

Group Theory and Crystal Lattices

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A method of obtaining the angular parts of one electron wave functions in all crystal lattices is discussed. The functions are shown to be bases for irreducible representations of rotation groups. Tables of these functions are given for use in cubic and close packed hexagonal lattices. Consideration is also given to angular wave functions in polyatomic crystals.

1. INTRODUCTION

THE effects of the symmetry properties of crystals on wave functions have been discussed in the literature¹ and functions which transform according to the operations of the full cubic group have been tabulated—the Kubic Harmonics.² Calculations on the band structure of solids are greatly simplified by the use of these and other similar functions and it was felt that their publication would be of great assistance to anyone undertaking such work. The functions given are for use in all cubic lattices and the close-packed hexagonal lattice but the general method of obtaining such functions is described and can be applied to all lattices.

A systematic presentation of the underlying theory, most of which can be found scattered through the literature, is given as an introduction.

2. CRYSTAL SYMMETRY

The one-electron wave functions in a crystal are solutions of Schrödinger's equation

$$\mathcal{H}\psi = \mathcal{E}\psi, \quad (1)$$

where the Hamiltonian \mathcal{H} is a function of the electron coordinates and \mathcal{E} is the energy.

For the ideal case of an infinite lattice there exists a translation group \mathcal{T} whose elements are defined by the equation

$$T_j \mathbf{r} = \mathbf{r} + n_{ji} \mathbf{a}_i,$$

where the \mathbf{a}_i 's ($i=1,2,3$) are the three smallest vectors such that the appearance of the lattice from a point $\mathbf{r} + \mathbf{a}_i$ is identical with that from the point \mathbf{r} . This means that the crystal potential $V(\mathbf{r})$ is invariant under the operations of \mathcal{T} . The three vectors \mathbf{a}_i define a unit cell in the lattice.

\mathcal{T} is an infinite Abelian group which commutes with both \mathcal{H} and \mathcal{E} in Eq. (1) and it can be shown that the

¹ H. A. Bethe, *Ann. Physik* **3**, 133 (1929); C. Eckart, *Revs. Modern Phys.* **2**, 344 (1930); D. H. Ewing and F. Seitz, *Phys. Rev.* **43**, 804 (1933); Bouckaert, Smoluchowski, and Wigner, *Phys. Rev.* **50**, 58 (1936); F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), and included references. F. C. Von der Lage, and H. A. Bethe, *Phys. Rev.* **71**, 612 (1947); C. Herring, *J. Franklin Inst.* **233**, 525 (1952); W. Doring and V. Zehler, *Ann. Physik* **13**, 214 (1953); Bell, Hum, Pincherle, Sciana, and Woodward, *Proc. Roy. Soc. (London)* **A71**, 217 (1953).

² See reference 1, F. C. Von der Lage and H. A. Bethe.

wave functions have the form

$$\psi(\mathbf{k}, \mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) u(\mathbf{k}, \mathbf{r}),$$

where

$$T_j u(\mathbf{k}, \mathbf{r}) = u(\mathbf{k}, \mathbf{r}). \quad (2)$$

Thus, it is only necessary to determine wave functions in the unit cell, for with the use of the wave vector \mathbf{k} they can then be found at any point in the crystal.

If a lattice in \mathbf{k} space, a reciprocal lattice, is defined by the three vectors \mathbf{b}_j , where $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$, the addition of $\mathbf{K} = n_j \mathbf{b}_j$ to the wave vector introduces a factor $\exp(i\mathbf{K} \cdot \mathbf{r})$ to the wave function; this has the periodicity of the lattice and can therefore be absorbed into $u(\mathbf{k}, \mathbf{r})$. Thus, the translational symmetry of the lattice can be completely described by taking the wave functions to be multivalued functions of the \mathbf{k} 's lying in the unit reciprocal lattice cell—the first Brillouin zone.

As the wave functions are to be considered as functions of \mathbf{k} it is obvious that the energy eigenvalue must also be a function of the wave vector, so that Eq. (1) can be written in the form

$$[-\frac{1}{2}\nabla^2 + V(\mathbf{r})]\psi(\mathbf{k}, \mathbf{r}) \equiv \mathcal{H}(\mathbf{r})\psi(\mathbf{k}, \mathbf{r}) = \mathcal{E}(\mathbf{k})\psi(\mathbf{k}, \mathbf{r}). \quad (3)$$

For given \mathbf{k} and $\mathcal{E}(\mathbf{k})$ this has in general n linearly independent degenerate solutions $\psi_s(\mathbf{k}, \mathbf{r})$, ($s=1, 2, \dots, n$).

About each point in the lattice one can define a rotation group \mathcal{R} , whose elements are rotations through $2\pi/n$ and inversion (i.e., the conversion of \mathbf{r} into $-\mathbf{r}$) such that

$$R_j V(\mathbf{r}) = V(\mathbf{r}).$$

It is shown in Appendix I that if R_j is an element of \mathcal{R} such that $R_j \mathbf{k} = \mathbf{k} + n_{ji} \mathbf{b}_i$ (when R_j is performed about the center of the first Brillouin zone) then it is possible to find an irreducible representation of the group of these elements made up of n -dimensional matrices $[J_{ts}]$ such that

$$R_j [\psi_s(\mathbf{k}, \mathbf{r})] \equiv [\psi_s(\mathbf{k}, R_j^{-1} \mathbf{r})] = [\psi_t(\mathbf{k}, \mathbf{r})] [J_{ts}]. \quad (4)$$

Thus in order to find the effect on the wave functions due to the rotational symmetry of the crystal lattice it is necessary to know

- (a) The rotational group \mathcal{R} to be associated with the point about which the wave functions are developed.

- (b) The subgroup $\mathcal{R}(\mathbf{k})$ of \mathcal{R} whose elements leave \mathbf{k} invariant or change it by a sum of reciprocal lattice vectors.

3. APPLICATION OF GROUP THEORY

In order to apply group theory to the crystal lattice the wave functions are expanded as a complete set of orthogonal functions about an atomic nucleus within the unit cell:

$$\psi_s(\mathbf{k}, \mathbf{r}) = \sum_l \sum_m A_{s,l,m} Y_l^m(\theta, \phi) S_l[\mathcal{E}(\mathbf{k}), \mathbf{r}],$$

where $Y_l^m(\theta, \phi)$ is a spherical harmonic; S is a function of r , the distance from the nucleus; and $A_{s,l,m}$ is a constant coefficient to be determined by boundary conditions. This equation can be rewritten in the form

$$\begin{aligned} \psi_s(\mathbf{k}, \mathbf{r}) &= \sum_L B_{sL} \sum_m C_{s,L,m} Y_L^m(\theta, \phi) S_L[\mathcal{E}(\mathbf{k}), \mathbf{r}] \\ &= \sum_L B_{sL} X_{sL} S_L[\mathcal{E}(\mathbf{k}), \mathbf{r}], \end{aligned}$$

where a particular value of L may appear more than once in the sum. The linear combinations of spherical harmonics, X_{sL} —the lattice harmonics—can be completely determined by group theory, for the only parts of the wave functions which can be affected by rotation are the lattice harmonics, and so from Eq. (4)

$$R_j[X_s] = [X_t][J_{ts}] \quad (\text{the suffix } L \text{ on both sides of the equation is dropped for convenience}).$$

Suppose that one has a group $\mathcal{R}(\mathbf{k}_a)$ which is completely determined, i.e., the matrices $[{}^a J_{ts}^m]$ which form its m th irreducible representation ${}^a \Gamma^m$, and the lattice harmonics ${}^a X_s^m$ corresponding to them are known. For each subgroup $\mathcal{R}(\mathbf{k}_b)$ of $\mathcal{R}(\mathbf{k}_a)$ it is possible to find a matrix M such that $M^{-1}[{}^a J_{ts}^m]M$ has a set of matrices $[{}^b J_{ts}^n]$ running down its diagonal for each element R_j in $\mathcal{R}(\mathbf{k}_b)$. That is, the representations ${}^a \Gamma^m$ can be reduced to give the irreducible representations ${}^b \Gamma^n$ of $\mathcal{R}(\mathbf{k}_b)$. The lattice harmonics corresponding to the irreducible representations of $\mathcal{R}(\mathbf{k}_b)$ are given by $[{}^a X_s^m]M$. The group $\mathcal{R}(\mathbf{k}_b)$ can then be used to determine a further group $\mathcal{R}(\mathbf{k}_c)$.

