APPLICATION OF THE FREE ELECTRON APPROXIMATION TO THE STRUCTURAL SPACE GROUP D_{4h}^{14}

By

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CHAPTER I

INTRODUCTION

Stannic Oxide (SnO_2), is one of a number of oxides and fluorides having the bipyramidal ditetragonal crystal structure commonly referred to as the rutile structure. The lattice dimensions as given by Wyckoff (1), are a = 4.72 Å and c = 3.16 Å. This substance occurs naturally as the mineral cassiterite and is chemically stable. The process of growing synthetic crystals of stannic oxide has proven somewhat elusive until recently (2). As a result, the majority of the experimental work done with this substance has involved the use of crystals that have been cut from samples of Bolivian cassiterite. The properties of these samples have been reviewed quite extensively by Kohnke (3) and the results have been analyzed in an attempt to construct a workable model of the conduction mechanism which may be compared with that postulated for the prototype compound TiO_2.

A full-scale symmetry analysis illustrating the interplay between crystallographic structure, wave vector groups and possible electronic wave functions is necessary if any of the theoretical methods thus far developed (4) are to be applied in construction of curves showing the configuration of the electron energy bands in momentum space. Such analyses have already been applied to several other crystal systems (5-11).

It is the purpose of this work to employ a similar treatment for crystals which display the rutile structure. For illustrative purposes free-electron energy bands and wave functions have been constructed as the first approximation to the possible energy band configuration actually present in this system.

CHAPTER II

MATHEMATICAL PRELIMINARIES

In order to begin an analysis of the symmetry properties associated with any crystallographic system it is necessary to use a mathematical approach in which the theory of groups and their class structure plays an integral role. For a purely mathematical analysis of the space groups D_{4h}^{1} to D_{4h}^{17} the reader is referred to the papers by Olbrychski (12) and Sek (13). These two papers present a comprehensive treatment of the generalized mathematical properties of the seventeen space groups in the tetragonal system. Although it is possible to use the method outlined in the papers to obtain the group properties of the particular structure in question, an alternative approach, used extensively by Jones (14), was chosen. Differences between the methods will be made evident later.

As mentioned, the symmetry properties of the space group under consideration may best be handled by utilizing the general mathematical theory of groups. Thus, several definitions and theorems from which all of these properties may be extracted must necessarily be stated. The majority of the definitions that shall be stated may be found in any book which treats the theory of groups and their representations. Since the language used in discussing groups and group properties varies from one book to the next, the following treatment shall use the definitions and notation of Mariot. (15).

The first definition of any importance embodies the idea of an ensemble of mathematical objects. An ensemble is a finite or infinite collection of arbitrary mathematical objects. These objects are called the elements of the ensemble. Given any ensemble, a law of combination of two arbitrary elements x and y is a rule which determines a third element z of the ensemble. We write

$$z = x \cdot y$$

and, in general, $x \cdot y \neq y \cdot x$.

A group G is then an ensemble whose law of combination satisfies the following three conditions:

(1) the law is <u>associative</u>

$$C_j \cdot (C_k \cdot C_1) = (C_j \cdot C_k) \cdot C_1$$

(C_j, C_k, and C_1 being members of G)

(2) the law requires a <u>unit element</u> E such that

$$E \cdot C_k = C_k \cdot E = C_k$$

(3) every element C_i has an <u>inverse</u> $(C_i)^{-1}$ such that

$$C_i \cdot (C_i)^{-1} = (C_i)^{-1} \cdot C_i = E .$$

As an example of how this definition may be applied, consider the ensemble of all integers. If the law of combination is defined to be ordinary addition then it is easily seen that this set (or ensemble) constitutes a group. However, if the law of combination is taken to be multiplication, the three restrictions on the law of combination will not all be satisfied. The first two conditions will be satisfied. However, the third condition cannot be satisfied unless the ensemble contains rational numbers from zero to one. Since the ensemble does not contain these elements, it cannot constitute a mathematical group.

If the system is finite in extent, the number of elements in the system is called the order of the group. If the law of combination is also commutative the group is said to be commutative or abelian. If A, B, and X are three members of a group G, B is said to be conjugate to A, or B is the transform of A with respect to X if $B = X^{-1} \cdot A \cdot X$. The fundamental definition is that all elements of the form $X^{-1} A\ X$, X being any element of G, constitute the class of A. It should be noted at this point that the class concept is non-trivial only if the group is non-abelian.

Given a group G, a subgroup H is a part of G obeying the following:

(a) If X and Y are members of H, then X·Y is also a member of H.

(b) The subgroup obeys all the laws of combination defining a group.

Notice here that the unit element of H must be that of G.

Let $(H) = (E, H_1, H_2, \ldots)$ be a subgroup of G and consider an element $x \epsilon G$. Forming the ensembles:

$$X \cdot (H) = X, X \cdot H_1, X \cdot H_2 \ldots . \tag{2.1}$$

$$(H) \cdot X = X, H_1 \cdot X, H_2 \cdot X \ldots . \tag{2.2}$$

If X is itself a member of H, the property $X \cdot (H) = (H) \cdot X$ is trivial, but if X does not belong to H, the ensemble of elements $X \cdot (H)$ is called the right coset of G associated with H. Similarly, the ensemble $(H) \cdot X$ is the left coset associated with H.

At this point a theorem shall be stated without proof. The proof of this and any following theorems stated can be found in any text that treats this subject.

Theorem 1:

The subgroup H and the coset $X \cdot (H)$ do not have a common element. This theorem shall be used later and has been stated at this point merely for convenience.

The next topic of interest is that of the invariant subgroup. A subgroup H of a group G is called an invariant subgroup if $X^{-1} \cdot (H) \cdot X = (H)$ for every X in G. Evidently, this is merely a formal statement of the fact that for this case the right and left cosets are equal.

Theorem 2:

The ensemble (H), $X \cdot (H)$, $Y \cdot (H)$,.... is a supergroup of which the unit element is (H).

Although this system is called the supergroup by Mariot, many authors refer to this ensemble as the factor group. The concept of a factor group shall be used extensively in the later work.

Notice that the general group properties that have thus far been outlined are independent of the type of elements contained in the group. A crystallographic group is merely a collection of operations that constitute an ensemble satisfying the group properties. In such an ensemble the elements are rotations, reflections, and translations.

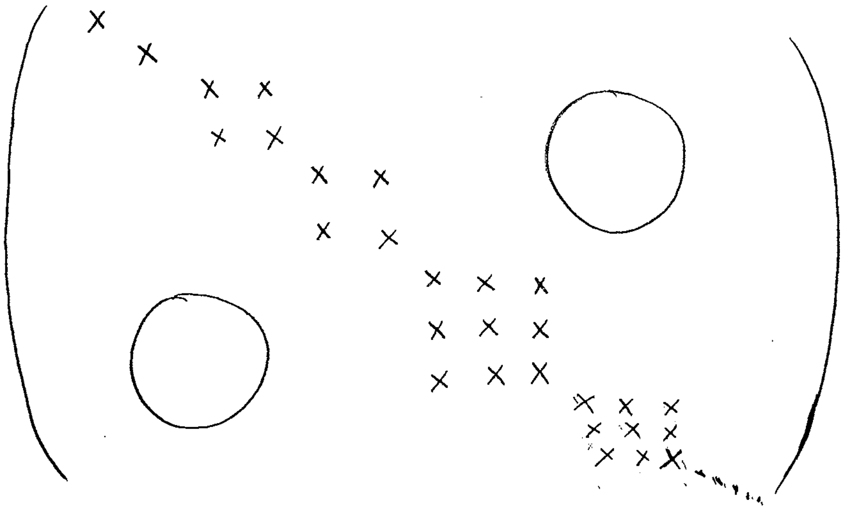
A particular group may be analyzed using several different techniques. One of the most widely applied techniques used in crystallography is dependent upon the theory of mathematical representations of a group. Before stating the two theorems necessary to extract the representations it is necessary to emphasize the importance of the concept of a class. It is this concept which plays the dominant role in the theory. As mentioned by Jones (14), the work involved in determining classes may be greatly reduced by noting that if the operations of the group are written in matrix form, the matrices corresponding to a given class all have the same trace. This follows from the definition of a class and the fact that a similarity transformation does not change the trace of a matrix. For further details of the work involved the reader is referred to Jones (pp 76-90).

Briefly, the idea of representation theory involves obtaining matrix representations for all group elements, reducing the set of matrices to diagonal form, and considering the traces of the matrices in this form.

The determination of the types of symmetry displayed by wave functions which represent allowed electronic states in crystals can best be accomplished by a systematic approach. The first step involves the construction of the regular representation of the crystallographic group. The fact that any group may be represented as a group of regular permutations is very important and, when coupled with the fact that every regular permutation can be represented as a gxg matrix, becomes the foundation of the work that follows. The representation of the group by these permutation matrices is known as the regular representation. Some of its properties can be seen at once. First, each matrix is of degree g (group order). Secondly, since there can be no diagonal element for any operation except the identity, it follows that:

$$\begin{aligned} \mathrm{Tr}\, A &= 0 \;\{A \neq E\} \\ \mathrm{Tr}\, A &= g \;\{A = E\} \end{aligned} \qquad (2.3)$$

Since in general the operations of the group do not all commute with each other, it is not possible to find a transformation matrix which will bring all matrices of the regular representation simultaneously into diagonal form. However, it is possible to find a transformation which will bring all matrices of the group into a form such as that shown below;



Such a matrix consists of single elements or sub-matrices of degree two or three along the diagonal. For general groups the sub-matrices may be of higher degree but for any crystallographic group none appears with more than three rows and columns.

When the regular group matrices have been transformed so as to make the sub-matrices as small as possible, the representation is said to be completely reduced and the sub-matrices themselves determine what are known as irreducible representations. The traces of the matrices of an irreducible representation are called characters. A character is denoted by a symbol $\chi_i^{(\nu)}$ where ν denotes the irreducible representation and the subscript i denotes the class of the operation to which the matrix refers. As previously mentioned, all matrices of a given class have the same character. Although it is sometimes necessary to obtain the complete matrices of the irreducible representations in order to solve the wave mechanical problem, in practice it is found that a knowledge of the characters is sufficient to enable one to extract the symmetry types without much difficulty.

The calculation of the character tables is dependent upon two theorems:

3. The number of irreducible representations is equal to the number of classes.
4. The number of equivalent matrices of an irreducible representation, in the regular representation, is equal to their degree.

The first theorem may be used to obtain immediately the number of wavefunctions of distinctive symmetry. The second theorem may be used to determine the degeneracy of each symmetry type.

In any irreducible representation, the matrix which represents the identity operation is simply the unit matrix. Consequently, the character of the identity operator for any irreducible representation is equal to the degree of the representation. Thus, by Theorem 4, if $\chi_E^{(\nu)}$ represents the character of the identify operator in the ν representation, then there are just $[\chi_E^{(\nu)}]^2$ diagonal positions occupied by an irreducible representation in the regular representation. Since the matrix of irreducible representations is of order gxg it follows that

$$(\chi_E^{(1)})^2 + (\chi_E^{(2)})^2 + \cdots (\chi_E^{(r)})^2 = g \qquad (2.4)$$

where r is the number of classes. As an example consider a group wherein $g = 16$ and $r = 10$. For this system the only combination of characters that will satisfy the condition given in equation (2.4) is

$$16 = 2^2 + 2^2 +1+1+1+1+1+1+1+1$$

and this yields valuable information about the character of the possible wave functions that may be constructed as well as the electronic states that may be present in a system defined by such a group. It may be seen that there are two doubly degenerate states and eight non-degenerate states for this system.

The calculation of character tables for any system is usually quite involved. The general procedure is to first obtain all class products, then use the class product coefficients to obtain elements of a gxg eigenvalued determinant. This determinant and its use is described in great detail by Jones (14). If the group order is large and the group does not commute, the calculation of characters using this systematic approach is tedious. An alternative method depending only on existing character tables and general orthogonality relations has been developed. It is this method which shall be used throughout the following work.

A crucial part of the alternative analysis involves the way by which a group may be decomposed. Suppose G is a group of order g with r classes and that H is a normal subgroup of G having order g/2. If x is an element of G (other than the identity) which commutes with all other elements of G and if X is not a member of H then the group G may be decomposed in the following fashion

$$G = H + XH. \tag{2.5}$$

The group G must contain twice as many classes as H, for if C is a class of H, XC is another class which cannot belong to H. This follows from the definitions of subgroup and normal subgroup. Since H is a normal subgroup, no operation of H can be transformed out of H. Since there are twice as many classes in G as in H, there are also twice as many irreducible representations of G as there are of H. Suppose now that the matrix (a_{mn}) is an irreducible representation of an operator

A in H. Then one irreducible representation of G will be obtained by allowing (a_{mn}) to represent XA as well as A. This representation satisfies the basic requirement that the matrix representing the product of any two operations of G is equal to the product of the matrices representing these operators. A second representation can be obtained in which if (a_{mn}) represents A, $(-a_{mn})$ represents XA.

If all irreducible representations of G for which A and XA have the same matrices are designated by r+ and those for which the matrices for A and XA differ in sign by r- then the character tables of G may be constructed readily if that of H is known. Using S to denote the character table of H, then the character table for G has the form:

	H	XH
r+	S	S
r-	S	-S

Thus if the characters and classes of H are known, those of G may be readily found and the character table set up immediately without calculation of eigenvalues and without the necessity of finding all irreducible representations. This is the basic difference between the procedure used herein and that outlined by Olbrychski (12).

Before any further procedure may be outlined it is necessary to distinguish between the point group and the space group of a crystallographic system. The point group is defined as being that group of rotations and reflections which bring the crystal into coincidence with itself. The space group differs from the point group in that it consists of the translation group and the product of this group with a complex of operations which may consist of rotations, reflections, glide reflections, and screw displacements. In most systems it is necessary to consider the space group although some systems such as the simple cubic system may be completely described using the point group.

The simplest way of obtaining the properties of the point group is to make use of the stereographic projections by which directions in space may be represented by points on a plane. In order to use the stereographic projection, it is first necessary to briefly discuss the properties of the projection and its applications.

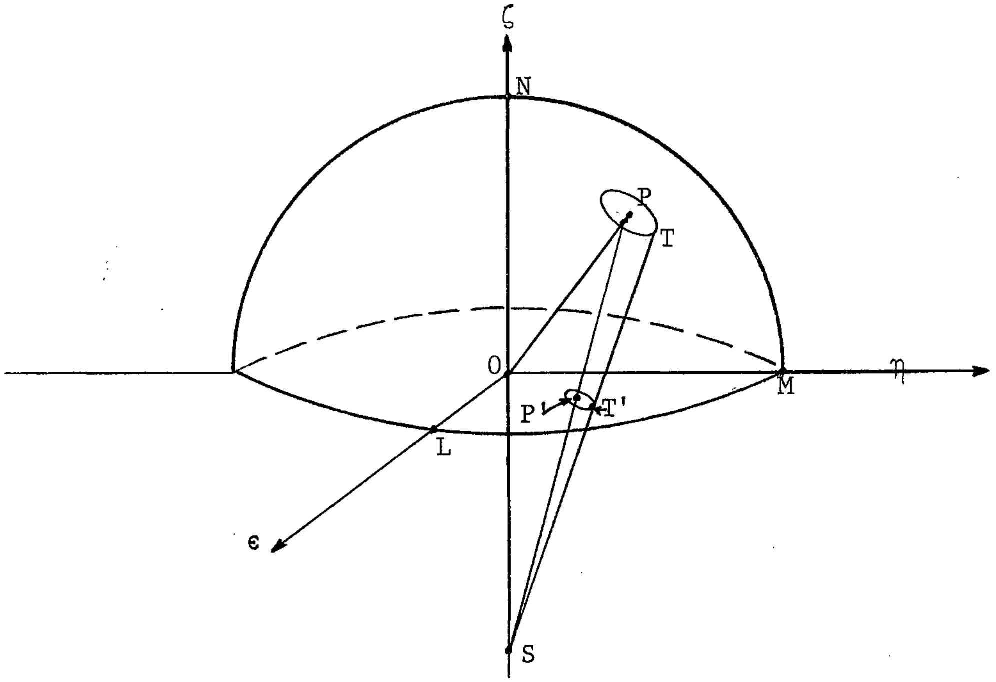


Figure 1. Construction of a Stereographic Projection [After Jones (14)]

Let P be a point on a sphere of unit radius whose coordinates in the rectangular system OL, OM, ON, are (l,m,n) so that these are the direction cosines of the line OP. S represents the south pole of the sphere. The point P', where the line SP cuts the equatorial plane, is the stereographic projection of P and its coordinates in the plane are

$$P' = \{\epsilon_{p'}, \eta_{p'}\} \qquad \epsilon_{p'} = \frac{l}{1+\eta} \qquad \eta'_p = \frac{m}{1+\eta} \tag{2.6}$$

Now, let a plane at right angles to OP whose equation is

$$lx + my + nz = p \qquad p<1 \tag{2.7}$$

cut the unit sphere in a circle of which T is one point. The coordinates (ϵ,η) of T', the projection of T, are given by eliminating (x,y,z) between (2.7) and the equations

$$x^2 + y^2 + z^2 = 1 \tag{2.8}$$

$$\epsilon = \frac{x}{1+z} \; ; \; \eta = \frac{y}{1+z} \tag{2.9}$$

The result is

$$(\epsilon - \frac{l}{P+n})^2 + (\eta - \frac{m}{P+n})^2 = \frac{1-P^2}{(P+n)^2} \tag{2.10}$$

Hence, a circle on the sphere is projected as a circle on the equatorial plane. The center of the projected circle is not P' but rather is obtained using equation (2.10) as $(\frac{l}{P+n}, \frac{m}{P+n})$. The rotation of a solid about a given direction in space can therefore be represented by a circular path about a fixed point in the stereogram.

If the rotation is about a diad axis in the equatorial plane, a point P in the northern hemisphere is transferred to a point in the southern hemisphere. A projection of this point from S would result in a point on the stereogram outside the unit circle. This is inconvenient, and a simpler method is to project points in the southern hemisphere from N and denote these points on the stereogram by small circles in contrast to the dots used when the projection is from S.

