available. Therefore, each of the g_ρ elements must pass through ($m \times h_\rho/g_\rho$) points (that is, leaves $m \times h_\rho/g_\rho$ atoms unshifted). The m points are equivalent, as are the g_ρ symmetry elements. Obviously, when $h_\rho = g_\rho$ each symmetry element must pass through all the points.

Finally, the number of atoms populating an equipoint must be equal to the rank of the equipoint in order for symmetry to be preserved. Thus the number of atoms which remain invariant under the factor group is related to the total number of atoms on a particular site either by

$$\omega_\rho = \omega_s \frac{h_\rho}{g_\rho}$$

where the formula refers to any crystallographic cell or by

$$\omega_\rho = \frac{g}{h} \frac{h_\rho}{g_\rho}$$

which automatically refers to the primitive cell. The invariance conditions can be tabulated for each sublattice, summed for each symmetry class, and the reducible character calculated in the usual manner.

SOME REPRESENTATIVE EXAMPLES

As an illustration of this procedure for factor group analysis we examine a few structures in detail.

i) Perovskite

The basic perovskite structure (e.g., $SrTiO_3$) is primitive cubic. There are several structures based on distortions of the perovskite structure. Two of these are the orthorhombic $GdFeO_3$ structure and the trigonal $LaAlO_3$ structure. Factor group analysis would allow a comparison of the expected IR and Raman spectra of the three structures.

The normal mode behavior of perovskite is very well understood and it makes a good illustrative example. The crucial steps are presented in Table 1. Perovskite belongs to symmorphic space group $O_h{}^1$, $Pm3m$ with one formula unit per unit cell. Using $SrTiO_3$ as a typical example, the Sr^{2+} is on the $1(a)$ site, the Ti^{4+} on the $1(b)$ site and the 3 oxygen

TABLE 1. INVARIANCE CONDITIONS FOR PEROVSKITE

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
1(a), O_h Sr^{++}	1	1	1	1	1	1	1	1	1	1
1(b), O_h Ti^{4+}	1	1	1	1	1	1	1	1	1	1
3(d), D_{4h}	E	–	$2C_2''$	$2C_4$ $2C_2'$ C_2		i	$2S_4$	–	σ_h $2\sigma_v$	$2\sigma_d$
3 0^{-2}	3	0	1	1 2 1		3	1	0	1 2	1
ω_p	5	2	3	3	5	5	3	2	5	3
Γ	15	0	–3	3	–5	–15	–3	0	5	3

$$\Gamma = 4T_{1u} + T_{2u}$$

ions on the $3(d)$ site. The point symmetries of these occupied sites are tabulated in the left column of table 1. The next step is to match the classes of the subgroup with the corresponding classes of the factor group. This step is trivial for the $1(a)$ and $1(b)$ sites, since the subgroup is the same as the factor group. The $3(d)$ sites are more complicated. The diagonal axes, $2C_2''$, of the D_{4h} subgroup correspond to the edge diagonals of the cube. However, both the class of $2C_2'$ and the class C_2 in D_{4h} correspond to the same $3C_2$ class of the factor group. This situation occurs rather frequently. The number of atoms in each sublattice that remain invariant can now be written down, by using equation 5 or 6. An atom will be invariant under a factor group operation only if that symmetry operation appears in the point symmetry of the sublattice. From the total population of the equipoint (sublattice), the proportion that remain invariant is determined by the ratio of the order of the subgroup class to the order of the corresponding factor group class. These are the numbers tabulated with each sublattice in Table 1. One then merely sums the invariant atoms over all equipoints and obtains the total invariant atoms, ω_p. From ω_p the reducible character and its decomposition into the irreducible representations of the factor group follow according to equations 2 and 3 and, of course, are the well known result.

The $GdFeO_3$ structure belongs to space group D_{2h}^{16}, *Pbnm* with 4

formula units in the primitive cell (Geller and Wood, 1956). Table 2 gives the distribution of atoms on the equipoints and their point symmetries. All rotation elements in this space group are screw axes and do not contribute to the character. Here we have to decide which factor group class of mirror planes to select as the unique subgroup class. This choice is made by the selection of crystallographic axes in an orthorhombic system. The space group symbol *Pbnm* places the true mirror perpendicular to the *c*-axis so $\sigma_{(xy)}$ is selected. Other orientations are frequently used and indeed Geller and Wood's choice is not that of the International Tables (*Pnma*). The remainder of the analysis follows as before.