It is always possible to start with the full rotation group for which the ${}^a X_s^m$ are the spherical harmonics Y_l^m , but for the results applicable to cubic lattices given at the end of this paper the full cubic group which has been determined by Von der Lage and Bethe² was used as a starting point.

4. DETERMINATION OF PROPER WAVE FUNCTIONS

By use of the lattice harmonics corresponding to a rotation group $\mathcal{R}(\mathbf{k})$ it is possible to find ψ 's centered on each atomic nucleus in a unit lattice cell. These ψ 's contain an infinite number of arbitrary constants B_L which must be determined by the condition that a proper wave function is smooth throughout the crystal. To determine the constants it is usual to divide the

unit cell into subcells, one surrounding each nucleus, and to match wave functions over the surfaces of these subcells.³

When matching wave functions it must be remembered that they are each developed about different points in the lattice—they are each centered on an atomic nucleus. It is shown in Appendix II that this has two important effects. Consider different atomic nuclei at A_p and A_q , where A_q is at a distance \mathbf{S}_{pq} from A_p ; then:

- (a) ψ_p should be joined smoothly on to $\exp(i\mathbf{k} \cdot \mathbf{S}_{pq})\psi_q$
 (b) ψ_p^n must be considered in conjunction with ψ_q^m

where:

$$[J_{ts}^m] = \exp\{i\mathbf{k} \cdot (E - {}_p R_j^{-1})\mathbf{S}_{pq}\}[J_{ts}^n].$$

APPENDIX I

It is possible to define a rotation group \mathcal{R} at any point in the direct lattice, the elements of which leave the lattice invariant. In the reciprocal lattice one can define a rotation group $\mathcal{S}(\mathbf{k})$ for each \mathbf{k} , whose operations S_i when performed about the center of the first Brillouin zone satisfy the equation

$$S_i \mathbf{k} = \mathbf{k} + n_{ij} \mathbf{b}_j \equiv \mathbf{k}.$$

Define $\mathcal{R}(\mathbf{k})$ as the subgroup of the elements common to \mathcal{R} and $\mathcal{S}(\mathbf{k})$.

In this appendix it is shown that one can find an irreducible representation of $\mathcal{R}(\mathbf{k})$ made up of matrices $[J_{ts}]$ such that

$$R_j[\psi_s(\mathbf{k}, \mathbf{r})] = [\psi_s(\mathbf{k}, R_j^{-1}\mathbf{r})] = [\psi_t(\mathbf{k}, \mathbf{r})][J_{ts}] \quad (4)$$

where R_j is any element of $\mathcal{R}(\mathbf{k})$.

The effect of a rotation R_j on a function $f(\mathbf{r})$ may be defined by the equations

$$R_j f(\mathbf{r}) = f(M_j \mathbf{r}) = [f(\mathbf{s})]_{\mathbf{s} = M_j \mathbf{r}}.$$

Then

$$\begin{aligned} R_k R_j f(\mathbf{r}) &= R_k \{R_j f(\mathbf{r})\} = [R_j f(\mathbf{t})]_{\mathbf{t} = M_k \mathbf{r}} \\ &= \{[f(\mathbf{s})]_{\mathbf{s} = M_j \mathbf{t}}\}_{\mathbf{t} = M_k \mathbf{r}} = [f(\mathbf{s})]_{\mathbf{s} = M_j M_k \mathbf{r}}. \end{aligned}$$

If $R_l = R_k R_j$ then $M_l = M_j M_k$, and it is logical and consistent to write $M_j = R_j^{-1}$ so that $R_j f(\mathbf{r}) = f(R_j^{-1}\mathbf{r})$ and, in particular, $R_j \psi(\mathbf{k}, \mathbf{r}) = \psi(\mathbf{k}, R_j^{-1}\mathbf{r})$.

Schrödinger's equation for a typical one-electron wave function is written in the form

$$[-\frac{1}{2}\nabla_r^2 + V(\mathbf{r})]\psi(\mathbf{k}, \mathbf{r}) = \mathcal{H}(\mathbf{r})\psi(\mathbf{k}, \mathbf{r}) = \mathcal{E}(\mathbf{k})\psi(\mathbf{k}, \mathbf{r}). \quad (3)$$

It is readily shown that

- (a) $R_j \nabla_r = \nabla_{R_j \mathbf{r}}$
 (b) $\mathbf{A} \cdot (R_j \mathbf{B}) = (R_j^{-1} \mathbf{A}) \cdot \mathbf{B}$ (\mathbf{A} and \mathbf{B} any vectors)

³ E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); J. C. Slater, Phys. Rev. **45**, 794 (1934); W. Shockley, Phys. Rev. **52**, 866 (1937); W. Kohn, Phys. Rev. **87**, 472 (1952); D. J. Howarth and H. Jones, Proc. Phys. Soc. (London) **A65**, 355 (1952); Bell, Hum, Pincherle, Sciana, and Woodward, reference 1; D. P. Jenkins and L. Pincherle, Phil. Mag., Ser. 7, **45**, 93 (1954); L. I. Schiff, Proc. Phys. Soc. (London) **A67**, 1 (1954).

and hence, that

$$\nabla^2_{R_j r} \equiv \nabla_r^2.$$

By definition $R_j V(\mathbf{r}) = V(\mathbf{r})$. Therefore the operator R_j commutes with the Hamiltonian $\mathcal{H}(\mathbf{r})$ as well as with the energy eigenvalue $\mathcal{E}(\mathbf{k})$. Thus, operating with R_j on both sides of Eq. (3) gives

$$\mathcal{H}(\mathbf{r})\psi(\mathbf{k}, R_j^{-1}\mathbf{r}) = \mathcal{E}(\mathbf{k})\psi(\mathbf{k}, R_j^{-1}\mathbf{r}). \quad (3a)$$

For a given \mathbf{k} and $\mathcal{E}(\mathbf{k})$ Eq. (3) has, in general, n degenerate solutions

$$\psi_s(\mathbf{k}, \mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) u_s(\mathbf{k}, \mathbf{r}) \quad (s=1, 2, \dots, n).$$

Therefore Eq. (3a) has n solutions

$$\begin{aligned} \psi_s(\mathbf{k}, R_j^{-1}\mathbf{r}) &= \exp(i\mathbf{k} \cdot R_j^{-1}\mathbf{r}) u_s(\mathbf{k}, R_j^{-1}\mathbf{r}) \\ &= \exp(iR_j \mathbf{k} \cdot \mathbf{r}) u_s(\mathbf{k}, R_j^{-1}\mathbf{r}). \end{aligned}$$

But these are wave functions having wave vector $R_j \mathbf{k}$. Therefore it is possible to define a set of n degenerate wave functions

$$\psi_t(R_j \mathbf{k}, \mathbf{r}) = \exp(iR_j \mathbf{k} \cdot \mathbf{r}) v_t(R_j \mathbf{k}, \mathbf{r}) \quad (t=1, 2, \dots, n)$$

which are also solutions of (3a). The functions $\psi_s(\mathbf{k}, R_j^{-1}\mathbf{r})$ must then be linear combinations of the functions $\psi_t(R_j \mathbf{k}, \mathbf{r})$; thus

$$[\psi_s(\mathbf{k}, R_j^{-1}\mathbf{r})] = [\psi_t(R_j \mathbf{k}, \mathbf{r})][J_{ts}].$$