In addition to rotations, reflections can also be represented on the stereogram. A reflection in the equatorial plane is represented by a dot surrounded by a small circle. These are the projections from S and N respectively of the two points in space related by the reflection. A reflection in a plane normal to the equatorial plane such as the plane LON is denoted by two dots or two circles on either side of the line in the stereogram which is the projection of this plane. Several pertinent stereograms are given in Chapter IV.

A plane which is inclined to the vertical but passes through the origin is represented by an arc of a great circle in the stereogram. For more detailed information as to the use of stereograms in describing the crystallographic point group, the reader is referred to Chapter III of the text by Jones (14).

In order to understand some of the language used when discussing various point groups it is necessary to define the symbolism used when discussing such systems. Throughout this work both the Schoenflies and the Hermann-Mauguin notation has been used. Whenever a symbol in either form of notation appears, the symbol will be explained at that point. For general information as to the use of these two types of notation, the reader is referred to Kittel (16).

To be able to illustrate the relationships existing between two mathematical groups, the concept of a mathematical mapping from one group to another shall be employed. The most general definition of a mapping from one group into another is embodied in the concept of homeomorphism. A homeomorphism is a mapping of one group into another with certain restraints placed upon the function that accomplishes the mapping, i.e., the mapping function. Let A and B be two mathematical groups. The function φ maps A into B if the relation

$$\varphi(a_1 \cdot a_2) = \varphi(a_1) \ \Theta \ \varphi(a_2) \tag{2.1}$$

holds. As may be seen, this definition embodies two different operations (one for each group) and a function that illustrates an equivalence between these two groups in a special manner. In the above equation, $\varphi(a_1) = b_1 \epsilon B$ and $\emptyset(a_2) = b_2 \epsilon B$. Briefly, then, one group is mapped into another if a_1 (the pre-image of b_1) and a_2 (the pre-image of b_2) may be combined under the operation in A yielding another element, a_3 having an image in B which is the same element as that found by combining the image of a_1 and the image of a_2 using the operation in B, i.e., $\varphi(a_1 \cdot a_2) = \varphi(a_3) = b_3 = b_1 \Theta b_2 = \varphi(a_1) \Theta \varphi(a_2)$. If this mapping is one to one, the mapping is called an isomorphism. Evidently, two groups that are mathematically isomorphic are equivalent. As a result, if they have the same structure as far as the number of classes is concerned, the fact that they are isomorphic will insure that the character systems of A and B are the same. Thus, if the groups used in the crystal system under study may be shown to be isomorphic to point groups already developed in the literature (14) and may be shown to have the same number of classes as the point groups with respect to which the isomorphism is constructed, the calculation of characters for groups may be circumvented simply by the construction of the isomorphism.

CHAPTER III

CONSTRUCTION OF THE BRILLOUIN ZONE

A complete symmetry analysis of any crystal system has as its basis the group properties of the unit cell of the crystal. However, if information is to be gained as to the configuration of the energy bands, the possible electronic states, and the wave functions describing these states, it is convenient to make a mathematical mapping from physical space to the space of the reciprocal lattice. This can be done in the following fashion.

Let $\underline{a}_1$, $\underline{a}_2$, $\underline{a}_3$ be three fixed vectors and let n_1, n_2, n_3 take all positive or negative integral values including zero. Then the set of points

$$n_1\underline{a}_1 + n_2\underline{a}_2 + n_3\underline{a}_3 \tag{3.1}$$

maps out a translation lattice. In order to specify the vectors $\underline{a}_i$, which are known as the primitive translations of the lattice, it is convenient to refer them to a rectangular coordinate system. The components of $\underline{a}_i$ will be written a_{ix}, a_{iy}, a_{iz} and these nine quantities, completely specify the lattice.

A useful notation for the present purpose is obtained by writing the nine vector components as a matrix and the three integers n_i as the components of a column vector. A lattice point is then specified by the symbol $\underline{\underline{A}}\underline{n}$,

$$\begin{pmatrix} a_{1x} & a_{2x} & a_{3x} \\ a_{1y} & a_{2y} & a_{2z} \\ a_{1z} & a_{2z} & a_{3z} \end{pmatrix} \cdot \begin{pmatrix} n_1 \\ n_2 \\ n_3 \end{pmatrix} = \underline{An} \qquad (3.2)$$

The usual rule for matrix multiplication then gives the rectangular components of $\underline{An}$ as a column vector. Since the sum of two lattice displacements $\underline{An}$ and $\underline{Am}$ is $\underline{A}(\underline{n}+\underline{m})$, a translation lattice is completely specified by the matrix $\underline{A}$.

In crystallography the translation lattices are classified into fourteen different types known as Bravais lattices. This classification arises from the relation which exists between the translation lattice and the other operators of the space group.

In order to specify the quantum states of an electron in a three-dimensional lattice a vector $\underline{k}$ is required which is a vector in the space of the reciprocal lattice. A reciprocal lattice may now be uniquely defined for every Bravais lattice. If $\underline{A}$ represents the Bravais lattice matrix and $\underline{B}$ the reciprocal lattice matrix, then the relation,

$$\underline{AB} = 2\Pi\underline{1} \qquad (3.3)$$

defines $\underline{B}$ in terms of $\underline{A}$ and the identity matrix. This definition is sometimes given without the factor 2Π which appears here. However, in the present case it simplifies the notation that follows. The three vectors of the matrix $\underline{B}$ may be obtained through a modified form of equation (3.3),

$$\underline{a}_i \cdot \underline{b}_j = 2\Pi\delta_{ij} \qquad (3.4)$$

In this relation, the $\underline{a}_i$ are the primitive translations of the Bravais lattice. This set of equations completely specifies the $\underline{b}_j$. In fact:

$$\underline{b}_1 = \frac{2\Pi}{D} \underline{a}_2 \times \underline{a}_3$$

$$\underline{b}_2 = \frac{2\Pi}{D} \underline{a}_3 \times \underline{a}_1 \tag{3.5}$$

$$\underline{b}_3 = \frac{2\Pi}{D} \underline{a}_1 \times \underline{a}_2$$

where $D = \underline{a}_1 \cdot (\underline{a}_2 \times \underline{a}_3) = \text{Det.}\, \underline{A}$. The fact that equations (3.5) are the solutions of (3.4) can be seen at once since $\underline{b}_1$ (for example) is at right angles to both $\underline{a}_2$ and $\underline{a}_3$ and therefore, the scalar products with these vectors vanish.

The lattice mapped out by the points

$$l_1\underline{b}_1 + l_2\underline{b}_2 + l_3\underline{b}_3 \tag{3.6}$$

as l_1, l_2, l_3 take all positive and negative integral values including zero is called the reciprocal lattice.

The unit polyhedron in reciprocal space is defined as the region enclosed by planes which bisect normally the lines joining the origin to the nearest points of the reciprocal lattice. As the points of the reciprocal lattice are given by the vectors $\underline{lB}$, the equation of any one of these planes is

$$\underline{K} \cdot \underline{lB} = \tfrac{1}{2} \left| \underline{lB} \right|^2. \tag{3.7}$$

The stannic oxide, or rutile crystal structure is composed of inter-penetrating, primitive tetragonal cells which differ in orientation by a ninety degree rotation. Although the resulting unit cell, as shown in Figure 1, has a metal atom at the body-centered position, it is the primitive tetragonal cell which determines the Brillouin zone.

The $\underline{A}$ matrix for the primitive tetragonal cell may be written as:

$$\underline{A} = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & c \end{pmatrix} \tag{3.8}$$

Since $\underline{A}$ is a scalar matrix, it may be inverted immediately. Thus, the matrix describing the reciprocal lattice may be written as:

$$\underline{B} = 2\Pi \begin{pmatrix} \frac{1}{a} & 0 & 0 \\ 0 & \frac{1}{a} & 0 \\ 0 & 0 & \frac{1}{c} \end{pmatrix} \tag{3.9}$$

Application of the vector form of the Bragg reflection law (i.e., equation (3.7), results in:

$$K_x\left(\frac{l_1}{a}\right) + K_y\left(\frac{l_2}{a}\right) + K_z\left(\frac{l_3}{c}\right) = \Pi\left[\left(\frac{l_1}{a}\right)^2 + \left(\frac{l_2}{a}\right)^2 + \left(\frac{l_3}{c}\right)^2\right] \tag{3.10}$$

The smallest polyhedron that may be constructed using this relation is obtained by using the following values of $\underline{l}$: (100); (010); (001); $(\bar{1}00)$; $(0\bar{1}0)$; $(00\bar{1})$.

Thus, the first Brillouin zone for this structure is a parallelopiped having a cross sectional area $(2\Pi/a)^2$ and height $2\Pi/c$. The volume of this cell is evidently $(2\Pi)^3/a^2c$, which is that corresponding to the required result given by Jones (14). Figure 2 illustrates the shape of the zone and has coordinates listed for points of high symmetry.

CHAPTER IV

CHARACTER TABLES AND WAVE VECTOR GROUPS

When an electron is constrained to move within a crystal lattice it is subject to many forces. As a result, only very restricted values of electron energies are allowed. In order to determine the possible energy states it is necessary to solve the time independent Schroedinger equation. This equation is usually written in operator form as

$$H\psi = E\psi \qquad (4.1)$$

In this form, H is the Hamiltonian operator and as such describes the total energy E of the electron. Using the simplest form for H, i.e.,

$$H = \frac{P^2}{2m} + V_{(r)} \qquad (4.2)$$

with the substitutions

$$\begin{aligned} P_k &\rightarrow \frac{\hbar}{i} \frac{\partial}{\partial x_K} \\ x_K &\rightarrow x_K \end{aligned} \qquad (4.3)$$

the spatially dependent Schroedinger equation may be written in standard form as

$$\Delta\psi + \frac{2m}{\hbar^2}(E - V(r))\psi = 0 \qquad (4.4).$$

The solutions of this equation play an integral role in the following work. Bloch (17) has shown that if the potential is periodic the solutions of this equation have the general form given by

$$\psi = e^{i\underline{K}\cdot\underline{r}}\, U(\underline{r}) \qquad (4.5).$$

In this relation U(r) has the periodicity of the potential, i.e., the periodicity of the lattice. Jones (14) has shown that this form of solution is valid even if the potential is chosen to be some arbitrary constant. Thus, this type of solution may be used for every situation wherein the potential is either constant or periodic.

The Brillouin zone as constructed in Chapter III has several points for which the co-ordinates have been listed. At each of these points a wave function may be written using equation (4.5). The group of the wave vector for each point is then defined to be that set of space group operations that leaves the wavefunction invariant or transforms it into a wavefunction at an equivalent point. Two points in the first Brillouin zone are called equivalent if they differ at most by a reciprocal lattice vector.

The space group symbol of the rutile structure is P4/mnm. This means that this structure differs from the most symmetric tetragonal point group with respect to the reflections in the (100) and (010) planes. These true reflections are replaced by diagonal glide reflections.

The nature of the glide operation must be considered in some detail in order to fully understand the properties of the space group at various points of high symmetry. First, it is necessary to define operators which denote the glides in question. These operators and their mathematical properties have been treated elsewhere (14), however, a general statement of the properties of such operations is a necessary preliminary to the work that follows.

If $T(\underline{r})$ denotes a translation through $\underline{r}$, and K denotes a point group operation, the symbol $KT(\underline{r})$ implies a displacement followed by the application of the point group operation in question. In general, the order of performance of these two operations is very important inasmuch as the operations KT and TK do not necessarily commute. The lack of commutativity is clearly illustrated in the following relation:

$$KT(\underline{r}) = T(K\underline{r})K. \tag{4.6}$$

The operations KT form a group which is a continuous group if K and $\underline{r}$ are unrestricted. If $\underline{r}$ is restricted to lattice translations, T to either integral multiples of the primitive vectors or rational fractions of these, and K is restricted to the operations of a crystallographic point group, then KT are the operations of the space group. If $\underline{S}$ denotes a fractional vector, that is, one whose components are proper fractions, then a glide reflection may be written $T(\underline{AS})m$, where m represents a mirror reflection.

These properties may now be applied to the unit cell of the crystal system in question. The unit cell has been drawn in Figure 1. From this figure it may be ascertained that there are three reflection planes which are mutually perpendicular. Two of the reflection planes have associated with them axes which may be classified as diad axes. Due to the presence of the body centered molecule, the unit cell lacks the ninety degree rotational symmetry characteristic of the holosymmetric point group P4/mmm. However, the unit cell does possess a one-hundred and eighty degree rotational symmetry. Thus the entire point group consists of an identity, (E), a reflection in the basal plane (m_3), two reflections in the inequivalent mirror planes (m_1 and m_2), two improper rotations associated with the diad axes (R_1 and R_2), a one-hundred and eighty degree rotation (C_2), and an inversion operation (J) included to insure closure of the group. These eight operations may be placed on a stereogram as in Figure 4. At this point, it should be noted that these operations may be obtained immediately from the holosymmetric point group P4/mmm (stereogram shown in Figure 5) simply by deleting all operations of this group that correspond to the two reflection planes (100) and (010).

The full space group of the crystal is obtained by multiplying all point group operations by the diagonal glide operation. This complex of sixteen distinct operations must be described in terms of the factor group. Here it should be stated that the point group is of order eight, commutes, and may be made isomorphic to that of the orthorhombic system. Thus the characters for this point group are well known and need not be calculated.

Since all of the point group elements play an important role in the following analysis, each operation has been listed in Table I with its inverse. In the third column the substitution corresponding to the operation in question is listed. This column should be scrutinized rather closely. The set of substitutions may be derived easily and merely indicates the manner in which the product xyz is transformed upon application of the operation in question. However, it is very important in the following work that this set of substitutions be valid. For this reason column four has been included in Table I and indicates the matrix representation of each operation.

The group of the wave vector at various points of the Brillouin

TABLE I

POINT GROUP ELEMENTS AND THEIR IRREDUCIBLE REPRESENTATIONS

Element	Inverse	Sub	Matrix
E	E	xyz	$\begin{pmatrix}1&0&0\\0&1&0\\0&0&0\end{pmatrix}$
M_1	M_1	$\bar{y}\bar{x}z$	$\begin{pmatrix}0&-1&0\\-1&0&0\\0&0&1\end{pmatrix}$
M_2	M_2	yxz	$\begin{pmatrix}0&1&0\\1&0&0\\0&0&1\end{pmatrix}$
M_3	M_3	$xy\bar{z}$	$\begin{pmatrix}1&0&0\\0&1&0\\0&0&-1\end{pmatrix}$
R_1	R_1	$\bar{y}\bar{x}\bar{z}$	$\begin{pmatrix}0&-1&0\\-1&0&0\\0&0&-1\end{pmatrix}$
R_2	R_2	$yx\bar{z}$	$\begin{pmatrix}0&1&0\\1&0&0\\0&0&-1\end{pmatrix}$
C_2	C_2	$\bar{x}\bar{y}z$	$\begin{pmatrix}-1&0&0\\0&-1&0\\0&0&1\end{pmatrix}$
J	J	$\bar{x}\bar{y}\bar{z}$	$\begin{pmatrix}-1&0&0\\0&-1&0\\0&0&-1\end{pmatrix}$

zone may be determined in a systematic way. The first step involves consideration of the Bloch function at that point and selecting all point group operations that will either leave the function invariant or transform it into another Bloch function at an equivalent point.

Consider the group of the wave vector at the point Γ. At this point of the zone, the wavefunction is merely V where V(r) has the same period as the Bravias lattice. Since the glide operations Tm and mT commute at this point, it will suffice to consider only the application of the elements (H) and Tm(H) to the wavefunction. In this notation (H) stands for the entire point group. Thus, the entire space group is to be applied to the wavefunction at the center of the Brillouin zone. This set is of order sixteen due to the inclusion of the product of the diagonal glide operation with all point group operations. This set of sixteen elements will not form a group in itself because the combination law stated for the product of a point group operation and a translation (included in the glide) introduces some other translations that were not in the original set. However, all of these translations are of such a nature that when they are applied to the Bloch function they reproduce the function exactly. As a result of the commutativity of the point group elements and the commutativity of T and m, the entire set of order sixteen is commutative. Thus, the character table consists only of positive and negatives 1's and may be constructed quickly by considering that (H) is a normal subgroup of the space group and Tm commutes with every element in the group. Following the argument given in Chapter II, the character table is set up using the characters given for the orthorhombic point group. The results are tabulated in Table II.

Consider next the point of the first zone designated X. The Bloch function at this point is given by:

$$\psi_X = e^{\frac{i\pi x}{a}} U(\underline{r}) \tag{4.7}$$

The only other point of the zone that is equivalent to this point is the one that has coordinates which are the negative of those given for X. Thus, the set of point group elements that belong to the group of the wave vector at X consists of the elements:

$$E,\ m_3,\ J,\ C_2.$$

Using the substitutions given in Table I, these elements operating on the wavefunction will either reproduce the wavefunction at X or at its equivalent point. If the operation Tm is considered, (m representing a reflection in the x=0 plane) then application of this operation to the wavefunction at X gives another Bloch-type function at the point equivalent to X. Inclusion of this diagonal glide operation increases the order of the set to be studied to eight. Note however, that the product

$$JTm \equiv JT(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})m = T(\tfrac{\bar{1}}{2}\tfrac{\bar{1}}{2}\tfrac{\bar{1}}{2})mJ = T(\bar{1}\bar{1}\bar{1})TmJ$$

$$JTm = T(\bar{1}\bar{1}\bar{1})TmJ$$

See eqn. (4.6)

and when it is applied to the wavefunction at X the sign of the wavefunction is changed. As a result, it is necessary to include all translations that change the sign of the wavefunction in this group. Such translations shall be designated by Q. However, this is not yet sufficient. The fact that the group must be closed requires that all elements of the form QTm be included. The complete set of the wave vector at X is therefore of order sixteen. The elements of this group and the inverse of each element are listed in Table III.

In order to determine the classes for this set, it is necessary to consider all products of the form $x^{-1}a\ x$ where x is allowed to take on all values in the group and a is a fixed element. Table IV contains a sample calculation for two of these classes. Table V contains the complete results of this calculation and as such contains all classes. These classes may be shown to be simply isomorphic to those obtained using the holosymmetric point group P4/mmm via drawing an isomorphism between these two groups. The group isomorphism used for this case is given in Table VI. A class isomorphism follows directly.