The structure of $LaAlO_3$ (Geller and Bala, 1956) is trigonal, space group $D_{3d}{}^5$, $R\bar{3}m$ with two formula units in the trigonal cell. The analysis is summarized in Table 3.

It should be noted here that although both D_{2h} and D_{3d} are subgroups of O_h, the normal mode distribution in tables 2 and 3 cannot be obtained by a simple descent of symmetry argument. The distor-

TABLE 2. INVARIANCE CONDITIONS FOR $GdFeO_3$ STRUCTURE

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma_{(xy)}$	$\sigma_{(xz)}$	$\sigma_{(yz)}$
4 (c), C_s	E	–	–	–	–	C_s	–	–
4 Gd^{3+}	4	0	0	0	0	4	0	0
4 (b), C_i	E	–	–	–	i	0	0	0
4 Fe^{3+}	4	0	0	0	4	0	0	0
4 (c), C_s	E	–	–	–	–	C_s	–	–
4 O^{-2} (I)	4	0	0	0	0	4	0	0
8 (d), C_1	E	–	–	–	–	–	–	–
8 O^{-2} (II)	8	0	0	0	0	0	0	0
ω_p	20	0	0	0	4	8	0	0
Γ	60	0	0	0	-12	8	0	0

$$\Gamma = 7\ A_g + 7\ B_{1g} + 5\ B_{2g} + 5\ B_{3g}$$
$$+\ 8\ A_u + 8\ B_{1u} + 10\ B_{2u} + 10\ B_{3u}$$

TABLE 3.   INVARIANCE CONDITIONS FOR $LaAlO_3$ STRUCTURE

D_{3d}	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_d$
1 (a) D_{3d}	1	1	1	1	1	1
1 (b) 2 Al^{3+}	1	1	1	1	1	1
2 (c), C_{3v}	E	$2C_3$	–	–	–	$3\sigma_v$
2 La^{3+}	2	2	0	0	0	2
6 (h), C_s	E	–	–	–	–	σ
6 0^{-2}	6	0	0	0	0	2
ω_ρ	10	4	2	2	2	6
Γ	30	0	-2	-6	0	6

$$\Gamma = 3\,A_{1g} + A_{2g} + 4\,E_g + A_{1u} + 5\,A_{2u} + 6\,E_u$$

tion of the structure and the enlarged unit cells make a full factor group analysis mandatory if the spectra of the three structures are to be properly compared.

ii) Pollucite

Pollucite, $Cs_{1-x}Na_xAlSi_2O_6 \cdot xH_2O$ $(x = 0.3)$, is a complex network silicate. It is cubic, space group O_h^{10}, $Ia3d$ with 16 formula units per unit cell (Newnham, 1967). An analysis given in Table 4 illustrates the simplicity of the method. Water and Na^+ are believed by Newnham to substitute on the cesium site and so are not included separately. The only difficulty is in placing the two-fold axes. The C_2 axis associated with the cesium sublattice must be perpendicular to the C_3 axis in D_3 symmetry, therefore is perpendicular to the cube body diagonal and must be an edge diagnoal, the $6C_2$ class of O_h. The other two-fold axis is associated with the SiO_4 and AlO_4 tetrahedra and its position must be determined by an examination of the structure.

Since the crystallographic cell is body-centered, the multiplicity of the equipoints listed in the International Tables for X-ray Crystallography refers to this cell and therefore is twice as large as that for the primitive cell which contains only 8 formula units. By using equa-

TABLE 4. INVARIANCE CONDITIONS FOR POLLUCITE

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
16 (b), D_3	E	$2C_3$	$3C_2$	–	–	–	–	–	–	–
Cs^+	8	2	4	0	0	0	0	0	0	0
48 (g), C_2	E	–	–	–	C_2	–	–	–	–	–
$Al^{3+}Si^{4+}$	24	0	0	0	8	0	0	0	0	0
96 (h), C_1	E	–	–	–	–	–	–	–	–	–
O^{-2}	48	0	0	0	0	0	0	0	0	0
ω_ρ	80	2	4	0	8	0	0	0	0	0
Γ	240	0	–4	0	–8	0	0	0	0	0

$$\Gamma = 4 A_{1g} + 5 A_{2g} + 9 E_g + 16 T_{1g} + 15 T_{2g}$$
$$+ 4 A_{1u} + 5 A_{2u} + 9 E_u + 16 T_{1u} + 15 T_{2u}$$

tion 6 the correct number of atoms for the primitive cell is obtained automatically. The symmetry restrictions are very powerful and only 16 *IR* modes are permitted for this very complex structure.