But $R_j \mathbf{k} \equiv \mathbf{k}$; therefore it is possible to find a set of matrices $[J_{ts}]$ such that

$$R_j[\psi_s(\mathbf{k}, \mathbf{r})] = [\psi_s(\mathbf{k}, R_j^{-1}\mathbf{r})] = [\psi_t(\mathbf{k}, \mathbf{r})][J_{ts}]. \quad (4)$$

These matrices are a representation of the group $\mathcal{R}(\mathbf{k})$. This is shown by considering the product of any two elements:

$$\begin{aligned} R_j[\psi_s] &= [\psi_u][J_{us}] \\ R_k R_j[\psi_s] &= R_k\{[\psi_u][J_{us}]\} \\ &= \{R_k[\psi_u]\}[J_{us}] \\ &= \{[\psi_t][K_{tu}]\}[J_{us}] \\ &= [\psi_t]\{[K_{tu}][J_{us}]\}. \end{aligned}$$

If $R_t = R_k R_j$ then

$$R_t[\psi_s] = [\psi_t][L_{ts}]$$

where

$$[L_{ts}] = [K_{tu}][J_{us}].$$

Thus the matrices obey the same multiplication rules as the elements of $\mathcal{R}(\mathbf{k})$ and so form a representation of this group.

The row matrix $[\psi_s(\mathbf{k}, \mathbf{r})]$ is itself the basis for a representation of $\mathcal{R}(\mathbf{k})$.

The n -dimensional representation Γ made up of the matrices $[J_{ts}]$ may itself be irreducible. In general, however, it will be possible to reduce it to obtain a number of representations, Γ^m , of $\mathcal{R}(\mathbf{k})$ which are irreducible, i.e., it will be possible to find a matrix Q such that

$$Q^{-1}[J_{ts}]Q = \text{diag}\{[J_{ts}^{(1)}], [J_{ts}^{(2)}], \dots\}$$

for all R_j in $\mathcal{R}(\mathbf{k})$; where the matrix $[J_{ts}^m]$, which is an element of the irreducible representation Γ^m , may appear more than once, say c_m times, in this equation. Then the direct sum for Γ is

$$\Gamma = c_m \Gamma^m.$$

Equation (4) may be written

$$R_j[\psi_s(\mathbf{k}, \mathbf{r})]Q = [\psi_t(\mathbf{k}, \mathbf{r})]Q Q^{-1}[J_{ts}^m]Q,$$

and the matrix $[\psi_s(\mathbf{k}, \mathbf{r})]Q$ can be split into several matrices $[\psi_s^m(\mathbf{k}, \mathbf{r})]$ each containing a number of terms equal to the dimension of Γ^m . Thus for each irreducible representation one can obtain the relation

$$R_j[\psi_s^m(\mathbf{k}, \mathbf{r})] = [\psi_t^m(\mathbf{k}, \mathbf{r})][J_{ts}^m]$$

for all R_j in $\mathcal{R}(\mathbf{k})$. $[\psi_s^m(\mathbf{k}, \mathbf{r})]$ is then a basis for the representation Γ^m .

APPENDIX II

One can develop wave functions about each atomic nucleus in a crystal. The proper wave function, however, must be smooth throughout the whole crystal. Therefore, one must consider the relations between the individual nuclear wave functions which will cause this condition to be satisfied. In this appendix it is shown that this is done if

- (a) ψ_p is continuous with $\exp(i\mathbf{k} \cdot \mathbf{S}_{pq})\psi_q$
- (b) ψ_p^n is considered in conjunction with ψ_q^m ,

where ψ_p is a wave function developed about a nucleus at A_p , \mathbf{S}_{pq} is the vector from the p th to the q th nucleus, and

$$[J_{ts}^m] = \exp\{i\mathbf{k} \cdot (\mathbf{E} - {}_p R_j^{-1})\mathbf{S}_{pq}\}[J_{ts}^n].$$

(a) A proper wave function, developed about an origin O , is

$$\psi(\mathbf{k}, \mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) u(\mathbf{k}, \mathbf{r}).$$

Consider different atomic nuclei at the points A_p each surrounded by a subcell; \mathbf{r}_{pq} is any point on the boundary between the p th and q th subcells; $\mathbf{S}_{pq} = \mathbf{O}A_q - \mathbf{O}A_p$ will not, in general, be an allowed lattice translation. The wave function developed about A_p can be written

$$\psi_p(\mathbf{k}, \mathbf{r}) = \exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{O}A_p)] v_p(\mathbf{k}, \mathbf{r} - \mathbf{O}A_p).$$

Within the p th subcell one can define a constant P such that:

$$\psi(\mathbf{k}, \mathbf{r}) = P \psi_p(\mathbf{k}, \mathbf{r}),$$

i.e.,

$$u(\mathbf{k}, \mathbf{r}) = P \exp[-(i\mathbf{k} \cdot \mathbf{O}A_p)] v_p(\mathbf{k}, \mathbf{r} - \mathbf{O}A_p).$$

Without the loss of generality one can define $P = \exp(i\mathbf{k} \cdot \mathbf{O}A_p)$ so that $u(\mathbf{k}, \mathbf{r}) = v_p(\mathbf{k}, \mathbf{r} - \mathbf{O}A_p)$ in the p th subcell. This imposes the condition that

$$v_p(\mathbf{k}, \mathbf{r}_{pq} - \mathbf{O}A_p) = v_q(\mathbf{k}, \mathbf{r}_{pq} - \mathbf{O}A_q)$$

and means that $\psi_p(\mathbf{k}, \mathbf{r})$ must be continuous with $\exp(i\mathbf{k} \cdot \mathbf{S}_{pq})\psi_q(\mathbf{k}, \mathbf{r})$.

In general there is an arbitrariness in the definition of P . It is obvious, however, that the one chosen leads to the most elegant formulation of the required condition. If the crystal is monatomic then \mathbf{S}_{pq} is a lattice translation so that

$$v_p(\mathbf{k}, \mathbf{r}_{pq} - \mathbf{O}A_p) \equiv v_p(\mathbf{k}, \mathbf{r}_{pq} - \mathbf{O}A_q)$$

and the condition that $\psi_p(\mathbf{k}, \mathbf{r})$ be continuous with $\exp(i\mathbf{k} \cdot \mathbf{S}_{pq})\psi_q(\mathbf{k}, \mathbf{r})$ is no longer arbitrary.

(b) Consider R_j , an element of the group of operations allowed about both A_p and A_q ; when performed about these points the operator is written ${}_pR_j$ and ${}_qR_j$. If E is the identity operator then:

$$\{{}_qR_j - {}_pR_j\}\mathbf{r} = \{E - {}_pR_j\}\mathbf{S}_{pq}$$

where \mathbf{r} is measured from any origin O . This is easily proved.

Let

$$\mathbf{r}' = \mathbf{r} - \mathbf{S}_{pq};$$

then

$$\begin{aligned} {}_qR_j\mathbf{r} &= {}_pR_j\mathbf{r}' + \mathbf{S}_{pq} \\ &= {}_pR_j\mathbf{r} - {}_pR_j\mathbf{S}_{pq} + \mathbf{S}_{pq} \end{aligned}$$

and

$$\{{}_qR_j - {}_pR_j\}\mathbf{r} = \{E - {}_pR_j\}\mathbf{S}_{pq}.$$

The expression on the left-hand side leaves the lattice unchanged, and that on the right-hand side can be only a translation which must therefore be a sum of lattice vectors.