Due to the relation between the two groups given in Table VI, the set of characters obtained for the group of the wave vector at the point X is the same as that obtained for the holosymmetric point group P4/mmm. This set has been rearranged as given in Table VII and must now be scrutinized rather closely. The function which has been used to generate the group of substitutions of the wave vector at X is the Bloch function at that point, (equation (4.7)). Once the operations of the wave vector group were selected, the only properties of the wavefunction subsequently used were: that $U(\underline{r})$ should be invariant under a lattice transformation; that Q=T(110) should transform the wavefunction into an equivalent Bloch function; and that Q^2 should leave the wavefunction invariant. The given wavefunction is not the only function with these properties; for example, $U(\underline{r})$ itself satisfies the conditions. Hence, amongst the representations of this group there will be some for which the character of Q is positive. These appear in the top eight rows in Table VI and they cannot refer to the wavefunction since

$Q\psi = -\psi$. The only representations that belong to the wave vector at X have been designated by X_1 and X_2 and each of these corresponds to a doubly degenerate state.

Consider a similar treatment applied to the states at Z. Since the wavefunction at this point is given by $\psi_z = e^{\frac{\pi i z}{c}} U(\underline{r})$ the set of point group operations that either leave the wavefunction invariant or transform it into a wavefunction at an equivalent point are given by all elements such that z is transformed into itself or its negative. Thus, all of the point group elements apply to this wave vector group. Using an analysis exactly similar to that just discussed for the point at X, the factor group is composed of all of the point group elements multiplied by E, Tm, Q, and QTm. The set of elements and their inverses are listed in Table VIII. The classes are calculated as before by considering all possible products of the form $x^{-1}a\ x$ and are given in Table IX. The full group is of order thirty-two and contains twenty classes. Therefore, the character table is not simply isomorphic to one of the character tables already worked out for the holosymmetric point groups.

Two alternatives are available if these characters are to be calculated. The first of these lies in a complete analysis based upon the solution of secular determinants whose elements are class product coefficients. The other alternative is to recognize that the elements given in Table X form a subgroup of the complete group. This subgroup is of order sixteen and is invariant. Multiplication of every element of this subgroup with the element m_1 (or m_2) produces the rest of the group. Since m_1 commutes with all members of the group, it is possible to use the procedure outlined in Chapter II wherein a knowledge of the characters of the subgroup is sufficient to allow the immediate calculation of the characters for the complete group. As a result of this analysis, it is seen that since the subgroup is isomorphic to the point group P4/mmm, it is possible to write the character table immediately. Using an argument very similar to that developed for the group of the wave vector at X it is seen that the table of characters may be re-arranged into a set which apply to the point in question (due to the restriction $Q\psi = -\psi$) and a set that do not apply. Again, it may be seen that only doubly degenerate states are allowed at this point. Table XI contains the characters for this group.

Consider now states at the point M. At this point the wavefunction is given by:

$$\psi_M = e^{\frac{i\pi}{a}(x+y)} U(\underline{r}) \qquad (4.8).$$

The point group elements which leave this wavefunction invariant or take it into a wavefunction at the equivalent point consist of all elements which take xy into yx, xy, $\bar{y}\bar{x}$ or $\bar{x}\bar{y}$. The entire point group (G) displays this property. The element Tm is not a member of the wave vector group at M. However, the product Tm_xTm_y is a member of this group. The product may be rewritten as:

$$\begin{aligned} Tm_xTm_y &= T(011)m_xm_y = T(011)C_2 = QC_2 \\ Tm_yTm_x &= T(101)m_ym_x = T(101)C_2 = QC_2 \end{aligned} \qquad (4.9)$$

where Q is a translation which changes the sign of the wavefunction and Q^2 is the identity. Thus, the full group of the wave vector at M consists of (G) and Q(G). This group is of order sixteen and is commutative. As a result, there are sixteen classes in this group that are simply isomorphic to those found at the center of the zone. The character table for this wave vector group is given as Table XII.

At the point A the wavefunction has the form:

$$\psi_A = e^{i(\frac{\pi}{a}x + \frac{\pi}{a}y + \frac{\pi}{c}z)} U(\underline{r}) \qquad (4.10)$$

Equivalent points have wavefunctions given by

$$e^{i(\frac{\pi}{a}x + \frac{\pi}{a}y - \frac{\pi}{c}z)} U(\underline{r})$$

$$e^{i(-\frac{\pi}{a}x - \frac{\pi}{a}y + \frac{\pi}{c}z)} U(\underline{r})$$

$$e^{-i(\frac{\pi}{a}x + \frac{\pi}{a}y + \frac{\pi}{c}z)} U(\underline{r})$$

The entire point group applies to this set without producing a new wavefunction. As was the case for the point at M, although neither Tm_x nor Tm_y is included in the wave vector group, their product is. However, for this set, the product does not introduce a translation and the resulting characters may be seen to be simply isomorphic with those obtained at the center of the zone. The character system for this wave vector group is given in Table XIII.

At the point R the wavefunction is given by

$$\psi_R = e^{i(\frac{\pi}{a}x + \frac{\pi}{c}z)} U(\underline{r}) \qquad (4.11).$$

The set of point group elements that take this wavefunction into itself or a wavefunction at an equivalent point are:

$$E,\ m_3,\ J,\ C_2.$$

Again, as at X, the wavevector group consists of this set (H) and the products Tm(H), Q(H) and QTm(H). Table XIV contains the appropriate elements and inverses. The characters are given in Table XV.

It is also necessary to consider the points that lie on the axis between the high symmetry points discussed so far. The first such point has been designated as Δ. Here the wavefunction is given by

$$\psi_{\Delta} = e^{\frac{2\pi\xi Xi}{a}} U(\underline{r}) \quad 0<\xi<\tfrac{1}{2} \tag{4.12}$$

The set of all elements in the space group which leave the form of this wavefunction invariant consists of all elements which do not change the sign of x. Only four elements fit into this category. They are: E, m_3, TmC_2, and TmJ. The characters for the system are determined by considering the set of substitutions generated by these elements. This set is shown in Table XVI along with the corresponding elements. Note that this set of substitutions corresponds to those provided by the elements E, m_2, m_3, and R_2 present in the holosymmetric point group P4/mmm. These elements constitute a commutative subgroup of the holosymmetric group. Due to the commutativity of this subgroup, its characters are well known. Since the wave vector group at Δ is composed of elements that have the same substitutions as this group, an isomorphism may be constructed between these two groups and their characters. The characters for the group of the wave vector at the point Δ are listed in Table XVII.

A similar analysis applies to every axial point. Rather than repeat the entire procedure for each axis, the results of the analyses of wave vector groups and characters at designated general points have been listed in Tables XVIII through XXVI.

TABLE II

CHARACTERS AT Γ

	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}
Γ_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Γ_2	1	-1	-1	1	1	-1	-1	1	1	-1	-1	1	1	-1	-1	1
Γ_3	1	1	-1	-1	1	1	-1	-1	1	1	-1	-1	1	1	-1	-1
Γ_4	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1
Γ_5	1	1	1	1	-1	-1	-1	-1	1	1	1	1	-1	-1	-1	-1
Γ_6	1	-1	-1	1	-1	1	1	-1	1	-1	-1	1	-1	1	1	-1
Γ_7	1	1	-1	-1	-1	-1	1	1	1	1	-1	-1	-1	-1	1	1
Γ_8	1	-1	1	-1	-1	1	-1	1	1	-1	1	-1	-1	1	-1	1
Γ'_1	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1
Γ'_2	1	-1	-1	1	1	-1	-1	1	-1	1	1	-1	-1	1	1	-1
Γ'_3	1	1	-1	-1	1	1	-1	-1	-1	-1	1	1	-1	-1	1	1
Γ'_4	1	-1	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1	-1	1
Γ'_5	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	1	1	1	1
Γ'_6	1	-1	-1	1	-1	1	1	-1	-1	1	1	-1	1	-1	-1	1
Γ'_7	1	1	-1	-1	-1	-1	1	1	-1	-1	1	1	1	1	-1	-1
Γ'_8	1	-1	1	-1	-1	1	-1	1	-1	1	-1	1	1	-1	1	-1
	E	R_1	R_2	C_2	J	m_2	m_1	m_3								

$C_i = TmC_{i-8} \qquad (i > 8)$

TABLE III

WAVE VECTOR GROUP ELEMENTS AT X

Element	Inverse
E	E
m_3	m_3
C_2	C_2
J	J
Tm	QTm
Tmm_3	$QTmm_3$
TmC_2	TmC_2
TmJ	TmJ
QTm	Tm
$QTmm_3$	Tmm_3
$QTmC_2$	$QTmC_2$
QTmJ	QTmJ
Q	Q
Qm_3	Qm_3
QC_2	QC_2
QJ	QJ

TABLE IV

TYPICAL CLASS CALCULATIONS $X^{-1}aX = C_a$

a = Tm	$a = C_2$
Tm	C_2
Tm	C_2
QTm	C_2
QTm	C_2
Tm	QC_2
Tm	QC_2
QT_m	QC_2
QTm	QC_2
Tm	QC_2
T_m	QC_2
QT_m	QC_2
QTm	QC_2
Tm	C_2
Tm	C_2
QTm	C_2
QTm	C_2

In Table IV x is taken from Table III directly

Example is

$$QTm\,(C_2)Tm = QTmQTmC_2 = Q^2(Tm)^2C_2 = QC_2$$

$$TmJ\,(Tm)TmJ = TmJQJ = TmQJ^2 = TmQ = QTm$$

TABLE V

CLASSES AT X

$C_1 = E$

$C_2 = Q$

$C_3 = Tm + QTm$

$C_4 = J + QJ$

$C_5 = TmJ + QTmJ$

$C_6 = m_3$

$C_7 = Qm_3$

$C_8 = Tmm_3 + QTmm_3$

$C_9 = C_2 + QC_2$

$C_{10} = TmC_2 + QTmC_2$

TABLE VI

GROUP ISOMORPHISM USED

Elements at X	Elements in P4/mmm
E	E
m_3	J
C_2	m_2
J	R_1
Tm	C_1
Tmm_3	JC_1
TmC_2	m_2^1
TmJ	R_1^1
QTm	C_1^{-1}
$QTmm_3$	JC_1^{-1}
$QTmJ$	R_2^1
$QTmC_2$	m_1^1
Q	C_2
Qm_3	m_3
QJ	R_2
QC_2	m_1

TABLE VII

CHARACTERS AT X

	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
	1	1	1	1	1	1	1	1	1	1
	1	1	1	-1	-1	1	1	1	-1	-1
	1	1	-1	1	-1	1	1	-1	1	-1
	1	1	-1	-1	1	1	1	-1	-1	1
	1	1	1	1	1	-1	-1	-1	-1	-1
	1	1	1	-1	-1	-1	-1	-1	1	1
	1	1	-1	1	-1	-1	-1	1	-1	1
	1	1	-1	-1	1	-1	-1	1	1	-1
X_1	2	-2	0	0	0	2	-2	0	0	0
X_2	2	-2	0	0	0	-2	2	0	0	0
	E	Q				m_3Qm_3				

TABLE VIII

ELEMENTS AND INVERSES AT Z

Element	Inverse	Element	Inverse
E	E	QTm	Tm
m_1	m_1	$QTmm_1$	Tmm_1
m_2	m_2	$QTmm_2$	Tmm_2
m_3	m_3	$QTmm_3$	$QTmm_3$
R_1	R_1	$QTmR_1$	$QTmR_1$
R_2	R_2	$QTmR_2$	$QTmR_2$
C_2	C_2	$QTmC_2$	TmC_2
J	J	QTmJ	QTmJ
Tm	QTm	Q	Q
Tmm_1	$QTmm_1$	Qm_1	Qm_1
Tmm_2	$QTmm_2$	Qm_2	Qm_2
Tmm_3	Tmm_3	Qm_3	Qm_3
TmR_1	TmR_1	QR_1	QR_1
TmR_2	TmR_2	QR_2	QR_2
TmC_2	$QTmC_2$	QC_2	QC_2
TmJ	TmJ	QJ	QJ

TABLE IX

CLASSES AT Z

$C_1 = E$

$C_2 = Q$

$C_3 = Tm + QTm$

$C_4 = m_3 + Qm_3$

$C_5 = Tmm_3 + QTmm_3$

$C_6 = C_2^*C_1 = C_2$

$C_7 = C_2^*C_2 = QC_2$

$C_8 = C_2^*C_3 = TmC_2 + QTmC_2$

$C_9 = C_2^*C_4 = J + QJ$

$C_{10} = C_2^*C_5 = TmJ + QTmJ$

$C_{11} = m_1 = m_1C_1$

$C_{12} = Qm_1 = m_1C_2$

$C_{13} = Tmm_1 + QTmm_1 = m_1C_3$

$C_{14} = R_1 + QR_1 = m_1C_4$

$C_{15} = TmR_1 + QTmR_1 = m_1C_5$

$C_{16} = m_2 = m_1C_6$

$C_{17} = Qm_2 = m_1C_7$

$C_{18} = Tmm_2 + QTmm_2 = m_1C_8$

$C_{19} = R_2 + QR_2 = m_1C_9$

$C_{20} = TmR_2 + QTmR_2 = m_1C_{10}$

---

*point group element rather than a class

TABLE X

NORMAL SUBGROUP OF Z

E
C_2
J
m_3
Q
QC_2
QJ
Qm_3
Tm
TmC_2
TmJ
Tmm_3
QTm
$QTmC_2$
QTmJ
$QTmm_3$

TABLE XI

CHARACTERS AT Z

	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}
	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
	1	1	1	-1	-1	1	1	1	-1	-1	1	1	1	-1	-1	1	1	1	-1	-1
	1	1	-1	1	-1	1	1	-1	1	-1	1	1	-1	1	-1	1	1	-1	1	-1
	1	1	-1	-1	1	1	1	-1	-1	1	1	1	-1	-1	1	1	1	-1	-1	1
	1	1	1	1	1	-1	-1	-1	-1	-1	1	1	1	1	1	-1	-1	-1	-1	-1
	1	1	1	-1	-1	-1	-1	-1	1	1	1	1	1	-1	-1	-1	-1	-1	1	1
	1	1	-1	1	-1	-1	-1	1	-1	1	1	1	-1	1	-1	-1	-1	1	-1	1
	1	1	-1	-1	1	-1	-1	1	1	-1	1	1	-1	-1	1	-1	-1	1	1	-1
	1	1	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1
	1	1	1	-1	-1	1	1	1	-1	-1	-1	-1	-1	1	1	-1	-1	-1	1	1
	1	1	-1	1	-1	1	1	-1	1	-1	-1	-1	1	-1	1	-1	-1	1	-1	1
	1	1	-1	-1	1	1	1	-1	-1	1	-1	-1	1	1	-1	-1	-1	1	1	-1
	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	1	1	1	1	1
	1	1	1	-1	-1	-1	-1	-1	1	1	-1	-1	-1	1	1	1	1	1	-1	-1
	1	1	-1	1	-1	-1	-1	1	-1	1	-1	-1	1	-1	1	1	1	-1	1	-1
	1	1	-1	-1	1	-1	-1	1	1	-1	-1	-1	1	1	-1	1	1	-1	-1	1
Z_1	2	-2	0	0	0	2	-2	0	0	0	2	-2	0	0	0	2	-2	0	0	0
Z_2	2	-2	0	0	0	-2	2	0	0	0	2	-2	0	0	0	-2	2	0	0	0
Z_3	2	-2	0	0	0	2	-2	0	0	0	-2	2	0	0	0	-2	2	0	0	0
Z_4	2	-2	0	0	0	-2	2	0	0	0	-2	2	0	0	0	2	-2	0	0	0
	E	Q				C_2	QC_2				m_1	Qm_1				m_2	Qm_2			

TABLE XII

CHARACTERS AT M

	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}
M_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
M_2	1	-1	-1	1	1	-1	-1	1	1	-1	-1	1	1	-1	-1	1
M_3	1	1	-1	-1	1	1	-1	-1	1	1	-1	-1	1	1	-1	-1
M_4	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1
M_5	1	1	1	1	-1	-1	-1	-1	1	1	1	1	-1	-1	-1	-1
M_6	1	-1	-1	1	-1	1	1	-1	1	-1	-1	1	-1	1	1	-1
M_7	1	1	-1	-1	-1	-1	1	1	1	1	-1	-1	-1	-1	1	1
M_8	1	-1	1	-1	-1	1	-1	1	1	-1	1	-1	-1	1	-1	1
M'_1	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1
M'_2	1	-1	-1	1	1	-1	-1	1	-1	1	1	-1	-1	1	1	-1
M'_3	1	1	-1	-1	1	1	-1	-1	-1	-1	1	1	-1	-1	1	1
M'_4	1	-1	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1	-1	1
M'_5	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	1	1	1	1
M'_6	1	-1	-1	1	-1	1	1	-1	-1	1	1	-1	1	-1	-1	1
M'_7	1	1	-1	-1	-1	-1	1	1	-1	-1	1	1	1	1	-1	-1
M'_8	1	-1	1	-1	-1	1	-1	1	-1	1	-1	1	1	-1	1	-1
	E	m_1	m_2	m_3	R_1	R_2	C_2	J		$C_i = Tm_x Tm_y C_{i-8}$ $\quad i > 8$						

C

TABLE XIII

CHARACTERS AT A

C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
1	-1	-1	1	1	-1	-1	1	1	-1	-1	1	1	-1	-1	1
1	1	-1	-1	1	1	-1	-1	1	1	-1	-1	1	1	-1	-1
1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1
1	1	1	1	-1	-1	-1	-1	1	1	1	1	-1	-1	-1	-1
1	-1	-1	1	-1	1	1	-1	1	-1	-1	1	-1	1	1	-1
1	1	-1	-1	-1	-1	1	1	1	1	-1	-1	-1	-1	1	1
1	-1	1	-1	-1	1	-1	1	1	-1	1	-1	-1	1	-1	1
1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1
1	-1	-1	1	1	-1	-1	1	-1	1	1	-1	-1	1	1	-1
1	1	-1	-1	1	1	-1	-1	-1	-1	1	1	-1	-1	1	1
1	-1	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1	-1	1
1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	1	1	1	1
1	-1	-1	1	-1	1	1	-1	-1	1	1	-1	1	-1	-1	1
1	1	-1	-1	-1	-1	1	1	-1	-1	1	1	1	-1	-1	-1
1	-1	1	-1	-1	1	-1	1	-1	1	-1	1	1	-1	1	-1
E	R_1	R_2	C_2	J	M_2	M_1	M_3	Tm_xTm_y							