SUMMARY

It is possible to make very routine calculations of the symmetry of normal modes and their selection rules for crystals of arbitrarily complex structure. The required data are the distributions of atoms on the equipoints of the space group. The steps in the analysis then are:

i. Determine the invariance conditions for each sublattice, using equation 5 or 6.
ii. Sum these over all sublattices and calculate the reducible repre sentation.
iii. Distribute the degrees of freedom among the irreducible representations of the factor group, using equation 3.
iv. Write the selection rules in the usual manner.

REFERENCES

ADAMS, D. M., AND D. C. NEWTON (1970) Tables for factor group analysis of the vibrational spectra of solids. *J. Chem. Soc.* (A), 2822–2827.

BERTIE, J. E., AND J. W. BELL (1971) Unit cell group and factor group in the theory of the electronic and vibrational spectra of crystals. *J. Chem. Phys.* **54**, 160–162.

BHAGAVANTAM, S., AND T. VENKATARAYUDU (1939) Raman effect in relation to crystal structure. *Proc. Indian Acad. Sci.* **9A**, 224–258.

BUERGER, M. J. (1960) *Crystal Structure Analysis*. John Wiley, New York, p. 249.

CHEN, S. H. (1967) Group-theoretical analysis of the lattice vibrations in metallic β-Sn. *Phys. Rev.* **163**, 532–546.

GELLER, S., AND E. A. WOOD (1956) Crystallographic studies of perovskite-like compounds. I. Rare earth orthoferrites and $YFeO_3$, $YCrO_3$, $YAlO_3$. *Acta Crystallogr.* **9**, 563–568.

———, AND V. B. BALA (1956) Crystallographic studies of perovskite-like compounds. II. Rare earth aluminates. *Acta Crystallogr.* **9**, 1019–1025.

HALFORD, RALPH S. (1946) Motions of molecules in condensed systems: I. Selection rules, relative intensities, and orientation effects for Raman and infrared spectra. *J. Chem. Phys.* **14**, 8–15.

HENRY, N. F., AND K. LONSDALE (1965) *International Tables for X-Ray Crystallography,* Vol. I. Kynoch Press, London. 558 pp.

HORNIG, DONALD F. (1948) The vibrational spectra of molecules and complex ions in crystals. I. General theory. *J. Chem. Phys.* **16**, 1063–1076.

JONES, H. (1962) *The Theory of Brillouin Zones and Electric States in Crystals.* North Holland, Amsterdam, 268 pp.

KOPELMAN, RAOUL (1967) Interchange symmetry. I. Molecules, crystals and excitons. *J. Chem. Phys.* **47**, 2631–2648.

KOSTER, G. F. (1957) Space groups and their representations. *In* F. Seitz and D. Turnbull (eds.) *Solid State Physics,* Vol. 5. Academic Press, New York, 84 pp.

MARADUDIN, A. A., AND S. H. VOSKO (1968) Symmetry properties of the normal vibrations of a crystal. *Rev. Mod. Phys.* **40**, 1-37.

MITRA, SHASHANKA S., AND PETER J. GIELISSE (1964) Infrared spectra of crystals. *In* Herman A. Szymanski (ed) *Progress in Infrared Spectroscopy,* Vol. II. Plenum Press, New York.

NEWNHAM, R. E. (1967) Crystal structure and optical properties of pollucite. *Amer. Mineral.* **52**, 1515–1518.

STREITWOLF, H. W. (1964) Über die Symmetrien bein Gitterproblem. *Phys. Stat. Sol.* **5**, 383–390.

WARREN, J. L. (1968) Further considerations on the symmetry properties of the normal vibrations of a crystal. *Rev. Mod. Phys.* **40**, 38–76.

WHITE, W. B., AND B. A. DE ANGELIS (1967) Interpretation of the vibrational spectra of spinels. *Spectrochim. Acta* **23A**, 985–995.

WILSON, E. BRIGHT, JR., J. C. DECIUS, AND PAUL C. CROSS (1955) *Molecular Vibrations.* McGraw-Hill, New York, 388 pp.

WINSTON, HARVEY, AND RALPH S. HALFORD (1949) Motions of molecules in condensed systems: V. Classification of motions and selection rules for spectra according to space symmetry. *J. Chem. Phys.* **17**, 607–616.