If $\psi_s(\mathbf{k}, \mathbf{r})$ is a wave function based on O then

$$\psi_s(\mathbf{k}, \mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r})u_s(\mathbf{k}, \mathbf{r})$$

and

$${}_pR_j\psi_s(\mathbf{k}, \mathbf{r}) = \exp(i\mathbf{k} \cdot {}_pR_j^{-1}\mathbf{r})u_s(\mathbf{k}, {}_pR_j^{-1}\mathbf{r});$$

therefore

$$\begin{aligned} {}_qR_j\psi_s(\mathbf{k}, \mathbf{r}) &= \exp(i\mathbf{k} \cdot {}_qR_j^{-1}\mathbf{r})u_s(\mathbf{k}, {}_qR_j^{-1}\mathbf{r}) \\ &= \exp\{i\mathbf{k} \cdot (E - {}_pR_j^{-1})\mathbf{S}_{pq}\}{}_pR_j\psi_s(\mathbf{k}, \mathbf{r}). \end{aligned}$$

But it is shown in Appendix I that

$${}_pR_j[\psi_s(\mathbf{k}, \mathbf{r})] = [\psi_t(\mathbf{k}, \mathbf{r})][{}_pJ_{ts}].$$

Thus

$$\begin{aligned} {}_qR_j[\psi_s(\mathbf{k}, \mathbf{r})] &= [\psi_t(\mathbf{k}, \mathbf{r})][{}_qJ_{ts}] \\ &= [\psi_t(\mathbf{k}, \mathbf{r})] \exp\{i\mathbf{k} \cdot (E - {}_pR_j^{-1})\mathbf{S}_{pq}\}[_pJ_{ts}]; \end{aligned}$$

therefore

$$[{}_qJ_{ts}] = \exp\{i\mathbf{k} \cdot (E - {}_pR_j^{-1})\mathbf{S}_{pq}\}[_pJ_{ts}].$$

So if a wave function is a basis for the representation Γ^n when centered on the nucleus at A_p it must be a basis for the representation Γ^m when centered on the nucleus at A_q , where

$$[J_{ts}^m] = \exp\{i\mathbf{k} \cdot (E - {}_pR_j^{-1})\mathbf{S}_{pq}\}[_pJ_{ts}^n].$$

Lattice Harmonics

Lattice harmonics having angular quantum number of less than or equal to six are given for the full cubic group (as Von der Lage and Bethe)³ and for the close-packed hexagonal group. They have been normalized to 4π . To shorten the tables the direction cosines, x/r , y/r , z/r are replaced by x , y , z ; unnormalized functions in the same set are denoted by letters in brackets (e.g., in $A_p(x)$, $(f) \equiv x^3 - 3(p)/5 \equiv x^3 - 3x/5$); and only one of three triply degenerate functions is given—the others are obtained by cyclic interchange of coordinates. For convenience, functions are orthogonalized over a sphere.

The harmonics which are bases of groups of lower order are given in terms of those of a convenient higher order. The actual functions required are readily obtained.

$$\text{e.g., } G_{p'} \text{ comes from } (\frac{1}{2})^{\frac{1}{2}}[C_{p'}(1) + C_{p'}(2)].$$

But

$$C_{p'}(1) \text{ comes from } A_p(y) \text{ and } A_{f'}(y)$$

and

$$C_{p'}(2) \text{ comes from } A_p(z) \text{ and } -A_{f'}(z),$$

so

$$G_{p'} \text{ comes from } (\frac{1}{2})^{\frac{1}{2}}[A_p(y) + A_p(z)]$$

$$\text{and } (\frac{1}{2})^{\frac{1}{2}}[A_{f'}(y) - A_{f'}(z)].$$

Thus the actual lattice harmonics which are bases of the representation $G_{p'}$ are

$$\begin{aligned} p & (3/2)^{\frac{1}{2}}[y+z] \\ f_1 & (175/8)^{\frac{1}{2}}[y^3+z^3-3(p)/5] \\ f_2 & (105/8)^{\frac{1}{2}}[(z^2-x^2)y-(x^2-y^2)z] \\ h_1 & (43659/128)^{\frac{1}{2}}[y^5+z^5-10(f_1)/9-3(p)/7] \\ h_2 & (3465/128)^{\frac{1}{2}}[(z^4+x^4-6z^2x^2)y+(x^4+y^4-6x^2y^2)z] \\ h_3 & (10395/32)^{\frac{1}{2}}[(z^2-x^2)y^3-(x^2-y^2)z^3-(f_2)/3]. \end{aligned}$$

The Schönflies notation for the various crystallographic point groups is given to assist anyone who wishes to consult character tables found in the literature and the harmonics are listed in the order in which they would appear according to such tables.

The relationship between the labeling used in this paper and that due to Bouckaert, Smoluchowski, and Wigner is given in Table I.

TABLE I. The relationship between the labeling used in this paper and that due to Bouckaert, Smoluchowski, and Wigner.

B.S.W.	D.G.B.	B.S.W.	D.G.B.
Γ, R, H	A	Λ	I
P	B	F	K
X	C	Σ, S	L
L, M	D	G	M
Δ, T	E	Z	N
W	F	D	O
N	G		

Cubic Symmetries

Ⓐ—an O_h group

$$A_s \quad s \quad 1$$

$$g \quad (525/16)^{\frac{1}{2}}[x^4+y^4+z^4-3/5]$$

$$i \quad (693693/32)^{\frac{1}{2}}[x^2y^2z^2+(g)/22-1/105]$$

$$A_i \quad i \quad (15015/32)^{\frac{1}{2}}[x^4(y^2-z^2)+y^4(z^2-x^2)+z^4(x^2-y^2)]$$

A_d (doubly degenerate)

$$A_d(1) \begin{cases} d & (5/4)^{\frac{1}{2}}[2x^2-y^2-z^2] \\ g & (735/16)^{\frac{1}{2}}[2x^4-y^4-z^4-6(d)/7] \\ i & (11011/32)^{\frac{1}{2}}[2x^6-y^6-z^6-15(g)/11-5(d)/7] \end{cases}$$

$$A_d(2) \begin{cases} d & (15/4)^{\frac{1}{2}}[y^2-z^2] \\ g & (2205/16)^{\frac{1}{2}}[y^4-z^4-6(d)/7] \\ i & (33033/32)^{\frac{1}{2}}[y^6-z^6-15(g)/11-5(d)/7] \end{cases}$$

$A_{d'}$ (triply degenerate)

$$A_{d'}(x) \begin{cases} d & (15)^{\frac{1}{2}}yz \\ g & (2205/4)^{\frac{1}{2}}[x^2yz-(d)/7] \\ i_1 & (1486485/128)^{\frac{1}{2}}[x^4yz-6(g)/11-(d)/21] \\ i_2 & (27027/128)^{\frac{1}{2}}[y^4+z^4-10y^2z^2/3]yz \end{cases}$$

A_g (triply degenerate)

$$A_g(x) \begin{cases} g & (315/4)^{\frac{1}{2}}[y^2-z^2]yz \\ i & (99099/16)^{\frac{1}{2}}[x^2yz(y^2-z^2)-(g)/11] \end{cases}$$

A_l No representation of order less than nine

$A_f \quad f \quad (105)^{\frac{1}{2}}xyz$

A_h (doubly degenerate)

$$A_h(1) \quad h \quad (1155/4)^{\frac{1}{2}}[2x^2-y^2-z^2]xyz$$

$$A_h(2) \quad h \quad (3465/4)^{\frac{1}{2}}[y^2-z^2]xyz$$

$A_{f'}$ (triply degenerate)

$$A_{f'}(x) \begin{cases} f & (105/4)^{\frac{1}{2}}[y^2-z^2]x \\ h & (10395/16)^{\frac{1}{2}}[(y^2-z^2)x^3-(f)/3] \end{cases}$$

A_p (triply degenerate)

$$A_p(x) \begin{cases} p & 3^{\frac{1}{2}}x \\ f & (175/4)^{\frac{1}{2}}[x^3-3(p)/5] \\ h_1 & (43659/64)^{\frac{1}{2}}[x^5-10(f)/9-3(p)/7] \\ h_2 & (3465/64)^{\frac{1}{2}}[y^4+z^4-6y^2z^2]x \end{cases}$$