$C_i = Tm_xTm_yC_{i-8}$ when $i > 8$

TABLE XIV

ELEMENTS AND INVERSES AT R

Element	Inverse
E	E
m_2	m_2
J	J
C_2	C_2
Tm	QTm
Tmm_3	Tmm_3
TmJ	QTmJ
TmC_2	TmC_2
QTm	Tm
$QTmm_3$	$QTmm_3$
QTmJ	TmJ
$QTmC_2$	$QTmC_2$
Q	Q
Qm_3	Qm_3
QJ	QJ
QC_2	QC_2

TABLE XV

CHARACTERS AT R

	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
	1	1	1	1	1	1	1	1	1	1
	1	1	1	-1	-1	1	1	1	-1	-1
	1	1	-1	1	-1	1	1	-1	1	-1
	1	1	-1	-1	1	1	1	-1	-1	1
	1	1	1	1	1	-1	-1	-1	-1	-1
	1	1	1	-1	-1	-1	-1	-1	1	1
	1	1	-1	1	-1	-1	-1	1	-1	1
	1	1	-1	-1	1	-1	-1	1	1	-1
R_1	2	-2	0	0	0	2	-2	0	0	0
R_2	2	-2	0	0	0	-2	2	0	0	0

$C_1 = E$
$C_2 = Q$
$C_3 = Tm + QTm$
$C_4 = m_3 + Qm_3$
$C_5 = Tmm_3 + QTmm_3$

$C_6 = J$
$C_7 = QJ$
$C_8 = TmJ + QTmJ$
$C_9 = C_2 + QC_2$
$C_{10} = TmC_2 + QTmC_2$

TABLE XVII

CHARACTERS AT Δ

	E	m_3	TmJ	TmC_2
Δ_1	1	1	1	1
Δ_6	1	1	-1	-1
Δ_3	1	-1	-1	1
Δ_4	1	-1	1	-1
	x	x	$x+a/2$	$x+a/2$
	y	y	$\bar{y}+a/2$	$\bar{y}+a/2$
	z	$\bar{z}$	$\bar{z}$	$\bar{z}$

TABLE XVI

SUBSTITUTIONS USED FOR THE GROUP AT Δ

Element	Substitution
E	xyz
m_3	$xy\bar{z}$
TmC_2	$x\bar{y}z$
TmJ	$x\bar{y}z^{-}$

TABLE XVIII

AXIAL WAVE VECTOR GROUPS AND CLASSES

Symmetry Point	Wavefunction	Wave-Vector Group	Classes	Location of Characters
Λ	$\psi_\Lambda = e^{\frac{2\pi i\zeta z}{c}} U(\underline{r})$	$E, m_1, m_2, C_2, Tm,$ Tmm_1, Tmm_2, TmC_2	Set of substitutions isomorphic to group with classes $C_1 = E$, $C_2 = C_2$ $C_3 = m_1+m_2$, $C_4 = Tmm_1+Tmm_2$ $C_5 = Tm+TmC_2$	Table XIX
W	$e^{i\{\frac{\pi x}{a} + \frac{2\pi\zeta z}{c}\}} U(\underline{r})$	E, C_2, Tm, TmC_2	Substitutions isomorphic with E, m_1, m_2, C_2 of P4/mmm point group	Table XX
S	$e^{2\pi i\{\frac{\xi(x+y)}{a} + \frac{z}{2c}\}} U(\underline{r})$	E, m_2, R_2, m_3	These commute	Table XXI
T	$e^{\pi i\{\frac{x}{a} + \frac{z}{c} + \frac{2\xi y}{a}\}}$	E, m_3, Tm, Tmm_3	Substitutions isomorphic to $\{E, m_1, R_1, m_3\}$ of p4/mmm point group	Table XXII
U	$e^{2\pi i\{\frac{x\xi}{a} + \frac{z}{2c}\}} U(\underline{r})$	E, m_3, TmC_2, TmJ	Same as Δ wave-vector group	Table XXIII
Σ	$e^{\frac{2\pi i}{a}\xi(x+y)} U(r)$	Same as S		Table XIV

TABLE XVIII (Continued)

Symmetry Point	Wavefunction	Wave-Vector Group	Classes	Location of Characters
V	$e^{\pi i\{\frac{(x+y)}{a} + \frac{2\zeta z}{c}\}} U(\underline{r})$	Same as Λ		Table XXV
Y	$e^{\frac{\pi i}{a}(x+2\xi y)} U(\underline{r})$	Same as T		Table XVI

TABLE XIX

CHARACTERS AT Λ

	C_1	C_2	C_3	C_4	C_5	
Λ_1	1	1	1	1	1	$C_1 = E$
Λ_2	1	1	1	-1	-1	$C_2 = C_2$
Λ_3	1	1	-1	1	-1	$C_3 = m_1+m_2$
Λ_4	1	1	-1	-1	1	$C_4 = Tm+TmC_2$
Λ_5	2	-2	0	0	0	$C_5 = Tmm_1+Tmm_2$

TABLE XX

CHARACTERS AT W

	C_1	C_2	C_3	C_4	
W_1	1	1	1	1	$C_1 = E$
W_2	1	-1	-1	1	$C_2 = C_2$
W_3	1	1	-1	-1	$C_3 = Tm$
W_4	1	-1	1	-1	$C_4 = TmC_2$

TABLE XXI

CHARACTERS AT S

	E	m_2	m_3	R_2
S_1	1	1	1	1
S_2	1	-1	-1	1
S_3	1	1	-1	-1
S_4	1	-1	1	-1

TABLE XXII

CHARACTERS AT T

	E	m_3	Tm	Tmm_3
T_1	1	1	1	1
T_2	1	-1	-1	1
T_3	1	1	-1	-1
T_4	1	-1	1	-1

TABLE XXIII

CHARACTERS AT U

	E	m_3	TmC_2	TmJ
U_1	1	1	1	1
U_2	1	-1	-1	1
U_3	1	1	-1	-1
U_4	1	-1	1	-1

TABLE XXIV

CHARACTERS AT Σ

	E	m_2	m_3	R_2
Σ_1	1	1	1	1
Σ_2	1	-1	-1	1
Σ_3	1	1	-1	-1
Σ_4	1	-1	1	-1

TABLE XXV

CHARACTERS AT V

	C_1	C_2	C_3	C_4	C_5
V_1	1	1	1	1	1
V_2	1	1	1	-1	-1
V_3	1	1	-1	1	-1
V_4	1	1	-1	-1	1
V_5	2	-2	0	0	0

TABLE XXVI

CHARACTERS AT Y

Y_1	1	1	1	1
Y_2	1	-1	-1	1
Y_3	1	1	-1	-1
Y_4	1	-1	1	-1

CHAPTER V

FREE ELECTRON ENERGY BANDS

In the majority of cases it is possible to determine the energy band configurations for any space group in a manner that is somewhat independent of the work outlined to this point. The symmetry analysis is used to indicate the allowed electronic states that may exist within a band and to reveal the amount and type of degeneracy present.

The principle by which compatible states are determined is extremely simple. The symmetry of any electronic state along an axis of the first Brillouin zone must be contained in the symmetry of the compatible states at the end of the axis. The rule which is used to determine the symmetry types along an axis which are compatible with a given type at the end of the axis states that the sum of the characters of the compatible representations along the axis must be equal to the character of the representation at the end point. The results of the symmetry analysis are used only for this purpose. It is the intent of this chapter to illustrate how such results may be applied to the designation of the possible electronic states in the simplest case, i.e., the free electron approximation.

As mentioned in Chapter IV, the time-independent Schroedinger equation has the form given by

$$\Delta\psi + \frac{2m}{\hbar^2}\left\{E - V(\vec{r})\right\}\psi = 0 \qquad (5.1)$$

If the Bloch form of wavefunction is used, i.e.,

$$\psi_{\underline{K}} = e^{i\underline{K}\cdot\underline{r}}\, U(\underline{r}) \tag{5.2}$$

direct substitution into the Schroedinger equation results in a differential equation that must be satisfied by the periodic function U(r).

This equation has the form

$$\Delta U + 2i\underline{K}\cdot \underline{\nabla U} + \frac{2m}{\hbar^2}\left[E - V(\underline{r})\right] U = 0. \tag{5.3}$$

In the free electron approximation, V(r) = 0. The use of this approximation results in a very much simplified mathematical problem for which a solution of equation (5.3) may be written as:

$$U_{\underline{1}}(\underline{r}) = e^{-i\underline{1B}\cdot\underline{r}} \tag{5.4}$$

The substitution of this solution into equation (5.1) results in a normalized energy $E_{\underline{k1}}$ given by:

$$E_{\underline{K1}} = \frac{2ma^2}{\hbar^2} E_{\underline{1}} = (\xi - 1_1)^2 + (\eta - 1_2)^2 + (\zeta - 1_3)^2\left(\frac{a}{c}\right)^2 \tag{5.5}$$

In obtaining this expression, the simplifying notation

$$\underline{K} = \frac{2\pi}{a}\left(\xi, \eta, \frac{a}{c}\zeta\right) \tag{5.6}$$

has been used. Such treatment involves the use of a wavefunction of the form

$$\psi_{\underline{K1}} = \exp[2\pi i\{(\xi-1_1)\frac{x}{a} + (\eta-1_2)\frac{y}{a} + (\zeta-1_3)\frac{z}{c}\}. \tag{5.7}$$

In order to obtain a wavefunction and energy corresponding to a particular state, it is necessary that the coordinates of the symmetry points be known. These coordinates have been given in Figure 2 and shall now be used when desired.

The first step in the treatment involves consideration of the possible states from Γ to Δ to X. The ξ, η and ζ coordinates of the points in question are:

$$\Gamma = (0,\ 0,\ 0) \qquad \Delta = (\xi,\ 0,\ 0) \qquad X = (\tfrac{1}{2},\ 0,\ 0). \tag{5.8}$$

The energies and wave functions at these points are given by

$$E_\Gamma = l_1^2 + l_2^2 + (\tfrac{a}{c})^2 l_3^2 \tag{5.9}$$

$$E_\Delta = (l_1 - \xi)^2 + l_2^2 + (\tfrac{a}{c})^2 l_3^2 \tag{5.10}$$

$$E_X = (l_1 - \tfrac{1}{2})^2 + l_2^2 + (\tfrac{a}{c})^2 l_3^2 \tag{5.11}$$

$$\psi_\Gamma = \exp[-2\pi i\{\frac{l_1 x}{a} + \frac{l_2 y}{a} + \frac{l_3 z}{c}\}] \tag{5.12}$$

$$\psi_\Delta = \exp[2\pi i\{(\xi - l_1)\frac{x}{a} - \frac{l_2 y}{a} - \frac{l_3 z}{c}\}] \tag{5.13}$$

$$\psi_X = \exp[2\pi i\{(\tfrac{1}{2} - l_1)\frac{x}{a} - \frac{l_2 y}{a} - \frac{l_3 z}{c}\}]. \tag{5.14}$$

In order to facilitate the proper combination of exponentials necessary to obtain the wavefunctions in terms of circular functions, Tables XXVII, XXVIII, and XXIX have been constructed. These tables are very similar to those used in the calculation of wave vector groups in that they indicate how each class operation in the compatible states transforms the set {xyz}. Use of these tables and the character tables given in the previous chapter enables one to construct allowed free-electron wavefunctions.

Since the l's must be integral, it follows that the Γ point is the point of lowest energy. This state is of type Γ_1 (i.e., it possesses the full symmetry of the space group and the wavefunction is merely a constant). Starting from this point and moving along the Δ axis, the energy and wavefunction are given by:

$$E_\Delta = \xi^2 \qquad \text{and} \qquad \psi_\Delta = e^{\frac{2\pi i \xi X}{a}} \tag{5.15}$$

From the character table, it may be seen that this function is of the type Δ_1. At the point X, the normalized energy is 1/4. The wavefunction at this point must be obtained by using the proper linear combination of the two exponentials;

$$\exp\left[\frac{\pi i X}{a}\right] \qquad \text{and} \qquad \exp\left[\frac{-\pi i X}{a}\right]. \tag{5.16}$$

Since all states at X are doubly degenerate, these must be combined into the following two functions which display the symmetry of the X_1 state.

$$\left(\cos \frac{\pi X}{a}\ ;\ \sin \frac{\pi X}{a}\right). \tag{5.17}$$

When $E_x = 1/4$, 1 may also have the value (100). Thus another Δ state starts at this point. The energy and wavefunction of this state are given by

$$E_\Delta = (1 - \xi)^2 \qquad \text{and} \qquad \psi_\Delta = \exp\left[\frac{2\pi i(\xi - 1)X}{a}\right]. \tag{5.18}$$

This function displays the symmetry of the Δ_6 state. At the end of the axis, at the point Γ, $E_\Gamma = 1$ and there are four possible values of 1 which give this energy. These four values are (100), (010), (100) and $(0\bar{1}0)$. The exponentials corresponding to these 1 values are:

$$\exp\left[\frac{\pm 2\pi i X}{a}\right] \qquad \text{and} \qquad \exp\left[\frac{\pm 2\pi i y}{a}\right]. \tag{5.19}$$

These must be combined to give functions with the symmetries dictated by the character table. Possible wavefunctions are listed below.

$$\mathrm{Sin}^2 \frac{2\pi X}{a} + \mathrm{Sin}^2 \frac{2\pi y}{a} \qquad \text{Type } \Gamma_1 \tag{5.20}$$

$$\mathrm{Cos} \frac{2\pi X}{a} + \mathrm{Cos} \frac{2\pi y}{a} \qquad \text{Type } \Gamma_1' \tag{5.21}$$

$$\mathrm{Cos} \frac{2\pi X}{a} - \mathrm{Cos} \frac{2\pi y}{a} \qquad \text{Type } \Gamma_2' \tag{5.22}$$

$$\mathrm{Cos}^2 \frac{2\pi X}{a} - \mathrm{Cos}^2 \frac{2\pi y}{a} \qquad \text{Type } \Gamma_2'. \tag{5.23}$$

In obtaining the symmetries used at the point $E_\Gamma = 1$, it was necessary to investigate the symmetries of the possible Δ states that enter and leave this point. Starting at $E_\Gamma = 1$ there are three new Δ bands. The energies of these bands and their corresponding 1 values are given below.

1	E_Δ	
$(010):(0\bar{1}0)$	$1 + \xi^2$	(5.24)
$(\bar{1}00)$	$(1 + \xi)^2$	(5.25)

These two bands terminate at different energies. The first band terminates at $E_x = 5/4$ and is doubly degenerate. The second band terminates at $E_x = 9/4$.

The exponentials appropriate to the above 1 values are:

1	Exponential	
$(\bar{1}00)$	$\exp[\frac{-2\pi i(\xi-1)X}{a}]$	(5.26)
(010)	$\exp[\frac{2\pi i}{a}(\xi X + y)]$	(5.27)
$(0\bar{1}0)$	$\exp[\frac{2\pi i}{a}(\xi X - y)]$.	(5.28)

The wavefunctions and symmetry types become:

1	Wavefunction	
$(\bar{1}00)$	$\psi_{\Delta_6} = \exp[\frac{-2\pi i}{a}(\xi+1)X]$	(5.26)
$(010):(0\bar{1}0)$	$\psi_{\Delta_6'} = \exp[\frac{2\pi i\xi X}{a}]\cos\frac{2\pi y}{a}$	(5.30)
	$\psi_{\Delta_1} = \exp[\frac{2\pi i\xi X}{a}]\sin\frac{2\pi y}{a}$.	(5.31)

At the point $E_x = 5/4$, another Δ band starts because it is also possible to obtain this energy using the 1 values (110) and $(1\bar{1}0)$. The wavefunctions may be obtained from the four exponentials

$$\exp[\frac{\pi i}{a}(X \pm 2y)] \quad \text{and} \quad \exp[\frac{-\pi i}{a}(X \pm 2y)] \tag{5.32}$$

and all may be combined into possible states at this point. The only symmetry type possible using these exponentials is that of the X_1 state, and for reasons of compatibility, two possible states of the symmetry X_1 must exist at this point. Then, possible wavefunctions have the form:

$$(\text{Cos}\,\frac{\pi X}{a}\;\text{Cos}\,\frac{2\pi y}{a}\;;\;\text{Cos}\,\frac{\pi X}{a}\;\text{Sin}\,\frac{2\pi y}{a}) \tag{5.33}$$

$$(\text{Sin}\,\frac{\pi X}{a}\;\text{Cos}\,\frac{2\pi y}{a}\;;\;\text{Sin}\,\frac{\pi X}{a}\;\text{Sin}\,\frac{2\pi y}{a}) \;. \tag{5.34}$$

In returning to the Γ point, the energies and wavefunctions along the axis are given by:

$$E'_{\Delta\;1=(100)} = E_{\Delta\;1=(1\bar{1}0)} = 1 + (1-\xi)^2 \qquad \text{and}$$

$$\exp[\frac{2\pi i}{a}\{(\xi - 1)X \pm y\}] \;. \tag{5.35}$$

Combination of the two exponentials yields the two wavefunctions listed below with the symmetries given.

$$e^{\frac{2\pi i(\xi-1)X}{a}} \text{ Cos } \frac{2\pi y}{a} = \psi_{\Delta_6} \tag{5.36}$$

$$e^{\frac{2\pi i(\xi-1)X}{a}} \text{ Sin } \frac{2\pi y}{a} = \psi_{\Delta_1} \tag{5.37}$$

At the center of the zone, the energy is given by $E_\Gamma = 2.0$. Again there are four possible ways of obtaining this energy, i.e., use of the (110), $(\bar{1}\bar{1}0)$, $(\bar{1}10)$ and $(1\bar{1}0)$ values of 1. Thus, there are four Γ states at this point with wavefunctions that can be ascertained by use of the character systems. Possible functions of the proper types are listed below.

$$\psi_{\Gamma_1} = \text{Cos } \frac{2\pi X}{a} \text{ Cos } \frac{2\pi y}{a} \tag{5.38}$$

$$\psi_{\Gamma_1'} = \text{Sin } \frac{2\pi X}{a} \text{ Sin } \frac{2\pi y}{a} \tag{5.39}$$

$$\psi_{\Gamma_2'} = \text{Sin}^2 \frac{2\pi X}{a} - \text{Sin}^2 \frac{2\pi y}{a} \tag{5.40}$$

$$\psi_{\Gamma_2} = \text{Sin } \frac{2\pi X}{a} \text{ Sin } \frac{2\pi y}{a} \left(\text{Sin}^2 \frac{2\pi X}{a} - \text{Sin}^2 \frac{2\pi y}{a}\right). \tag{5.41}$$

The singly degenerate Δ state terminates at $E_x = 9/4$. Another band starts at this point with 1 value (200). The exponentials to be combined here are:

$$\exp\left[\frac{3\pi iX}{a}\right] \quad \text{and} \quad \exp\left[\frac{-3\pi iX}{a}\right]. \tag{5.42}$$

Evidently these may be combined to yield the wavefunctions given below which again display the X_1 type of symmetry.

$$(\text{Cos}\ \frac{3\pi X}{a}\ ;\ \ \text{Sin}\ \frac{3\pi X}{a}) \qquad (5.43)$$

In returning to the Γ point, the energy along the Δ axis is given by (5.10) as:

$$E_{\Delta} = (2 - \xi)^2 \qquad (5.44)$$

while the wavefunction has the form

$$\psi_{\Delta_1} = \exp[\frac{2\pi i(\xi-2)X}{a}]. \qquad (5.45)$$

The energy at the center of the zone is $E_\Gamma = 4.0$. This value may also be obtained using $(\bar{2}00)$, (020) and $(0\bar{2}0)$. The analysis now is exactly like that used for $E_\Gamma = 1$ wherein the possible Δ bands were obtained in order to determine the symmetries of the states at this point. Such procedure results in allowed wavefunctions of the form:

$$\text{Cos}\ \frac{4\pi X}{a} + \text{Cos}\ \frac{4\pi y}{a} = \psi_{\Gamma_1} \qquad (5.46)$$

$$\text{Cos}\ \frac{4\pi X}{a} - \text{Cos}\ \frac{4\pi y}{a} = \psi_{\Gamma_2'} \qquad (5.47)$$

$$\text{Sin}\ \frac{4\pi X}{a}\ \text{Sin}\ \frac{4\pi y}{a} = \psi_{\Gamma_1'} \qquad (5.48)$$

$$\text{Sin}\ \frac{4\pi X}{a}\ \text{Sin}\ \frac{4\pi y}{a}\ \{\text{Cos}\ \frac{4\pi X}{a} - \text{Cos}\ \frac{4\pi y}{a}\} = \psi_{\Gamma_2} \qquad (5.49)$$

This analysis may be carried on indefinitely merely by the repeated application of the procedures outlined thus far. It is incomplete because all possible l values for the {(100)} set have not been used. In the past analysis all normalized energies at the center of the zone have been integral. This is not always the case, however, because of the a/c ratio. Consideration of the (001) and $(00\bar{1})$ set of l values leads to different values of the energy at the Γ point than those used thus far. Their use gives the energy at the center of the zone as $E_\Gamma = (a/c)^2$. Also, for this set the lowest energy wavefunction, ψ_Γ, is not a constant. Instead, the two exponentials

$$\exp\left[\frac{-2\pi i z}{c}\right] \quad \text{and} \quad \exp\left[\frac{2\pi i z}{c}\right] \tag{5.50}$$

must combine into states with symmetries dictated by the character table. Possible wavefunctions are:

$$\psi_{\Gamma_1'} = \text{Cos}\,\frac{2\pi z}{c} \tag{5.51}$$

$$\psi_{\Gamma_6'} = \text{Sin}\,\frac{2\pi z}{c} \quad . \tag{5.52}$$

Moving along the Δ axis results in an energy and wavefunctions given by:

$$E_\Delta = \xi^2 + \left(\frac{a}{c}\right)^2 \tag{5.53}$$

$$\psi_{\Delta_6} = e^{\frac{2\pi i X \xi}{a}}\ \text{Cos}\,\frac{2\pi z}{c} \tag{5.54}$$

$$\psi_{\Delta_4} = e^{\frac{2\pi i X \xi}{a}}\ \text{Sin}\,\frac{2\pi z}{c} \quad . \tag{5.55}$$

At X the appropriate energy is $1/4 + (a/c)^2$. The energy may be obtained using either the (001) and (00$\bar{1}$) values of 1 or by using the (101) and (10$\bar{1}$) set. Thus, possible wavefunctions at X must now be written as linear combinations of the exponentials:

$$\exp\left[2\pi i\left(\frac{X}{2a} + \frac{z}{c}\right)\right] \tag{5.56}$$

$$\exp\left[2\pi i\left(\frac{X}{2a} - \frac{z}{c}\right)\right] \tag{5.57}$$

$$\exp\left[2\pi i\left(\frac{-X}{2a}+\frac{z}{c}\right)\right] \tag{5.58}$$

$$\exp\left[2\pi i\left(\frac{-X}{2a}-\frac{z}{c}\right)\right] \tag{5.59}$$

which may be combined into the two wavefunctions

$$\psi_{X_1} : \left(\mathrm{Cos}\,\frac{\pi X}{a}\,\mathrm{Cos}\,\frac{2\pi z}{c}\ ;\ \mathrm{Sin}\,\frac{\pi X}{a}\,\mathrm{Cos}\,\frac{2\pi z}{c}\right) \tag{5.60}$$

and

$$\psi_{X_2} : \left(\mathrm{Cos}\,\frac{\pi X}{a}\,\mathrm{Sin}\,\frac{2\pi z}{c}\ ;\ \mathrm{Sin}\,\frac{\pi X}{a}\,\mathrm{Sin}\,\frac{2\pi z}{c}\right) . \tag{5.61}$$

For the 1 values (101) and $(10\bar{1})$, other Δ states begin having energy $E_{\Delta\ 1=(101)} = E_{\Delta\ 1=(10\bar{1})} = (\frac{a}{c})^2 + (1-\xi)^2$. Wavefunctions describing these states are

$$\psi_{\Delta_1} = e^{\frac{2\pi i(\xi-1)X}{a}}\ \mathrm{Cos}\,\frac{2\pi z}{c} \tag{5.62}$$

$$\psi_{\Delta_4} = e^{\frac{2\pi i(\xi-1)X}{a}}\ \mathrm{Sin}\,\frac{2\pi z}{c} \tag{5.63}$$

This band ends at $E_\Gamma = 1 + (a/c)^2$. At this point there are six other possible 1 values consistent with this energy, i.e., $(01\bar{1})$, $(0\bar{1}1)$, (011), $(\bar{1}01)$, $(\bar{1}0\bar{1})$, and $(0\bar{1}\bar{1})$. The exponentials obtained using all 1 values giving $E_\Gamma = 1 + (a/c)^2$ must now be combined in such a way as to yield Γ states that are compatible with the incoming and outgoing Δ states. Along the outgoing Δ axis energies and wavefunctions are given by

$$E_{\Delta\ 1=(011)} = E_{\Delta\ (01\bar{1})} = E_{\Delta\ (0\bar{1}1)} = E_{\Delta\ (0\bar{1}\bar{1})} = 1 + \left(\frac{a}{c}\right)^2(\xi)^2 \tag{5.64}$$

$$\psi_{\Delta_1} = e^{\frac{2\pi i X\xi}{a}}\ \mathrm{Cos}\,\frac{2\pi y}{a}\ \mathrm{Cos}\,\frac{2\pi z}{c} \tag{5.65}$$

$$\psi_{\Delta_4} = e^{\frac{2\pi i X\xi}{a}} \text{Sin} \frac{2\pi y}{a} \text{ Sin} \frac{2\pi z}{c} \tag{5.66}$$

$$\psi_{\Delta_3} = e^{\frac{2\pi i X\xi}{a}} \text{Cos} \frac{2\pi y}{a} \text{ Sin} \frac{2\pi z}{c} \tag{5.67}$$

$$\psi_{\Delta_6} = e^{\frac{2\pi i X\xi}{a}} \text{Sin} \frac{2\pi y}{a} \text{ Cos} \frac{2\pi z}{c} \tag{5.68}$$

$$E_{\Delta_{(\bar{1}01)}} = E_{\Delta_{(\bar{1}0\bar{1})}} = (\frac{a}{c})^2 + (1 + \xi)^2 \tag{5.69}$$

$$\psi_{\Delta_1} = e^{\frac{2\pi i(\xi+1)X}{a}} \text{Cos} \frac{2\pi z}{c} \tag{5.70}$$

$$\psi_{\Delta_2} = e^{\frac{2\pi i(\xi+1)X}{a}} \text{Sin} \frac{2\pi z}{c} \tag{5.71}$$

Using the symmetries of these states and the corresponding Γ states, eight wavefunctions may be constructed at the center of the zone and several representative possibilities are listed below.

$$\psi_{\Gamma_1} = \{\text{Cos} \frac{2\pi X}{a} + \text{Cos} \frac{2\pi y}{a}\} \text{ Cos} \frac{2\pi z}{c} \tag{5.72}$$

$$\psi_{\Gamma'_1} = \{\text{Sin}^2 \frac{2\pi X}{a} + \text{Sin}^2 \frac{2\pi y}{a}\} \text{ Cos} \frac{2\pi z}{c} \tag{5.73}$$

$$\psi_{\Gamma'_2} = \{\text{Sin}^2 \frac{2\pi X}{a} + \text{Sin}^2 \frac{2\pi y}{a}\}\{\text{Cos} \frac{2\pi X}{a} - \text{Cos} \frac{2\pi y}{a}\} \text{ Cos}^2 \frac{2\pi z}{c} . \tag{5.74}$$

In analogy with the previous treatment, this discussion may be carried out indefinitely. The results of the total analysis are shown in Figure 6.

In order to fully exploit the application of the free electron approximation to this structure, it is necessary to consider the electronic states present along all symmetry axes. For this reason, the past analysis should be repeated for other symmetry axes.

Consider as an additional illustration the axis from Γ to Λ to Z. In order to facilitate the classification of electronic states along this axis, Tables XXX and XXXI have been constructed. The energies and wavefunctions are obtained as before and are tabulated below:

$$E_\Gamma = l_1^2 + l_2^2 + (\tfrac{a}{c})^2\ l_3^2 \qquad (5.75)$$

$$E_\Lambda = l_1^2 + l_2^2 + (\tfrac{a}{c})^2 (l_3 - \zeta)^2 \qquad (5.76)$$

$$E_z = l_1^2 + l_2^2 + (\tfrac{a}{c})^2 (l_3 - \tfrac{1}{2})^2 \qquad (5.77)$$

$$\psi_\Gamma = e^{-2\pi i(\frac{l_1 X}{a} + \frac{l_2 y}{a} + \frac{l_3 z}{c})} \qquad (5.78)$$

$$\psi_\Delta = e^{-2\pi i\{\frac{l_1 X}{a} + \frac{l_2 y}{a} + (l_3 - \zeta)\frac{z}{c}\}} \qquad (5.79)$$

$$\psi_z = e^{-2\pi i\{\frac{l_1 X}{a} + \frac{l_2 y}{a} + (l_3 - \frac{1}{2})\frac{z}{c}\}}\ . \qquad (5.80)$$

As in the previous case, the lowest energy occurs at the center of the zone, corresponds to l=(000), and is zero. The wavefunction is constant and the state is of the type Γ_1. Using this value of l, the energy along the Λ axis has the form

$$E_\Lambda = (\tfrac{a}{c})^2\ \zeta^2 \qquad (5.81)$$

and the wavefunction is given by equation (5.79) as:

$$\psi_\Lambda = \exp[\tfrac{2\pi i \zeta z}{c}]\ . \qquad (5.82)$$

This state is one which displays the Λ_1 symmetry and is compatible with the Γ_1 state at the center of the zone.

As the top of the zone is approached, the energy has the magnitude $1/4(a/c)^2$ and may be obtained by using the (001) value of 1 as well as the (000) value. Since the states at the Z point are doubly degenerate, the two exponentials given by equation (5.79) may be combined into the wavefunctions

$$\psi_{z_1} : \{\mathrm{Cos}\,\frac{\pi z}{c}\ ;\ \mathrm{Sin}\,\frac{\pi z}{c}\} . \tag{5.83}$$

Because two values of 1 give the same energy here, another Λ band begins. The new energy and wavefunction for this band are

$$E_{\Lambda\ (001)} = (1 - \xi)^2\ (\frac{a}{c})^2 \tag{5.84}$$

$$\psi_{\Lambda_2} = \exp[\frac{2\pi i(\zeta-1)}{c}z] . \tag{5.85}$$

At the center of the zone, the energy obtained using (001) is the same as that obtained for $(00\bar{1})$ and has the value

$$E_{\Gamma\ (001)} = E_{\Gamma\ (00\bar{1})} = (\frac{a}{c})^2 . \tag{5.86}$$

Combinations of the exponentials resulting from the use of these 1 values allows the two possible wavefunctions

$$\psi_{\Gamma'_1} = \mathrm{Cos}\,\frac{2\pi z}{c} \tag{5.87}$$

and

$$\psi_{\Gamma'_6} = \mathrm{Sin}\,\frac{2\pi z}{c} . \tag{5.88}$$

This value $(00\bar{1})$ gives rise to another Λ band at this point described by the energy and wavefunction

$$E_{\Lambda\ (00\bar{1})} = (1 + \zeta)^2 (\frac{a}{c})^2 \qquad (5.89)$$

$$\psi_{\Lambda_2} = \exp[\frac{2\pi i(\zeta+1)}{c} z] \qquad (5.90)$$

Energy and wavefunctions obtained at the other end point, i.e. at Z, are listed below.

$$E_{z\ (00\bar{1})} = E_{z\ (002)} = (\frac{3}{2})^2\ (\frac{a}{c})^2 \qquad (5.91)$$

$$\psi_{z_1} : (\text{Cos}\ \frac{3\pi z}{c}\ ;\ \text{Sin}\ \frac{3\pi z}{c})\ . \qquad (5.92)$$

Again as in the past treatment, a whole new series of bands originates at $E_\Gamma = 1$. This energy may be obtained by the use of either of the four l values (100), $(\bar{1}00)$, (010) or $(0\bar{1}0)$. Wavefunctions which are appropriate have been obtained in the usual manner and are listed below.

$$\psi_{\Gamma_1} = \text{Sin}^2\ \frac{2\pi X}{a} + \text{Sin}^2\ \frac{2\pi y}{a} \qquad (5.93)$$

$$\psi_{\Gamma'_1} = \text{Cos}\ \frac{2\pi X}{a} + \text{Cos}\ \frac{2\pi y}{a} \qquad (5.94)$$

$$\psi_{\Gamma'_2} = \text{Cos}\ \frac{2\pi X}{a} - \text{Cos}\ \frac{2\pi y}{a} \qquad (5.95)$$

$$\psi_{\Gamma_2} = \text{Cos}^2\ \frac{2\pi X}{a} - \text{Cos}^2\ \frac{2\pi y}{a}\ . \qquad (5.96)$$

Compatible Λ states may be represented by

$$E_{\Lambda_{(100)}} = E_{\Lambda_{(\bar{1}00)}} = E_{\Lambda_{(010)}} = E_{\Lambda_{(0\bar{1}0)}} = 1 + \left(\frac{a}{c}\right)^2 \zeta^2 \tag{5.97}$$

$$\psi_{\Lambda_1} = \exp\left[\frac{-2\pi i\zeta z}{c}\right] \mathrm{Cos}\ \frac{2\pi X}{a}\ \mathrm{Cos}\ \frac{2\pi y}{a} \tag{5.98}$$

$$\psi_{\Lambda_3} = \exp\left[\frac{-2\pi i\zeta z}{c}\right] \left(\mathrm{Cos}\ \frac{2\pi X}{a} - \mathrm{Cos}\ \frac{2\pi y}{a}\right) \tag{5.99}$$

$$\psi_{\Lambda_2} : \exp\left[\frac{-2\pi i\zeta z}{c}\right] \left(\mathrm{Cos}\ \frac{2\pi X}{a} + \mathrm{Cos}\ \frac{2\pi y}{a}\right) \tag{5.100}$$

$$\psi_{\Lambda_4} = \exp\left[\frac{-2\pi i\zeta z}{c}\right] \left(\mathrm{Cos}^2\ \frac{2\pi X}{a} - \mathrm{Cos}^2\ \frac{2\pi y}{a}\right). \tag{5.101}$$

This four-fold degenerate Λ band terminates at the Z point with an energy of $1 + 1/4(a/c)^2$. For illustration, possible wavefunctions for two of the four doubly degenerate electronic states are

$$\psi_{z_1} : \mathrm{Cos}\ \frac{\pi z}{c} \left\{\mathrm{Cos}\ \frac{2\pi X}{a}\ \mathrm{Cos}\ \frac{2\pi y}{a}\ ;\ \mathrm{Sin}\ \frac{2\pi X}{a}\ \mathrm{Sin}\ \frac{2\pi y}{a}\right\} \tag{5.102}$$

$$\psi_{z_1} : \mathrm{Sin}\ \frac{\pi z}{c} \left\{\mathrm{Cos}\ \frac{2\pi X}{a}\ \mathrm{Cos}\ \frac{2\pi y}{a}\ ;\ \mathrm{Sin}\ \frac{2\pi X}{a}\ \mathrm{Sin}\ \frac{2\pi y}{a}\right\}. \tag{5.103}$$

Results of the total analysis are given in Figure 7. The general trend should now be evident. Treatment of the simplest l values yields the first few bands whereas the inclusion of all possible l values merely shifts the energy band scheme upward and in fact yields no new information. Thus, in the following tables and figures, only the first few bands are considered. The tables contain l values and corresponding energies along the other symmetry axes. The shape of the free electron bands is also conveniently illustrated by using the information in the tables to plot electron energies over selected plane circuits in k-space. Results of this kind have been utilized in obtaining Figures 8-12.