Ⓑ—a T_d group

$B_s \quad A_s \text{ and } A_f$

$B_i \quad A_i \text{ and } A_l$

B_d (doubly degenerate) A_d and A_h

B_p (triply degenerate) A_p and $A_{d'}$

B_f (triply degenerate) $A_{f'}$ and A_g

Ⓒ—a D_{4h} group

$C_s \quad A_s \text{ and } A_d(1)$

$C_g \quad A_g(x)$

$C_{d'}$ $A_d(2)$ and A_i

$C_d \quad A_{d'}(x)$

$C_{d''}$ (doubly degenerate)

$$C_{d''}(1) \begin{cases} A_{d'}(y) \\ A_g(y) \end{cases}$$

$$C_{d''}(2) \begin{cases} A_{d'}(z) \\ -A_g(z) \end{cases}$$

$C_h \quad A_h(2) \text{ and } A_l$

$C_p \quad A_p(x)$

$C_{f'} \quad A_f \text{ and } A_h(1)$

$C_f \quad A_{f'}(x)$

$C_{p'}$ (doubly degenerate)

$$C_{p'}(1) \begin{cases} A_p(y) \\ A_{f'}(y) \end{cases}$$

$$C_{p'}(2) \begin{cases} A_p(z) \\ -A_{f'}(z) \end{cases}$$

Ⓓ—a D_{3d} group

$D_s \quad A_s \text{ and } (1/3)^{\frac{1}{2}}[A_{d'}(x)+A_{d'}(y)+A_{d'}(z)]$

$D_g \quad A_i \text{ and } (1/3)^{\frac{1}{2}}[A_g(x)+A_g(y)+A_g(z)]$

D_d (doubly degenerate)

$$D_d(1) \begin{cases} A_d(1) \\ (1/6)^{\frac{1}{2}}[2A_{d'}(x)-A_{d'}(y)-A_{d'}(z)] \\ (1/2)^{\frac{1}{2}}[A_g(z)-A_g(y)] \end{cases}$$

$$D_d(2) \begin{cases} A_d(2) \\ (1/2)^{\frac{1}{2}}[A_{d'}(y)-A_{d'}(z)] \\ (1/6)^{\frac{1}{2}}[2A_g(x)-A_g(y)-A_g(z)] \end{cases}$$

$D_f \quad A_l \text{ and } (1/3)^{\frac{1}{2}}[A_{f'}(x)+A_{f'}(y)+A_{f'}(z)]$

$D_p \quad A_f \text{ and } (1/3)^{\frac{1}{2}}[A_p(x)+A_p(y)+A_p(z)]$

$D_{p'}$ (doubly degenerate)

$$D_{p'}(1) \begin{cases} A_h(1) \\ (1/6)^{\frac{1}{2}}[2A_p(x)-A_p(y)-A_p(z)] \\ (1/2)^{\frac{1}{2}}[A_{f'}(z)-A_{f'}(y)] \end{cases}$$

$$D_{p'}(2) \begin{cases} A_h(2) \\ (1/2)^{\frac{1}{2}}[A_p(y)-A_p(z)] \\ (1/6)^{\frac{1}{2}}[2A_{f'}(x)-A_{f'}(y)-A_{f'}(z)] \end{cases}$$

Ⓔ—a C_{4v} group

$E_s \quad C_s \text{ and } C_p$

$E_g \quad C_g \text{ and } C_h$

$E_{d'}$ $C_{d'}$ and C_f

$E_d \quad C_d \text{ and } C_{f'}$

E_p (doubly degenerate)

$$E_p(1) \begin{cases} C_{p'}(1) \\ C_{d''}(2) \end{cases}$$

$$E_p(2) \begin{cases} C_{p'}(2) \\ C_{d''}(1) \end{cases}$$

Ⓕ—a D_{2d} group

$F_s \quad C_s \text{ and } C_f$

$F_f \quad C_{f'} \text{ and } C_g$

$F_d \quad C_d \text{ and } C_h$

$F_p \quad C_p \text{ and } C_{d'}$

$F_{p'}$ (doubly degenerate)

$$F_{p'}(1) \begin{cases} C_{p'}(1) \\ C_{d''}(2) \end{cases}$$

$$F_{p'}(2) \begin{cases} C_{p'}(2) \\ -C_{d''}(1) \end{cases}$$

Ⓖ—a D_{2h} group

$G_s \quad C_s \text{ and } C_d$

$G_d \quad C_{d'} \text{ and } C_g$

$G_{d'} \quad (1/2)^{\frac{1}{2}}[C_{d''}(1)-C_{d''}(2)]$

$$\begin{aligned} G_{d''} & (1/2)^{\frac{1}{2}}[C_{d''}(1)+C_{d''}(2)] \\ G_f & C_f \text{ and } C_h \\ G_p & C_p \text{ and } C_{f'} \\ G_{p'} & (1/2)^{\frac{1}{2}}[C_{p'}(1)+C_{p'}(2)] \\ G_{p''} & (1/2)^{\frac{1}{2}}[C_{p'}(1)-C_{p'}(2)] \end{aligned}$$

$\mathfrak{J}\mathfrak{C}$ —a D_{2d} group

$$\begin{aligned} H_s & C_s \text{ and } C_{f'} \\ H_f & C_f \text{ and } C_g \\ H_d & C_{d'} \text{ and } C_h \\ H_p & C_p \text{ and } C_d \\ H_{p'} & \text{(doubly degenerate)} \end{aligned}$$

$$\begin{aligned} H_{p'}(1) & \begin{cases} C_{p'}(1) \\ C_{d''}(1) \end{cases} \\ H_{p'}(2) & \begin{cases} C_{p'}(2) \\ C_{d''}(2) \end{cases} \end{aligned}$$

\mathfrak{J} —a C_{3v} group

$$\begin{aligned} I_s & D_s \text{ and } D_p \\ I_f & D_f \text{ and } D_g \\ I_p & \text{(doubly degenerate)} \end{aligned}$$

$$\begin{aligned} I_p(1) & \begin{cases} D_{p'}(1) \\ D_d(1) \end{cases} \\ I_p(2) & \begin{cases} D_{p'}(2) \\ D_d(2) \end{cases} \end{aligned}$$

\mathfrak{K} —a C_3 group

$$\begin{aligned} K_s & B_s \text{ and } (1/3)^{\frac{1}{2}}[B_p(x)-B_p(y)-B_p(z)] \\ K_f & B_f \text{ and } (1/3)^{\frac{1}{2}}[B_f(x)-B_f(y)-B_f(z)] \\ K_p & \text{(doubly degenerate)} \end{aligned}$$

$$\begin{aligned} K_p(1) & \begin{cases} (1/6)^{\frac{1}{2}}[2B_p(x)+B_p(y)+B_p(z)] \\ B_d(1) \\ (1/2)^{\frac{1}{2}}[B_f(y)-B_f(z)] \end{cases} \\ K_p(2) & \begin{cases} (1/2)^{\frac{1}{2}}[B_p(z)-B_p(y)] \\ B_d(2) \\ (1/6)^{\frac{1}{2}}[2B_f(x)+B_f(y)+B_f(z)] \end{cases} \end{aligned}$$

\mathfrak{L} —a C_{2v} group

$$\begin{aligned} L_s & G_s \text{ and } G_{p'} \\ L_{p'} & G_p \text{ and } G_{d'} \\ L_d & G_{d'} \text{ and } G_f \\ L_p & G_{p''} \text{ and } G_d \end{aligned}$$