TABLE XXVII

CLASSES AND SUBSTITUTIONS AT Γ

Class	X	Y	Z
$C_1 = E$	X	Y	Z
$C_2 = R_1$	-Y	-X	-Z
$C_3 = R_2$	Y	X	-Z
$C_4 = C_2$	-X	-Y	+Z
$C_5 = J$	-X	-Y	-Z
$C_6 = m_2$	+Y	+X	+Z
$C_7 = m_1$	-Y	-X	+Z
$C_8 = m_3$	+X	+Y	-Z
$C_9 = Tm$	-X + a/2	Y + a/2	Z + C/2
$C_{10} = TmR_1$	-Y + a/2	X + a/2	-Z + C/2
$C_{11} = TmR_2$	Y + a/2	-X + a/2	-Z + C/2
$C_{12} = TmC_2$	X + a/2	-Y + a/2	+Z + C/2
$C_{13} = TmJ$	X + a/2	-Y + a/2	-Z + C/2
$C_{14} = Tmm_2$	+Y +a/2	-X + a/2	+Z + C/2
$C_{15} = Tmm_1$	-Y + a/2	+X + a/2	+Z + C/2
$C_{16} = Tmm_3$	-X + a/2	Y + a/2	-Z + C/2

TABLE XXVIII

CLASSES AND SUBSTITUTIONS AT Δ

Class	X	Y	Z
$C_1 = E$	X	Y	Z
$C_2 = m_3$	X	Y	-Z
$C_3 = TmJ$	X + a/2	-Y + a/2	Z + C/2
$C_4 = TmC_2$	X + a/2	-Y + a/2	Z + C/2

TABLE XXIX

CLASSES AND SUBSTITUTIONS AT X

Class	X	Y	Z
$C_1 = E$	X	Y	Z
$C_2 = Q$	X + a	Y + a	Z + C
$C_9 = m_3$	X	Y	-Z
$C_{10} = Qm_3$	X + a	Y + a	-Z + C

TABLE XXX

CLASSES AND SUBSTITUTIONS AT Λ

Class	X	Y	Z
$C_1 = E$	X	Y	Z
$C_2 = C_2$	-X	-Y	Z
$C_3 = m_1 + m_2$	Y or -Y	X or -X	Z
$C_4 = Tmm_1 + Tmm_2$	Y + a/2 or -Y + a/2	X + a/2	Z + C/2
$C_5 = Tm + TmC_2$	-X + a/2 or +X + a/2	-Y + a/2 or Y + a/2	Z + C/2

TABLE XXXI

CLASSES AND SUBSTITUTIONS AT Z

Class	X	Y	Z
$C_1 = E$	X	Y	Z
$C_2 = Q$	X + a	Y + a	Z + C
$C_6 = C_2$	-X	-Y	Z
$C_7 = QC_2$	-X + a	-Y + a	Z + C
$C_{11} = m_1$	-Y	-X	Z
$C_{12} = QM_1$	-Y + a	-X + a	Z + C
$C_{16} = m_2$	Y	X	Z
$C_{17} = QM_2$	Y + a	X + a	Z + C

TABLE XXXII

SOME ENERGIES AND 1 VALUES ALONG THE AXIS Z-U-R

1	E_z	E_u	E_R
$(1_1 1_2 1_3)$	$1_1^2+1_2^2+(1_3-\frac{1}{2})^2(\frac{a}{c})^2$	$(1_1-\xi)^2+1_2^2+(1_3-\frac{1}{2})^2$ $(\frac{a}{c})^2$	$(1_1-\frac{1}{2})^2+1_2^2+$ $(\frac{a}{c})^2(1_3-\frac{1}{2})^2$
$(000),(001)$	$\frac{1}{4}(\frac{a}{c})^2$	$\xi^2+\frac{1}{4}(\frac{a}{c})^2$	$\frac{1}{4}+\frac{1}{4}(\frac{a}{c})^2$
$(100),(101)$	$1+\frac{1}{4}(\frac{a}{c})^2$	$\frac{1}{4}(\frac{a}{c})^2+(1-\xi)^2$	$\frac{1}{4}+\frac{1}{4}(\frac{a}{c})^2$
$(\bar{1}00),(\bar{1}01)$	$\left\{1+\frac{1}{4}(\frac{a}{c})^2\right\}$	$\frac{1}{4}(\frac{a}{c})^2+(1+\xi)^2$	$(\frac{3}{2})^2+\frac{1}{4}(\frac{a}{c})^2$
$(011),(0\bar{1}1)$ $(010),(0\bar{1}0)$		$1+\xi^2+\frac{1}{4}(\frac{a}{c})^2$	$1+\frac{1}{4}+\frac{1}{4}(\frac{a}{c})^2$

TABLE XXXIII

SOME ENERGIES AND 1 VALUES ALONG THE AXIS R-W-X

1	E_x	E_w	E_R
$(1_1 1_2 1_3)$	$(1_1-\frac{1}{2})^2+1_2^2+(\frac{a}{c})^2 1_3^2$	$(1_1-\frac{1}{2})^2+1_2^2+$ $(1_3-\zeta)^2(\frac{a}{c})^2$	$(1_1-\frac{1}{2})^2+1_2^2+$ $(1_3-\frac{1}{2})^2(\frac{a}{c})^2$
$(000)(100)$	$\frac{1}{4}$	$\frac{1}{4}+\zeta^2(\frac{a}{c})^2$	$\frac{1}{4}+\frac{1}{4}(\frac{a}{c})^2$
$(001),(101)$	$\frac{1}{4}+(\frac{a}{c})^2$	$\frac{1}{4}+(\frac{a}{c})^2(1-\zeta)^2$	$\frac{1}{4}+\frac{1}{4}(\frac{a}{c})^2$
$(00\bar{1}),(10\bar{1})$	$\frac{1}{4}+(\frac{a}{c})^2$	$\frac{1}{4}+(\frac{a}{c})^2(1+\zeta)^2$	$\frac{1}{4}+(\frac{3}{4})^2(\frac{a}{c})^2$
$(102),(002)$	$\frac{1}{4}+4(\frac{a}{c})^2$	$\frac{1}{4}+(\frac{a}{c})^2(2-\zeta)^2$	$\frac{1}{4}+(\frac{3}{2})^2(\frac{a}{c})^2$

TABLE XXXIV

SOME ENERGIES AND l VALUES ALONG THE AXIS Γ-Σ-M

l	E_Γ	E_Σ	E_M
$(l_1 l_2 l_3)$	$l_1^2+l_2^2+(\frac{a}{c})^2 l_3^2$	$(l_1-\xi)^2+(l_2-\xi)^2$ $+l_3^2(\frac{a}{c})^2$	$(l_1-\frac{1}{2})^2+(l_2-\frac{1}{2})^2$ $+l_3^2(\frac{a}{c})^2$
(000)	0	$2\xi^2$	$\frac{1}{2}$
(100),(010)	1	$(1-\xi)^2+\xi^2$	$\frac{1}{2}$
(100),(110)	2	$2(1-\xi)^2$	$\frac{1}{2}$
$(\bar{1}\bar{1}0)$,$(\bar{1}10)$	2	$\xi^2+(1+\xi)^2$	$\frac{1}{4}+(\frac{3}{2})^2$
$(\bar{1}\bar{1}0)$	2	$2(1+\xi)^2$	$2(\frac{3}{2})^2$
$(\bar{1}00)$,$(0\bar{1}0)$	1	$(1+\xi)^2+\xi^2$	$(\frac{3}{2})^2+\frac{1}{4}$
(220)	8	$2(2-\xi)^2$	$2(\frac{3}{2})^2$
(200),(020)	4	$(2-\xi)^2+\xi^2$	$(\frac{3}{2})^2+\frac{1}{4}$

TABLE XXXV

SOME ENERGIES AND l VALUES ALONG THE AXIS M-V-A

l	E_M	E_V	E_A
$(l_1 l_2 l_3)$	$(l_1-\frac{1}{2})^2+(l_2-\frac{1}{2})^2$ $+l_3^2(\frac{a}{c})^2$	$(l_1-\frac{1}{2})^2+(l_2-\frac{1}{2})^2$ $+(\frac{a}{c})^2(l_3-\zeta)^2$	$(l_1-\frac{1}{2})^2+(l_2-\frac{1}{2})^2$ $+(l_3-\frac{1}{2})^2(\frac{a}{c})^2$
(000),(110) (010),(100)	$\frac{1}{2}$	$\frac{1}{2}+\zeta^2(\frac{a}{c})^2$	$\frac{1}{2}+\frac{1}{4}(\frac{a}{c})^2$
(001),(101) (011),(111)	$\frac{1}{2}+(\frac{a}{c})^2$	$\frac{1}{2}+(\frac{a}{c})^2(1-\zeta)^2$	$\frac{1}{2}+\frac{1}{4}(\frac{a}{c})^2$
$(00\bar{1})$,$(10\bar{1})$ $(01\bar{1})$,$(11\bar{1})$	$\frac{1}{2}+(\frac{a}{c})^2$	$\frac{1}{2}+(\frac{a}{c})^2(1+\zeta)^2$	$\frac{1}{2}+(\frac{3}{2})^2(\frac{a}{c})^2$
(002),(102) (012),(112)	$\frac{1}{2}+4(\frac{a}{c})^2$	$\frac{1}{4}+(\frac{a}{c})^2(2-\zeta)^2$	$\frac{1}{2}+(\frac{3}{2})^2(\frac{a}{c})^2$

TABLE XXXVI

SOME ENERGIES AND 1 VALUES ALONG THE AXIS Z-S-A

1	E_Z	E_S	E_A
$(l_1 l_2 l_3)$	$l_1^2+l_2^2+(l_3-\frac{1}{2})^2(\frac{a}{c})^2$	$(l_1-\xi)^2+(l_2-\xi)^2$ $+(l_3-\frac{1}{2})^2(\frac{a}{c})^2$	$(l_1-\frac{1}{2})^2+(l_2-\frac{1}{2})^2$ $+(l_3-\frac{1}{2})^2(\frac{a}{c})^2$
(000),(001)	$\frac{1}{4}(\frac{a}{c})^2$	$2\xi^2+\frac{1}{4}(\frac{a}{c})^2$	$\frac{1}{2}+\frac{1}{4}(\frac{a}{c})^2$
(111),(110)	$2+\frac{1}{4}(\frac{a}{c})^2$	$2(1-\xi)^2+\frac{1}{4}(\frac{a}{c})^2$	$\frac{1}{2}+\frac{1}{4}(\frac{a}{c})^2$
(100),(010)	$1+\frac{1}{4}(\frac{a}{c})^2$	$\xi^2+(1-\xi)^2+\frac{1}{4}(\frac{a}{c})^2$	
(101),(011)			
$(\bar{1}00),(0\bar{1}0)$	$1+\frac{1}{4}(\frac{a}{c})^2$	$\xi^2+(1+\xi)^2+\frac{1}{4}(\frac{a}{c})^2$	$(\frac{3}{2})^2+\frac{1}{4}+\frac{1}{4}(\frac{a}{c})^2$
$(\bar{1}01),(0\bar{1}1)$			
$(\bar{1}\bar{1}\bar{1}),(\bar{1}\bar{1}0)$	$2+\frac{1}{4}(\frac{a}{c})^2$	$(1+\xi)^2+\frac{1}{4}(\frac{a}{c})^2$	$(\frac{3}{2})^2+(\frac{3}{2})^2+\frac{1}{4}(\frac{a}{c})^2$
$(1\bar{1}1),(1\bar{1}0)$			
$(\bar{1}11),(\bar{1}10)$		$(1+\xi^2)+\xi^2+\frac{1}{4}(\frac{a}{c})^2$	$\frac{1}{4}+(\frac{3}{2})^2+\frac{1}{4}(\frac{a}{c})^2$

TABLE XXXVII

SOME ENERGIES AND 1 VALUES ALONG THE AXIS X-Y-M

1	E_X	E_Y	E_M
$(l_1 l_2 l_3)$	$(l_1-\frac{1}{2})^2+l_2^2+(\frac{a}{c})^2 l_3$	$(l_1-\frac{1}{2})^2+(l_2-\xi)^2$ $+(\frac{a}{c})^2 l_3^2$	$(l_1-\frac{1}{2})^2+(l_2-\frac{1}{2})^2$ $+l_3^2(\frac{a}{c})^2$
(000),(100)	$\frac{1}{4}$	$\frac{1}{4}+\xi^2$	$\frac{1}{2}$
(010),(110)	5/4	$\frac{1}{4}+(1-\xi)^2$	$\frac{1}{2}$
$(0\bar{1}0),(1\bar{1}0)$	5/4	$\frac{1}{4}+(1+\xi)^2$	$\frac{1}{4}+9/4=10/4$
$(\bar{1}00),(200)$	9/4	$9/4+\xi^2$	10/4
$(\bar{1}10),(210)$	13/4	$9/4(1-\xi)^2$	10/4
$(120),(1\bar{2}0)$	17/4	$\frac{1}{4}+(2-\xi)^2$	10/4

TABLE XXXVIII

SOME ENERGIES AND l VALUES ALONG THE AXIS A-T-R

l	E_R	E_T	E_A
$(l_1 l_2 l_3)$	$(l_1-\frac{1}{2})^2+l_2^2+(\frac{a}{c})^2$ $(l_3-\frac{1}{2})^2$	$(l_1-\frac{1}{2})^2+(l_2-\xi)^2$ $+(\frac{a}{c})^2(l_3-\frac{1}{2})^2$	$(l_1-\frac{1}{2})^2+(l_2-\frac{1}{2})^2$ $+(\frac{a}{c})^2(l_3-\frac{1}{2})^2$
(000),(101) (100),(001)	$\frac{1}{4}+\frac{1}{4}(\frac{a}{c})^2$	$\frac{1}{4}+\xi^2+\frac{1}{4}(\frac{a}{c})^2$	$\frac{1}{2}+\frac{1}{4}(\frac{a}{c})^2$
(010),(011) (110),(111)	$\frac{1}{4}+1+\frac{1}{4}(\frac{a}{c})^2$	$\frac{1}{4}+(1-\xi)^2+\frac{1}{4}(\frac{a}{c})^2$	$\frac{1}{2}+\frac{1}{4}(\frac{a}{c})^2$
$(0\bar{1}0),(0\bar{1}1)$ $(1\bar{1}0),(1\bar{1}1)$	$\frac{1}{4}+1+\frac{1}{4}(\frac{a}{c})^2$	$\frac{1}{4}+(1+\xi)^2+\frac{1}{4}(\frac{a}{c})^2$	$(\frac{3}{2})^2+\frac{1}{4}+\frac{1}{4}(\frac{a}{c})^2$

TABLE XXXIX

SOME ENERGIES AND l VALUES OF DEGENERATE STATES ALONG THE AXIS Γ-Λ-Z

l	E_Γ	E_Λ	E_Z
$(l_1 l_2 l_3)$	$l_1^2+l_2^2+(\frac{a}{c})^2 l_3^2$	$l_1^2+l_2^2+(\frac{a}{c})^2(l_3-\zeta)^2$	$l_1^2+l_2^2+(l_3-\frac{1}{2})^2$ $(\frac{a}{c})^2$
(100),(010) $(\bar{1}00),(0\bar{1}0)$	1	$1+(\frac{a}{c})^2\zeta^2$	$1+\frac{1}{4}(\frac{a}{c})^2$
(101),(011) $(\bar{1}01),(0\bar{1}1)$	$1+(\frac{a}{c})^2$	$1+(\frac{a}{c})^2(1-\zeta)^2$	$1+\frac{1}{4}(\frac{a}{c})^2$
$(10\bar{1}),(01\bar{1})$ $(\bar{1}0\bar{1}),(0\bar{1}\bar{1})$	$1+(\frac{a}{c})^2$	$1+(\frac{a}{c})^2(1+\zeta)^2$	$1+(\frac{3}{2})^2(\frac{a}{c})^2$
(102),(012) $(\bar{1}02),(0\bar{1}2)$	$1+4(\frac{a}{c})^2$	$1+(2-\zeta)^2(\frac{a}{c})^2$	$1+(\frac{3}{2})^2(\frac{a}{c})^2$

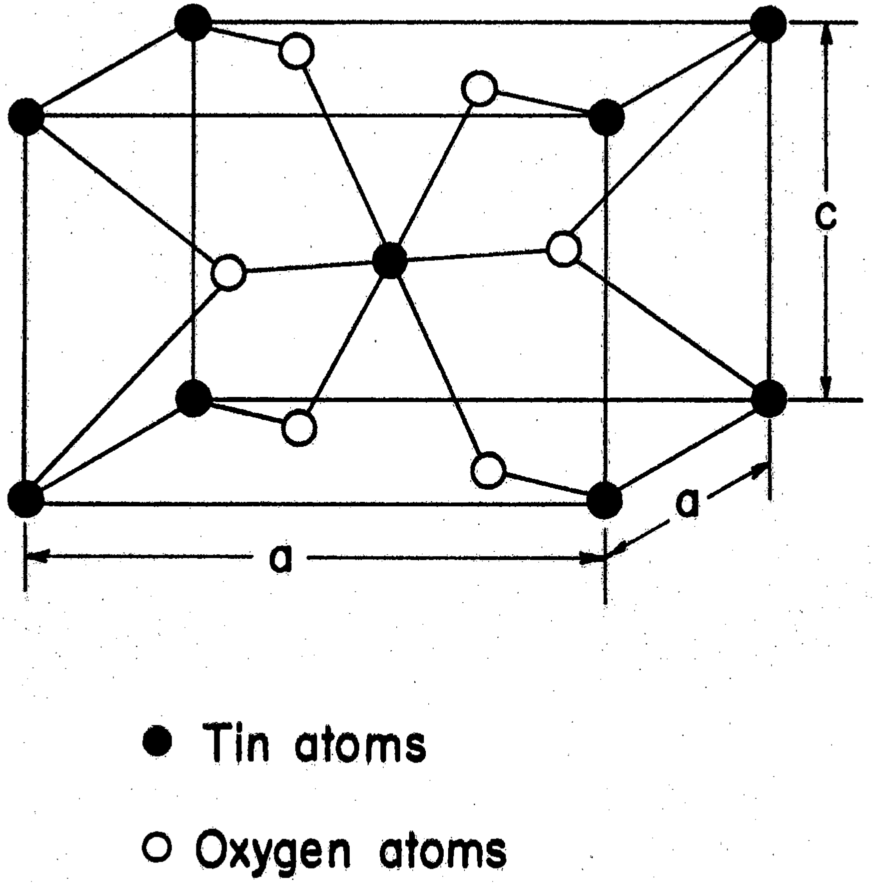
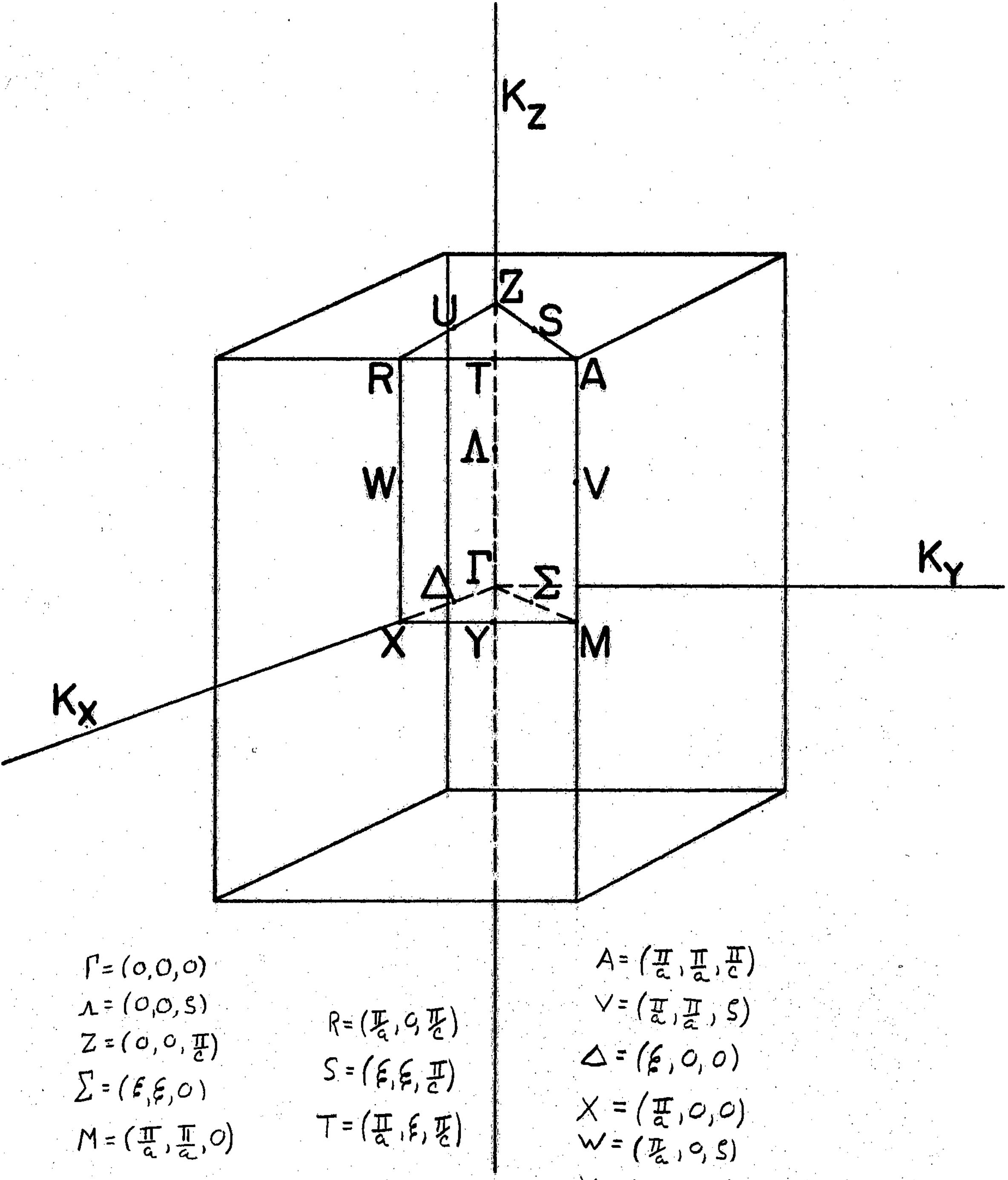


Figure 2. Unit Cell of the Space Group D_{4h}^{14}.



$\Gamma = (0,0,0)$

$\Lambda = (0,0,\zeta)$

$Z = (0,0,\frac{\pi}{c})$

$\Sigma = (\xi,\xi,0)$

$M = (\frac{\pi}{a},\frac{\pi}{a},0)$

$U = (\xi,0,\frac{\pi}{c})$

$R = (\frac{\pi}{a},0,\frac{\pi}{c})$

$S = (\xi,\xi,\frac{\pi}{c})$

$T = (\frac{\pi}{a},\xi,\frac{\pi}{c})$

$A = (\frac{\pi}{a},\frac{\pi}{a},\frac{\pi}{c})$

$V = (\frac{\pi}{a},\frac{\pi}{a},\zeta)$

$\Delta = (\xi,0,0)$

$X = (\frac{\pi}{a},0,0)$

$W = (\frac{\pi}{a},0,\zeta)$

$Y = (\frac{\pi}{a},\xi,0)$

Figure 3. First Brillouin Zone for the Primitive Tetragonal System.

Point Group Element	Substitution
E	xyz
M_1	$\bar{y}\bar{x}z$
M_2	yxz
R_1	$\bar{y}\bar{x}\bar{z}$
C_2	$\bar{x}\bar{y}z$
J	$\bar{x}\bar{y}\bar{z}$
M_3	$xy\bar{z}$
R_2	$yx\bar{z}$

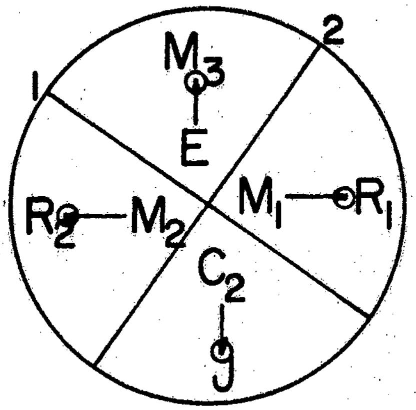
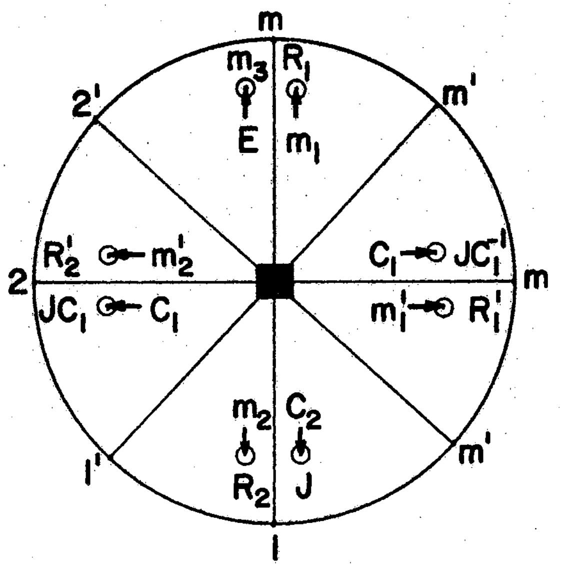


Figure 4. Stereogram for the Rutile Structure.



Element	Substitution	Classes
E	xyz	$C_1 = E$
m_1	$\bar{x}yz$	$C_2 = C_2$
C_1	$y\bar{x}z$	$C_3 = C_1 + C_1^{-1}$
m_1'	$\bar{y}\bar{x}z$	$C_4 = R_1 + R_2$
C_2	$\bar{x}\bar{y}z$	$C_5 = R_1' + R_2'$
m_2	$x\bar{y}z$	$C_6 = JC_1 = J$
C_1^{-1}	$\bar{y}xz$	$C_7 = JC_2 = m_3$
m_2'	yxz	$C_8 = JC_3 = JC_1^{-1} + JC_1$
m_3	$xy\bar{z}$	$C_9 = JC_4 = m_1 + m_2$
R_1	$\bar{x}y\bar{z}$	$C_{10} = JC_5 = m_1' + m_2'$
JC_1^{-1}	$y\bar{x}\bar{z}$	
R_1'	$\bar{y}\bar{x}\bar{z}$	
J	$\bar{x}\bar{y}\bar{z}$	
R_2	$x\bar{y}\bar{z}$	
JC_1	$\bar{y}x\bar{z}$	
R_2'	$yx\bar{z}$	

Figure 5. Stereogram for the Holosymmetric Point Group P4/mmm.

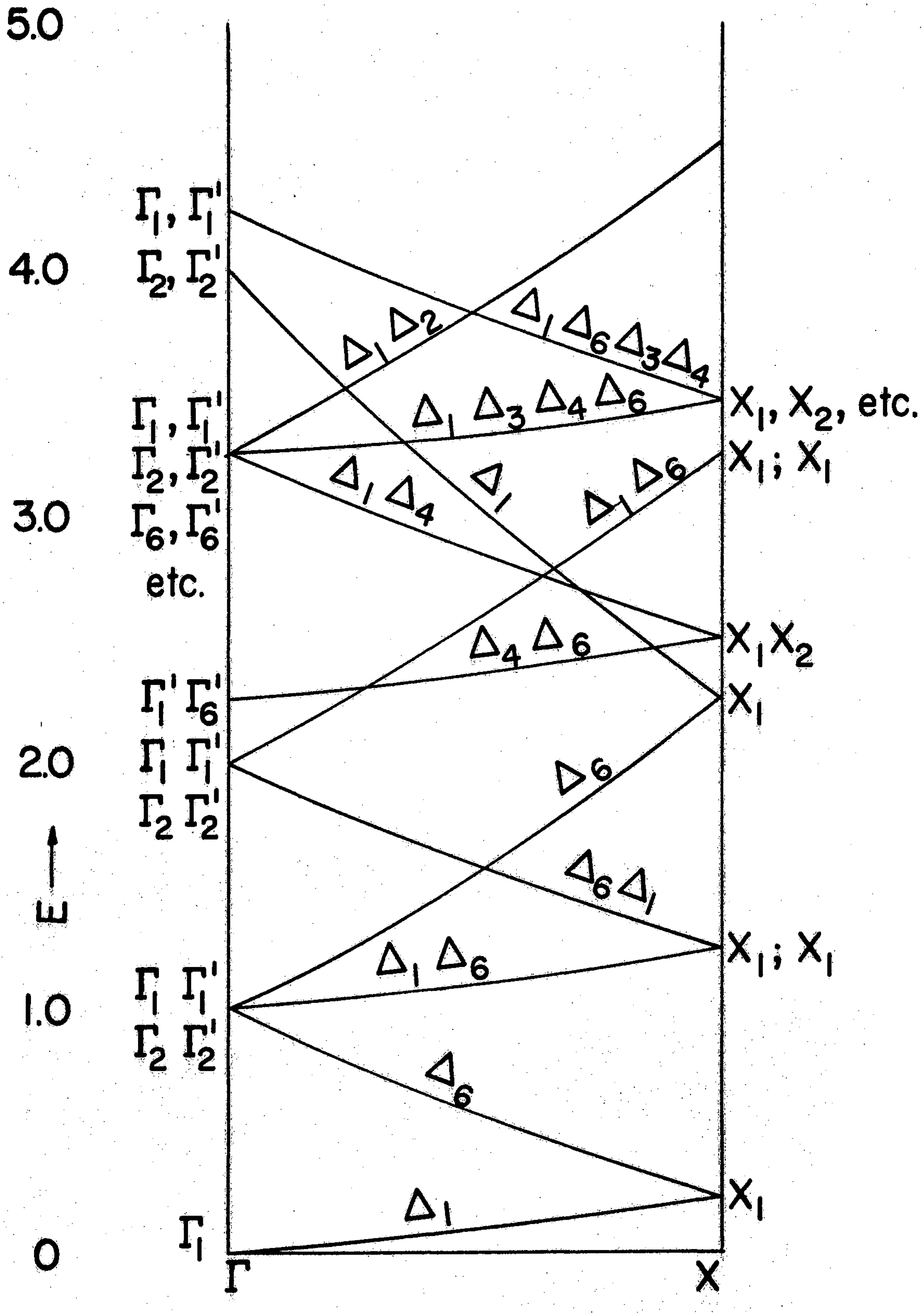


Figure 6. Free Electron Energy Band Configuration Along the Axis Γ-Δ-X.

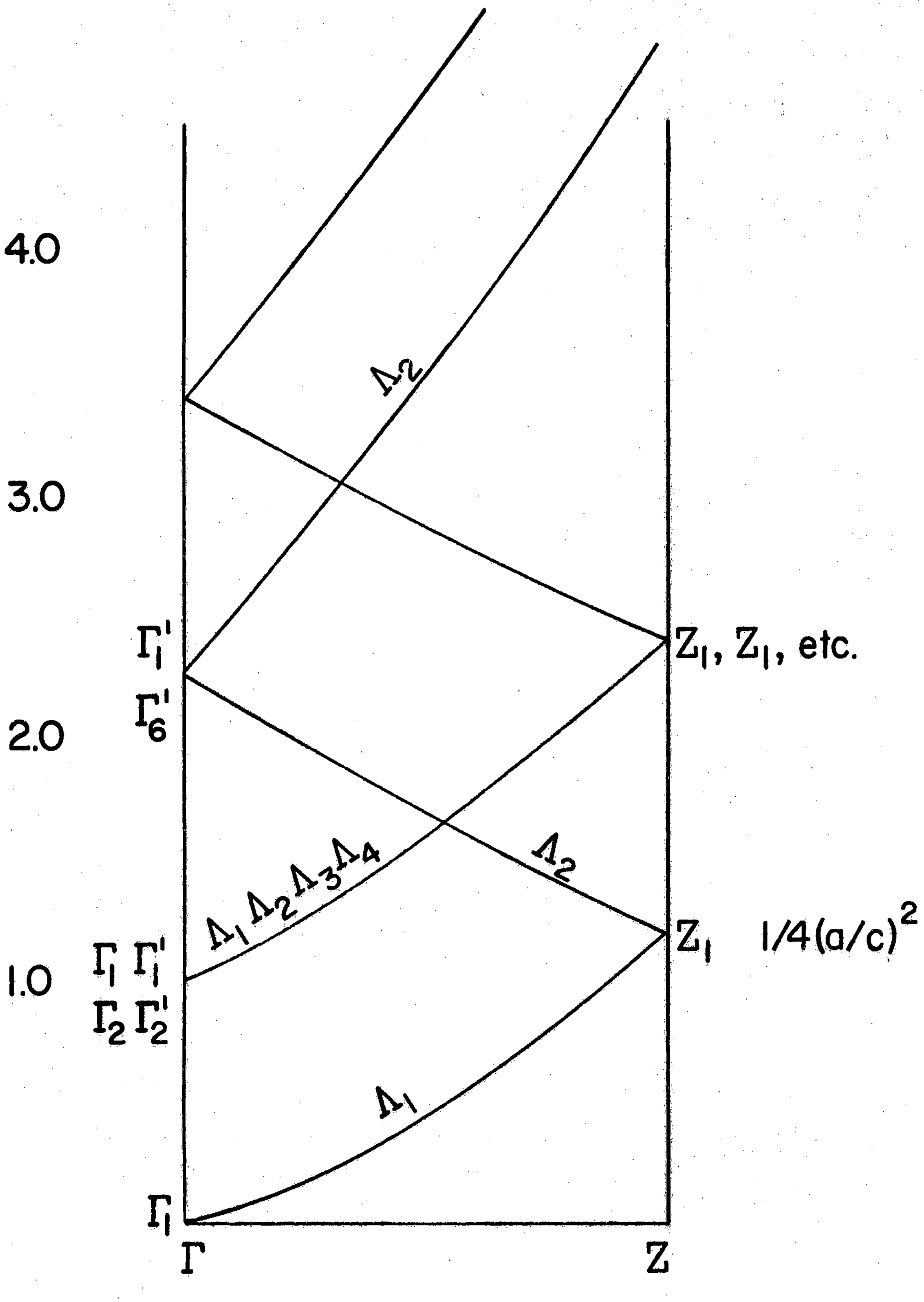


Figure 7. Free Electron Energy Band Configuration Along the Axis Γ-Λ-Z.

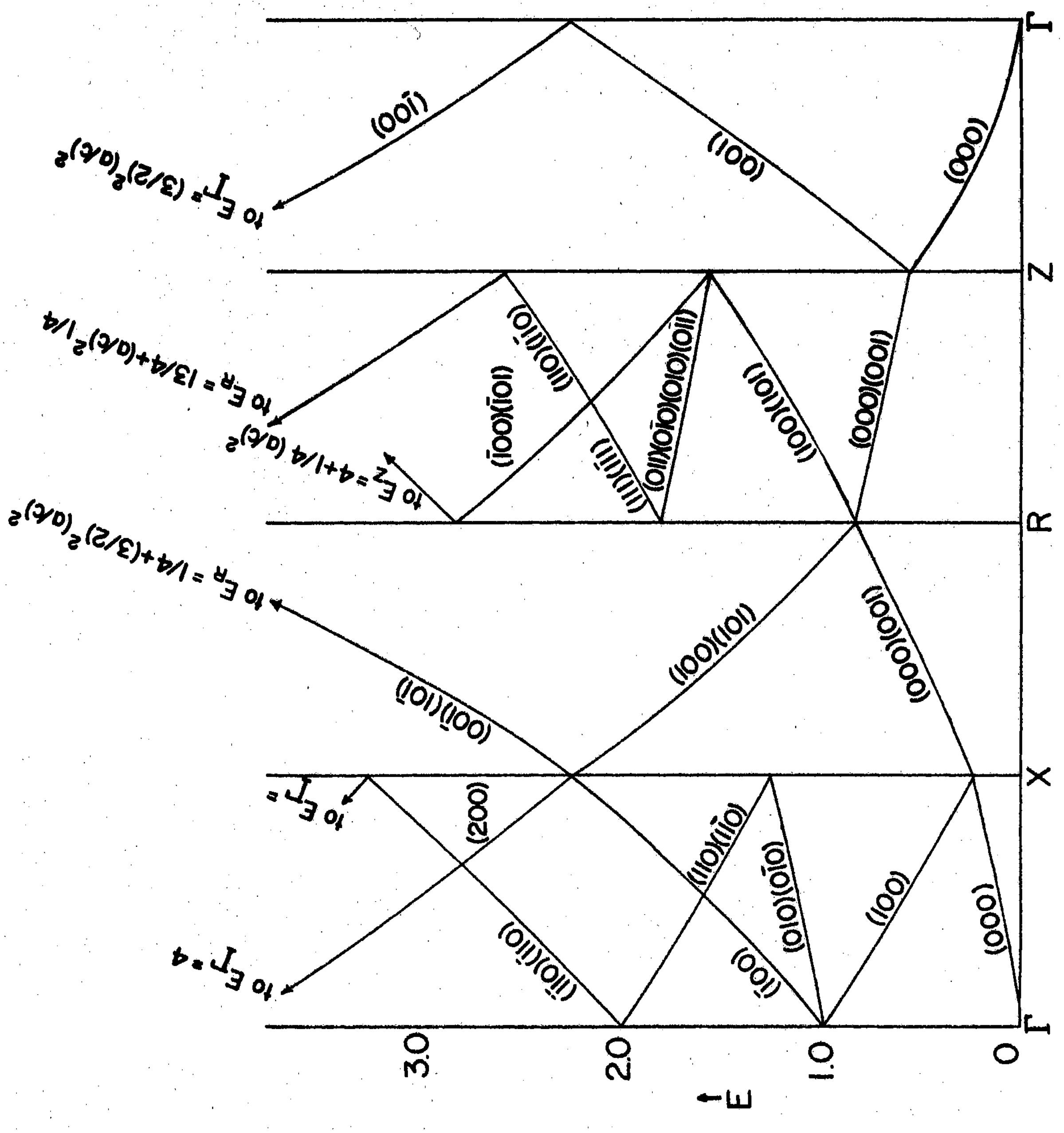


Figure 8. Free Electron Band Structure Around the Circuit Γ-X-R-Z-Γ.