\mathfrak{M} —a C_{2v} group

$$\begin{aligned} M_s & G_s \text{ and } G_{p''} \\ M_{p'} & G_p \text{ and } G_{d'} \\ M_d & G_{d''} \text{ and } G_f \\ M_p & G_{p'} \text{ and } G_d \end{aligned}$$

\mathfrak{N} —a C_{2v} group

$$\begin{aligned} N_s & F_s \text{ and } F_p \\ N_{p'} & F_{p'}(1) \\ N_d & F_d \text{ and } F_f \\ N_p & F_{p'}(2) \end{aligned}$$

\mathfrak{O} —a C_{2v} group

$$\begin{aligned} O_s & G_s \text{ and } G_p \\ O_{p'} & G_{p'} \text{ and } G_{d''} \\ O_d & G_d \text{ and } G_f \\ O_p & G_{p''} \text{ and } G_{d'} \end{aligned}$$

\mathfrak{P} —an S_4 group

$$\begin{aligned} P_s & F_s \text{ and } F_f \\ P_p & F_p \text{ and } F_d \\ P_{p'} & (1/2)^{\frac{1}{2}}[F_{p'}(1)+iF_{p'}(2)] \\ P_{p''} & (1/2)^{\frac{1}{2}}[F_{p'}(2)+iF_{p'}(1)] \end{aligned}$$

\mathfrak{Q} —a C_{1h} group

$$\begin{aligned} Q_s & M_s \text{ and } M_p \\ Q_p & M_{p'} \text{ and } M_d \end{aligned}$$

\mathfrak{R} —a C_{1h} group

$$\begin{aligned} R_s & L_s \text{ and } L_{p'} \\ R_p & L_p \text{ and } L_d \end{aligned}$$

\mathfrak{S} —a C_{1h} group

$$\begin{aligned} S_s & M_s \text{ and } M_{p'} \\ S_p & M_p \text{ and } M_d \end{aligned}$$

\mathfrak{T} —a C_2 group

$$\begin{aligned} T_s & M_s \text{ and } M_d \\ T_p & M_p \text{ and } M_{p'} \end{aligned}$$

\mathfrak{U} —a C_2 group

$$\begin{aligned} U_s & N_s \text{ and } N_d \\ U_p & N_p \text{ and } N_{p'} \end{aligned}$$

\mathfrak{V} —a C_1 group

$$V_s \quad U_s \text{ and } U_p$$

Close-Packed Hexagonal Symmetries

a —a D_{3h} group

$$\begin{aligned} a_s & s \quad 1 \\ d & (45/4)^{\frac{1}{2}}[x^2-1/3] \\ f & (35/8)^{\frac{1}{2}}[3y^2-z^2]z \\ g & (11025/64)^{\frac{1}{2}}[x^4-6(d)/7-1/5] \\ h & (31185/128)^{\frac{1}{2}}[(3y^2-z^2)zx^2-(f)/9] \\ i_1 & (693693/256)^{\frac{1}{2}}[x^6-15(g)/11-5(d)/7-1/7] \\ i_2 & (3003/1024)^{\frac{1}{2}}[y^6-15y^4z^2+15y^2z^4-z^6] \end{aligned}$$

$$\begin{aligned} a_f & f \quad (35/8)^{\frac{1}{2}}[y^2-3z^2]y \\ h & (31185/128)^{\frac{1}{2}}[(y^2-3z^2)x^2y-(f)/9] \\ i & (27027/128)^{\frac{1}{2}}[y^4+z^4-10y^2z^2/3]yz \end{aligned}$$

$$\begin{aligned} a_g & g \quad (315/8)^{\frac{1}{2}}[y^2-3z^2]xy \\ i & (165165/128)^{\frac{1}{2}}[x^3y(y^2-3z^2)-3(g)/11] \end{aligned}$$

TABLE IIa. Face-centered cubic lattice. The symmetry types for various points in the reciprocal lattice when the potential has full cubic symmetry or full tetrahedral symmetry.

\mathbf{k}	Full cubic	Full tetrahedral
(0,0,0)	<i>A</i>	<i>B</i>
$\pi/a(1,0,0)$	<i>C</i>	<i>H</i>
$\pi/2a(1,1,1)$	<i>D</i>	<i>I</i>
$\pi/a(\alpha,0,0)$ $0 < \alpha < 1$	<i>E</i>	<i>O</i>
$\pi/2a(1,2,0)$	<i>F</i>	<i>P</i>
$\pi/2a(\alpha,\alpha,\alpha)$ $0 < \alpha < 1$	<i>I</i>	<i>I</i>
$3\pi/4a(0,\alpha,\alpha)$ $0 < \alpha \leq 1$	<i>L</i>	<i>R</i>
$\pi/a(1,\alpha,\alpha)$ $0 < \alpha \leq \frac{1}{2}$	<i>L</i>	<i>R</i>
$\pi/a(\alpha,0,1)$ $0 < \alpha < \frac{1}{2}$	<i>N</i>	<i>U</i>
$\pi/a(0,\alpha,\beta)$	<i>Q</i>	<i>V</i>
$\pi/a(1,\alpha,\beta)$	<i>Q</i>	<i>V</i>
$\pi/a(\alpha,\beta,\beta)$	<i>R</i>	<i>R</i>
$\pi/2a(1,2-\alpha,\alpha)$ $0 < \alpha < 1$	<i>T</i>	<i>V</i>
$\pi/a(\alpha,\beta,\gamma)$	<i>V</i>	<i>V</i>

Thus, the unit lattice cell is a rhombo-dodecahedron bounded by the planes $\pm x \pm y = a$, $\pm y \pm z = a$, and

(i) $\mathbf{k} = \pi/2a(1,1,1)$								
Representation about Na	D_s	D_g	$D_d(1)$	$D_d(2)$	D_f	D_p	$D_{p'}(1)$	$D_{p'}(2)$
Representation about Cl	D_p	D_f	$D_{p'}(1)$	$D_{p'}(2)$	D_g	D_s	$D_d(1)$	$D_d(2)$
(ii) $\mathbf{k} = \pi/2a(1,2,0)$								
Representation about Na	F_s	F_p	F_d	F_f	F_f	$F_{p'}(1)$	$F_{p'}(2)$	$F_{p'}(2)$
Representation about Cl	F_p	F_s	F_f	F_d	F_f	$F_{p'}(1)$	$-F_{p'}(2)$	$-F_{p'}(2)$
(iii) $\mathbf{k} = \pi/2a(1,2-\alpha,\alpha)$								
Representation about Na				T_s				T_p
Representation about Cl				T_p				T_s

3. Crystals having zinc blende structure are again built up of two interpenetrating face-centered lattices, but one, the Zn lattice, is based on (0,0,0) and the other, the S lattice, on $a/2(1,1,1)$. The potential about each

(i) $\mathbf{k} = \pi/a(1,0,0)$								
Representation about Zn	H_s	H_f	H_d	H_p	$H_{p'}(1)$	$H_{p'}(2)$	$H_{p'}(2)$	$H_{p'}(1)$
Representation about S	H_p	H_d	H_f	H_s	$H_{p'}(2)$	$H_{p'}(1)$	$H_{p'}(1)$	$H_{p'}(2)$
(ii) $\mathbf{k} = \pi/2a(1,2,0)$								
Representation about Zn			P_s	P_p	$P_{p'}$	$P_{p'}$	$P_{p''}$	$P_{p''}$
Representation about S			$P_{p''}$	$P_{p'}$	$P_{p'}$	P_s	$P_{p''}$	$P_{p''}$

4. Calcium fluoride is taken as an example of a more complex crystal. It is made up of three interpenetrating face-centered lattices, a calcium lattice based on (0,0,0) and two fluorine lattices, $F^{(1)}$ based on $a/2(1,1,1)$, and $F^{(2)}$ based on $a/2(1,1,-1)$. The lattice potential, there-