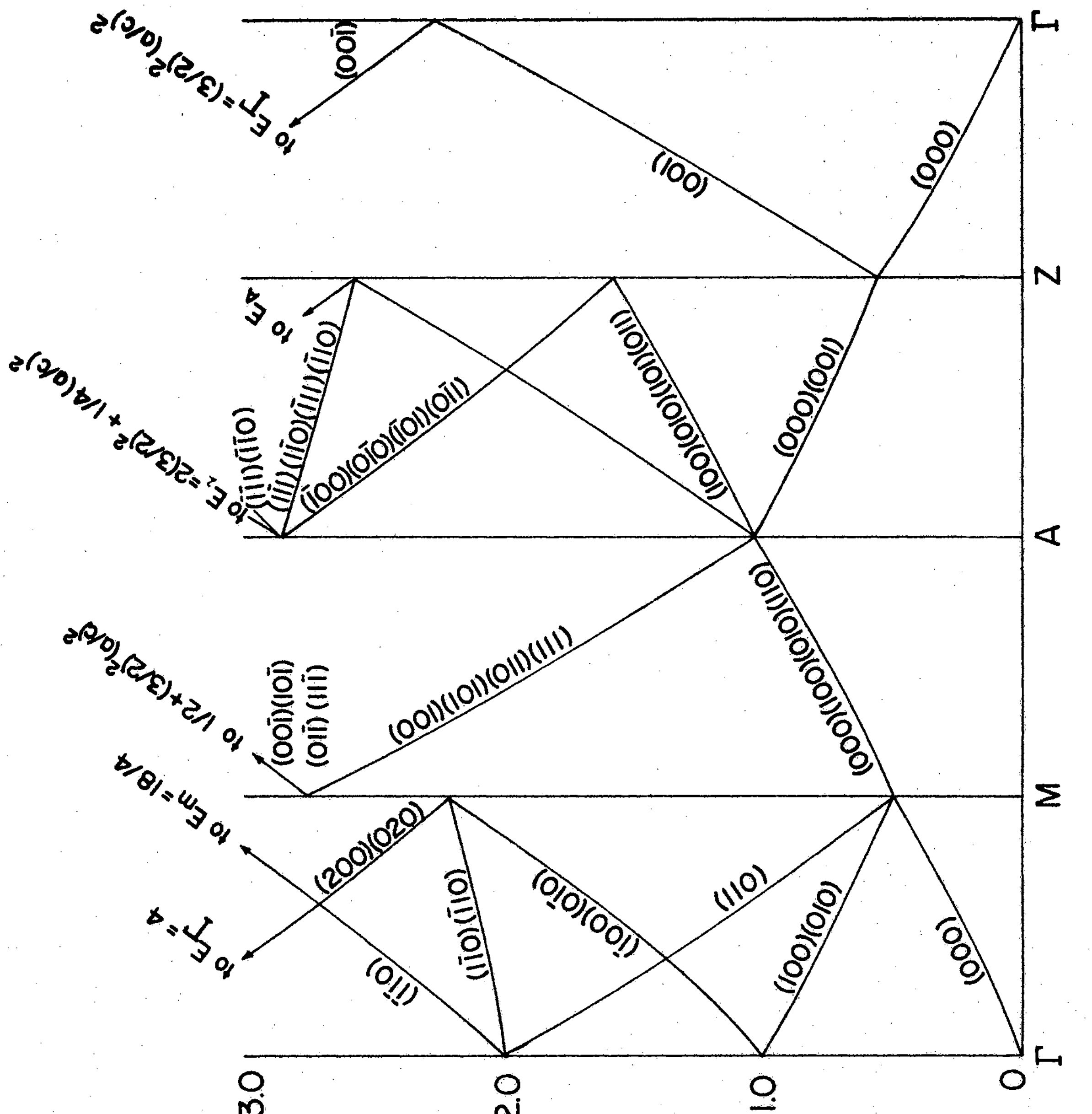


Figure 9. Free Electron Band Structure Around the Circuit Γ-M-A-Z-Γ.

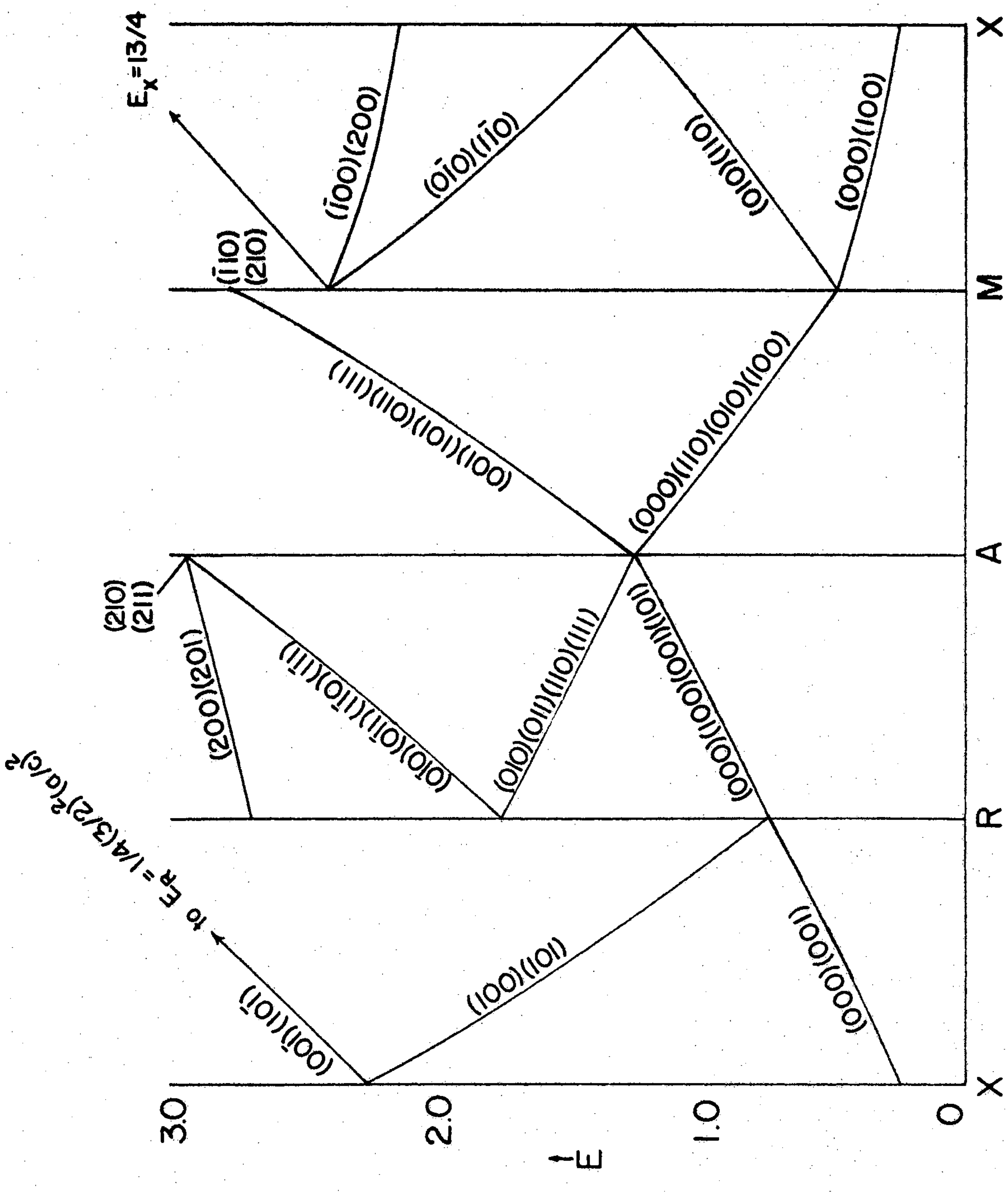


Figure 10. Free Electron Band Structure Around the Circuit X-R-A-M-X.

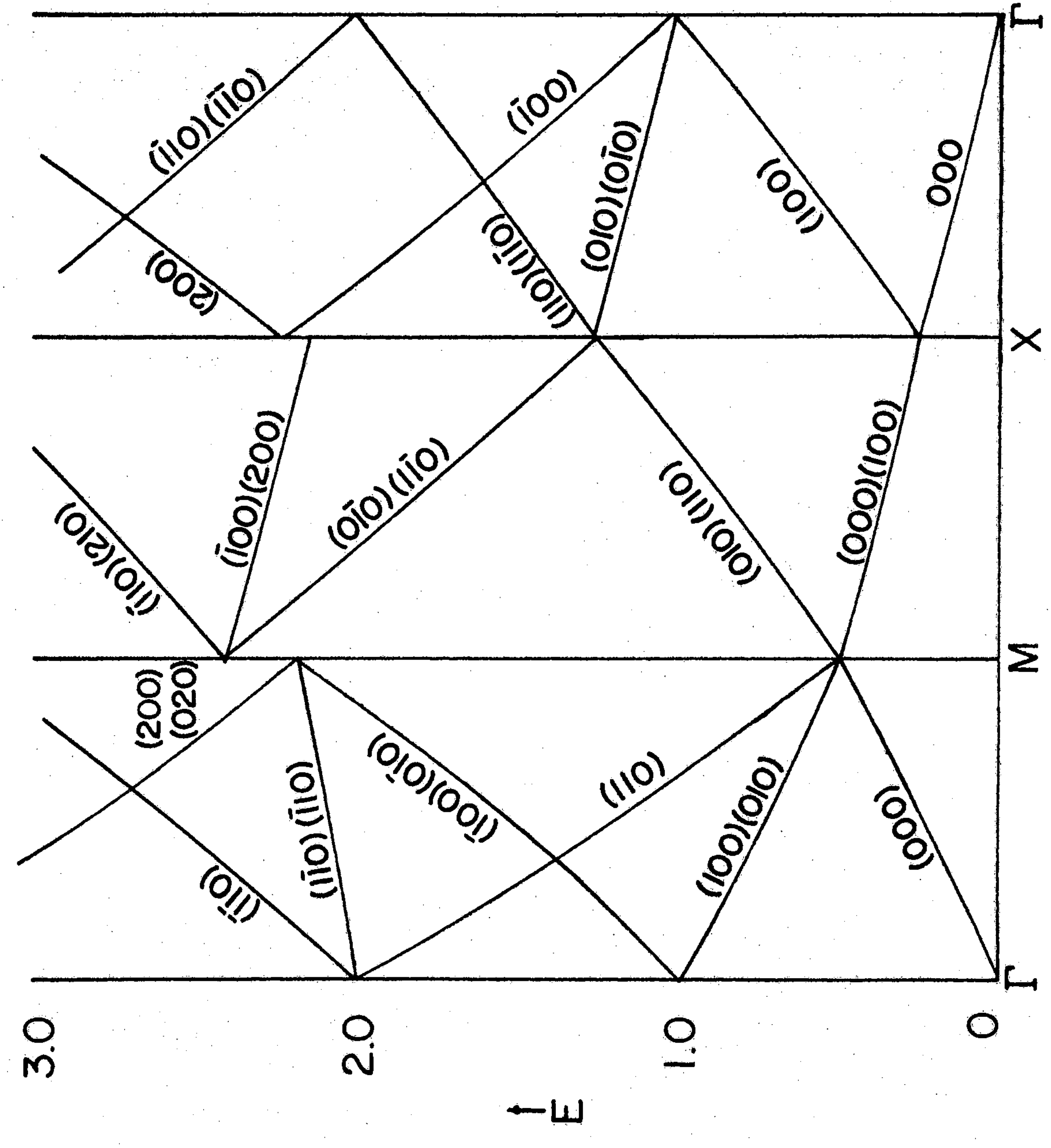


Figure 11. Free Electron Band Structure Around the Circuit Γ-M-X-Γ.

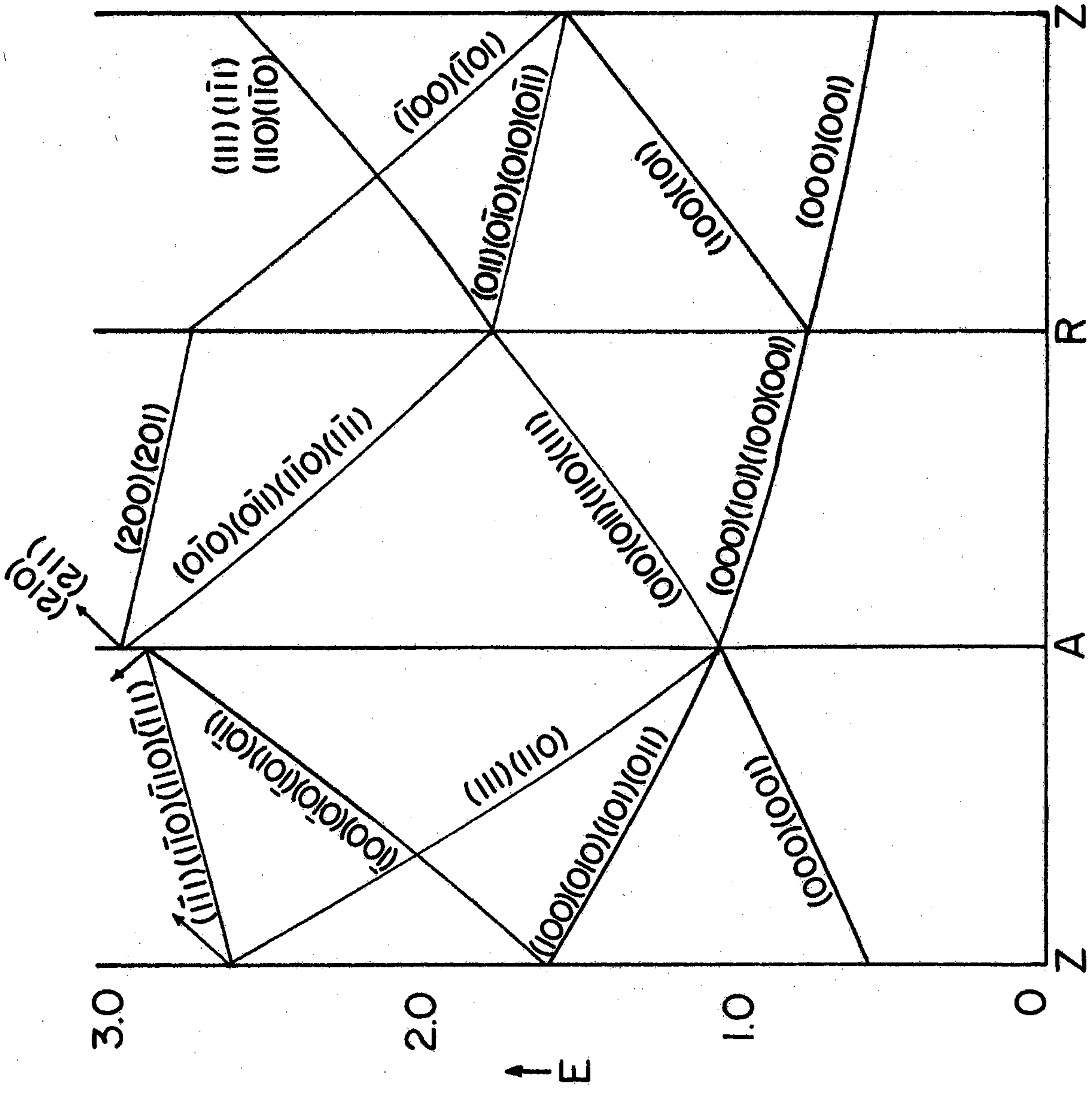


Figure 12. Free Electron Band Structure Around the Circuit Z-A-R-Z.

CHAPTER VI

CONCLUSIONS AND SUGGESTIONS FOR FURTHER STUDY

The system of characters developed in Chapter IV may be used for every substance which displays the rutile structure; however, the results of the analysis have been applied only to the most rudimentary model in this report. Such treatment is not only illustrative but constitutes a valuable first step in determining compatible electronic states within any band and may be extended in the manner given by Nutkins (18) to obtain a qualitative idea as to the free electron density of the states. However, the free electron approximation is not of significant value in itself because the effect of the periodic potential has been neglected.

A comprehensive review of the various theoretical methods available for the calculation of the energy band configurations from first principles has been given by Pincherele (4). Each of these methods involves the solution of the Schroedinger equation with a nonzero potential. As might be expected, the inclusion of a potential in the Schroedinger equation results in a very complex mathematical problem that may be solved only by the incorporation of various approximations concerning its nature and that of the wavefunctions. The choice of a "proper potential" is very difficult and requires a great deal of knowledge regarding the nature of the chemical bond, the magnitude of the exchange forces and the effect of spin-orbit coupling. As a result, a purely theoretical calculation has little value unless it may be correlated with experimental evidence concerning the band structure.

Logical extensions of the work performed thus far must be two-fold. Priority should be given to acquiring specific experimental data yielding information concerning the band structure. With such in hand, any of the more sophisticated theoretical approaches given in the literature may be applied.

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