(i) $\mathbf{k} = (0,0,0)$										
Representation about Ca	A_s	A_i	A_d	A_d'	A_g	A_l	A_f	A_h	$A_{f'}$	A_p
Representation about $F^{(1)}$	B_s	B_i	B_d	B_p	B_f	B_i	B_s	B_d	$B_{f'}$	B_p
Representation about $F^{(2)}$	B_s	B_i	B_d	B_p	B_f	B_i	B_s	B_d	$B_{f'}$	B_p
(ii) $\mathbf{k} = \pi/a(1,0,0)$										
Representation about Ca	C_s	C_g	C_d'	C_d	$C_{d''}(1)$	$C_{d''}(2)$	C_h	C_p	$C_{f'}$	C_f
Representation about F	H_p	H_d	H_f	H_s	$H_{p'}(2)$	$H_{p'}(1)$	H_f	H_s	H_p	H_d
(iii) $\mathbf{k} = \pi/2a(1,1,1)$										
Representation about Ca	D_s	D_g	$D_d(1)$	$D_d(2)$	D_f	D_p	$D_{d'}(1)$	$D_{d'}(2)$	$D_{d'}(1)$	$D_{d'}(2)$
Representation about F	I_s	I_f	$I_p(1)$	$I_p(2)$	I_f	I_s	$I_p(1)$	$I_p(2)$	$I_p(1)$	$I_p(2)$
(iv) $\mathbf{k} = \pi/a(\alpha,0,0)$										
Representation about Ca	E_s	E_g	E_d'	E_d	$E_p(1)$			$E_p(2)$		
Representation about F	O_s	O_d	O_d	O_s	$(\frac{1}{2})^{\frac{1}{2}}(O_{p'} - O_p)$			$(\frac{1}{2})^{\frac{1}{2}}(O_p + O_{p'})$		
(v) $\mathbf{k} = \pi/2a(1,2,0)$										
Representation about Ca	F_s	F_f	F_d	F_p	$F_{p'}(1)$			$F_{p'}(2)$		
Representation about $F^{(1)}$	$P_{p''}$	$P_{p''}$	$P_{p'}$	$P_{p'}$	$(\frac{1}{2})^{\frac{1}{2}}(P_s + iP_p)$			$(\frac{1}{2})^{\frac{1}{2}}(P_p - iP_s)$		
Representation about $F^{(2)}$	$P_{p'}$	$P_{p'}$	$P_{p''}$	$P_{p''}$	$(\frac{1}{2})^{\frac{1}{2}}(P_s - iP_p)$			$(\frac{1}{2})^{\frac{1}{2}}(P_p + iP_s)$		

$\pm z \pm x = a$, and the first Brillouin zone is a truncated octahedron—the square faces being the planes $k_x, k_y, k_z = \pm \pi/a$ and the hexagonal faces the planes $\pm k_x \pm k_y \pm k_z = 3\pi/2a$.

Table IIa gives the symmetry types for various points in the reciprocal lattice when the potential has full cubic symmetry or full tetrahedral symmetry.

1. In monatomic face-centered lattices, such as Ca, Cu, and Pb, the potential has full cubic symmetry and a wave function belongs to the same representation about each nucleus in the lattice.

2. The NaCl type lattice is made up of two interpenetrating face-centered lattices—the Na lattice based on (0,0,0) and the Cl lattice based on $a(1,0,0)$. Here again the potential has full cubic symmetry about all nuclei but at various points in \mathbf{k} space a wave function must belong to a different representation about each type of nucleus. (See Appendix II.)

nucleus, therefore, has full tetrahedral symmetry. Once again, at certain points in \mathbf{k} space a wave function must belong to different representations about the two types of nuclei.

fore, has full cubic symmetry about the calcium nucleus but only full tetrahedral symmetry about the fluorine nuclei. Thus a wave function will in general be the basis for an irreducible representation of different groups about the different nuclei.

At all other points in \mathbf{k} space there is a simple and obvious relationship between various representations.

b. Simple Cubic Lattice

The direct lattice vectors \mathbf{a}_i and the reciprocal lattice vectors \mathbf{b}_j are

$$\begin{aligned} \mathbf{a}_1 &= a(1,0,0); & \mathbf{b}_1 &= 2\pi/a(1,0,0); \\ \mathbf{a}_2 &= a(0,1,0); & \mathbf{b}_2 &= 2\pi/a(0,1,0); \\ \mathbf{a}_3 &= a(0,0,1). & \mathbf{b}_3 &= 2\pi/a(0,0,1). \end{aligned}$$

Thus, the unit lattice cell is a cube of side a and the first Brillouin zone a cube of side $2\pi/a$. Symmetry types for various points in the reciprocal lattice when the potential has full cubic or full tetrahedral symmetry are given in Table IIB.

There are no monatomic simple cubic crystals. The simplest ones are diatomic, made up of two interpenetrating simple cubic lattices of different atoms based on the points $(0,0,0)$ and $a/2(1,1,1)$, such that the potential has full cubic symmetry about each nucleus, e.g., CsCl and CuZn.

TABLE IIB. Simple cubic lattice. Symmetry types for various points in the reciprocal lattice when the potential has full cubic or full tetrahedral symmetry.

\mathbf{k}	Full cubic	Full tetrahedral
$(0,0,0)$	A	B
$\pi/a(1,1,1)$	A	B
$\pi/a(0,1,1)$	C	H
$\pi/a(1,0,0)$	C	H
$\pi/a(\alpha,0,0)$ $0 < \alpha < 1$	E	O
$\pi/a(\alpha,1,1)$ $0 < \alpha < 1$	E	O
$\pi/a(\alpha,\alpha,\alpha)$ $0 < \alpha < 1$	I	I
$\pi/a(0,\alpha,\alpha)$ $0 < \alpha < 1$	L	R
$\pi/a(1,\alpha,\alpha)$ $0 < \alpha < 1$	L	R
$\pi/a(\alpha,0,1)$ $0 < \alpha < 1$	N	U
$\pi/a(1,\alpha,\beta)$ $0 < \alpha, \beta < 1$	Q	V
$\pi/a(0,\alpha,\beta)$ $0 < \alpha, \beta < 1$	Q	V
$\pi/a(\alpha,\beta,\beta)$ $0 < \alpha, \beta < 1$	R	R
$\pi/a(\alpha,\beta,\gamma)$ $0 < \alpha, \beta, \gamma < 1$	V	V

For values of \mathbf{k} lying on the boundary of the first Brillouin zone a wave function must be a basis for a different representation about each type of nucleus. The relationship between these representations is given.

(i) $\mathbf{k}=\pi/a(1,1,1)$												
Representation about Cs	A_s	A_i	A_d	$A_{d'}$	A_g	A_l	A_f	A_h	$A_{f'}$	A_p		
Representation about Cl	A_f	A_l	A_h	A_p	$A_{f'}$	A_i	A_s	A_d	A_g	$A_{d'}$		
(ii) $\mathbf{k}=\pi/a(0,1,1)$												
Representation about Cs	C_s	C_g	$C_{d'}$	C_d	$C_{d''}(1)$	$C_{d''}(2)$	C_h	C_p	$C_{f'}$	C_f	$C_{p'}(1)$	$C_{p'}(2)$
Representation about Cl	C_d	$C_{d'}$	C_g	C_s	$C_{d''}(2)$	$C_{d''}(1)$	C_f	$C_{f'}$	C_p	C_h	$C_{p'}(2)$	$C_{p'}(1)$
(iii) $\mathbf{k}=\pi/a(1,0,0)$												
Representation about Cs	C_s	C_g	$C_{d'}$	C_d	$C_{d''}(1)$	$C_{d''}(2)$	C_h	C_p	$C_{f'}$	C_f	$C_{p'}(1)$	$C_{p'}(2)$
Representation about Cl	C_p	C_h	C_f	$C_{f'}$	$C_{p'}(2)$	$C_{p'}(1)$	C_g	C_s	C_d	$C_{d'}$	$C_{d''}(2)$	$C_{d''}(1)$
(iv) $\mathbf{k}=\pi/a(\alpha,1,1)$												
Representation about Cs	E_s		E_g		$E_{d'}$		E_d		$E_p(1)$		$E_p(2)$	
Representation about Cl	E_d		$E_{d'}$		E_g		E_s		$E_p(1)$		$E_p(2)$	
(v) $\mathbf{k}=\pi/a(1,\alpha,\alpha)$												
Representation about Cs		L_s			$L_{p'}$		L_d				L_p	
Representation about Cl		$L_{p'}$			L_s		L_p				L_d	
(vi) $\mathbf{k}=\pi/a(\alpha,0,1)$												
Representation about Cs		N_s			$N_{p'}$		N_d				N_p	
Representation about Cl		N_p			N_d		$N_{p'}$				N_s	
(vii) $\mathbf{k}=\pi/a(1,\alpha,\beta)$												
Representation about Cs					Q_s					Q_p		
Representation about Cl					Q_p					Q_s		

c. Body-Centered Cubic Lattice

The lattice vectors are:

$$\begin{aligned} \mathbf{a}_1 &= a(1,1,-1) & \mathbf{b}_1 &= \pi/a(1,1,0) \\ \mathbf{a}_2 &= a(1,-1,1) & \mathbf{b}_2 &= \pi/a(1,0,1) \\ \mathbf{a}_3 &= a(-1,1,1) & \mathbf{b}_3 &= \pi/a(0,1,1). \end{aligned}$$

The unit lattice cell is a truncated octahedron bounded by the planes $x, y, z = \pm a$ and $\pm x \pm y \pm z = 3a/2$. The first Brillouin zone is a rhombo dodecahedron bounded by the planes $\pm k_x \pm k_y = \pi/a$; $\pm k_y \pm k_z = \pi/a$ and $\pm k_z \pm k_x = \pi/a$. Symmetry types are listed in Table IIC.

The commonest lattices are monatomic, e.g., Na, Cs, Ba. In these a wave function must belong to the same representation throughout the crystal.

TABLE IIC. Body-centered cubic lattice. The symmetry types for various points in the reciprocal lattice when the potential has full cubic symmetry or full tetrahedral symmetry.

\mathbf{k}	Full cubic	Full tetrahedral
$(0,0,0)$	A	B
$\pi/a(1,0,0)$	A	B
$\pi/2a(1,1,1)$	B	B
$\pi/a(\alpha,0,0)$ $0 < \alpha < 1$	E	O
$\pi/2a(0,1,1)$	G	O
$\pi/2a(\alpha,\alpha,\alpha)$ $0 < \alpha < 1$	I	I
$\pi/2a(2-\alpha,\alpha,\alpha)$ $0 < \alpha < 1$	K	K
$\pi/2a(0,\alpha,2)$ $0 < \alpha < 1$	L	R
$\pi/a(0,1-\alpha,\alpha)$ $0 < \alpha < \frac{1}{2}$	M	S
$\pi/2a(\alpha,1,1)$ $0 < \alpha < 1$	O	O
$\pi/2a(\alpha,2-\beta,\beta)$ $0 < \alpha < \beta < 1$	S	S
$\pi/2a(0,\alpha,\beta)$ $0 < \alpha, \beta < 1$	Q	V
$\pi/2a(\alpha,\beta,\beta)$ $0 < \alpha < \beta < 1$	R	R
$\pi/2a(\alpha,\beta,\alpha)$	V	V

d. Close-Packed Hexagonal Lattice

The lattice vectors are

$$\begin{aligned} \mathbf{a}_1 &= (c, 0, 0) & \mathbf{b}_1 &= 2\pi/c(1, 0, 0) \\ \mathbf{a}_2 &= (0, a, 0) & \mathbf{b}_2 &= 2\pi/a(0, 1, -1/\sqrt{3}) \\ \mathbf{a}_3 &= (0, a/2, \sqrt{3}a/2) & \mathbf{b}_3 &= 2\pi/a(0, 0, 2/\sqrt{3}). \end{aligned}$$

The unit lattice cell is an hexagonal prism bounded by the planes $x = \pm c/2$; $y = \pm a/2$; $y + \sqrt{3}z = \pm a/2$; and $\sqrt{3}y + z = \pm a/2$. The first Brillouin zone is also an hexagonal prism having as its faces the planes $k_x = \pm \pi/c$; $k_z = \pm 2\pi/a\sqrt{3}$; $k_y + \sqrt{3}k_z = \pm 4\pi/a\sqrt{3}$; and $\sqrt{3}k_y + k_z = \pm 4\pi/a\sqrt{3}$.

All close-packed hexagonal lattices are diatomic made up of two interpenetrating lattices based on (0,0,0) and $(c/2, 0, a/\sqrt{3})$. The symmetry types for various points in the reciprocal lattice are given in Table IIId.

TABLE IIId. Close-packed hexagonal lattice. The symmetry types for various points in the reciprocal lattice.

\mathbf{k}	Symmetry type
(0,0,0)	<i>a</i>
$\pi(1/c, 0, 0)$	<i>a</i>
$2\pi(1/2c, 2/3a, 0)$	<i>b</i>
$2\pi(\alpha, 0, 0)$ $0 < \alpha < c/2$	<i>c</i>
$2\pi(1/2c, 0, \gamma)$ $0 < \gamma \leq 1/a\sqrt{3}$	<i>d</i>
$2\pi(\alpha, 2/3a, 0)$ $0 < \alpha < c/2$	<i>e</i>
$2\pi(1/2c, \beta, \gamma)$ $0 < \beta < 2/3a$ $0 \leq \gamma \leq 1/a\sqrt{3}$	<i>f</i>
$2\pi(\alpha, 0, \gamma)$ $0 < \alpha < c/2$ $0 < \gamma \leq 1/a\sqrt{3}$	<i>g</i>
$2\pi(\alpha, \beta, \gamma)$	<i>h</i>

At a number of points on the boundary of the first Brillouin zone the wave function must be a basis for different representations about each nucleus. The relationship between representations at such points is given.

$\mathbf{k} = \pi(1/c, 0, 0)$								
Representation about (1)	a_s	a_f	a_g	a_p	$a_{p'}(1)$	$a_{p'}(2)$	$a_d(1)$	$a_d(2)$
Representation about (2)	a_p	a_g	a_f	a_s	$a_d(1)$	$a_d(2)$	$a_{p'}(1)$	$a_{p'}(2)$
$\mathbf{k} = 2\pi(1/2c, 2/3a, 0)$								
Representation about (1)	b_s		b_p	$b_{p'}$	$b_{p''}$	b_d	$b_{d'}$	$b_{d''}$
Representation about (2)	$b_{d'}$		$b_{p''}$	b_d	$b_{p'}$	b_s	b_p	$b_{p''}$
$\mathbf{k} = 2\pi(1/2c, 0, 1/a\sqrt{3})$								
Representation about (1)	d_s			d_d		d_p		$d_{p'}$
Representation about (2)	d_p			$d_{p'}$		d_s		d_d
$\mathbf{k} = 2\pi(\alpha, 2/3a, 0)$								
Representation about (1)		e_s			e_p		$e_{p'}$	
Representation about (2)		$e_{p'}$			e_s		e_p	
$\mathbf{k} = 2\pi(1/2c, \beta, 0)$								
Representation about (1)				f_s			$f_{p'}$	
Representation about (2)				$f_{p'}$			f_s	

ACKNOWLEDGMENTS

The author wishes to record her sincere thanks to her colleagues at R.R.E. for their helpful discussions and criticisms.

Acknowledgment is made to the Chief Scientist, British Ministry of Supply, and the Controller, Her Britannic Majesty's Stationery Office, for permission to publish this paper. British Crown Copyright reserved.