ENERGY BAND STRUCTURE OF CHROMIUM

BY

THE SLATER-KOSTER INTERPOLATION SCHEME.

A Thesis

Presented to The

School of Graduate studies

and

The Faculty of Science

Addis Ababa University

In Partial Fulfillment of the

Requirements for the Degree

Master of Science in Physics

by

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June, 1985

This work is dedicated to my parents.

ACKNOWLEDGMENTS

My gratitude to my advisor and instructor Dr. Peter Mikusik for his help in guiding and supervising this work is boundless. His rich research background and his invaluable advice without which this thesis would not have materialised facilitated my progress in the work and has inspired me for further research activities in the field.

A special acknowledgment must also be made for the help and encouragement of Ato G/Amanuel Gessese in setting the Computer programme. Thanks are also due to System Analysis and Data processing Center of Addis Ababa University (AAU) for having very kindly offered the possibility of using their computer and for assistance in computing.

I am indepted to the International Center For Theoretical Physics (ICTP) library for their kind cooperation in sending me articles which are not available here. I also thank the AAU library for its generous help in ordering articles from abroad.

At last, I would like to express my deep indeptedness to Ato Girma Dagne and W/t Zenebech Woldetsadik for their skillful typing of the manuscript.

ABSTRACT

The matrix elements of the Hamiltonian between nine localized wave functions in tight-binding formalism are derived. The symmetry adapted wave-functions and the secular equations are formed by the group theory method for high symmetry points in the Brillouin Zone. A set of interaction integrals is chosen on physical grounds and fitted via the Slater -Koster interpolation scheme to the abinitio band structure of chromium calculated by the Green's function method. Then the energy band structure of chromium is interpolated and extrapolated in the Brillouin Zone. These results may be directly used for computation of the complex energy band structure at any point of the Brillouin Zone and density of states of chromium.

CONTENTS

	Page
List of Tables	i
List of Figures	ii
Introduction	1
Chapter 1. Energy Band Structure	4
Chapter 2. The Tight Binding Approximation and Slater-Koster Interpolation Scheme	7
Chapter 3..Group Theory	15
3-1 Symmetry Group Operators ..	15
3-2 Space Groups	16
3-3 Matrix Representation of a Group	18
3-4 Group Character and Class .	21
3-5 Projection Operator Method and Symmetry Adapted Wave Functions	22
3-6 Brillouin Zone of the Body Centered Cubic Lattice	26
3-7 Projection Operator Method Applied to the symmetry line Σ in the Brillouin Zone of BCC Lattice	29
Chapter 4. Energy Bands of Cr via Green's Function Method	31
Chapter 5. Interpolation and Extrapolation of the Energy Bands of Cr	36

Page

5-1 Energy Band Structure of Cr by Slater-Koster interpolation scheme 36

5-2 Numerical Method and Computer Programming employed to Evaluate the Parameters 47

Chapter 6. Results and Discussion 58

Conclusion 63

References 64

Appendix A.

Symmetrized Wave functions and Secular equations 67

Appendix B.

Flow Chart and FORTRAN programme for the interpolation scheme 80

Appendix C.

$E(\vec{k})$-values calculated by the Green's function method..... 86

Appendix D.

$E(\vec{k})$-curves calculated by the Slater-Koster interpolation scheme together with $E(\vec{k})$-values computed by the Green's function method 91

LIST OF TABLES

		Page
1.	Character table, for Group of $\mathcal{X}$, C_{2v}	29
2.	Energy values computed by Green's function method	35
3.	The complete set of matrix elements of the Hamiltonian	43
4.	Values of the interaction integrals for Iron	50
5.	Values of the first four interaction integrals obtained by the first process	51
6.	Energy values computed using the different values of the four interaction integrals in Table 5	51
7.	Values of the interaction integrals for Cr ..	52
8.	E(k)-values computed by the Slater-Koster interpolation scheme	55

LIST OF FIGURES

Page

1. Energy Band of a crystalline solid 5
2. Brillouin zone of bcc lattice 28
3. Faces of the 1/48 part of the Brillouin zone showing the points at which $E(\vec{k})$ is calculated by the Green's function method 34
4. to 6. The s-,p-,d-type atomic orbitals 37
7. $E(\vec{k})$-values of Cr computed using the different values of the first four interaction integrals in Table 5 and interaction integrals of Iiron 53
8. Faces of the 1/48 part of the Brillouin zone showing the points at which $E(\vec{k})$ is computed by the interpolation scheme 54

INTRODUCTION

The electronic energy band calculation is one of the complicated problems in solid state physics. The success with which we are now able to understand the electronic energy levels of many solids may be ascribed principally to two sources:

1. The existence of sophisticated first-principles band calculations, which begin with a carefully chosen one-electron potential and are frequently carried out self-consistently. These calculations can be carried out at few high symmetry points in the Brillouin zone (BZ).

2. The development of interpolation schemes, which short circuit many of the calculational complexities inherent in a band calculationsby the judicious use of symmetry arguments and group theory method, thereby leading to a deeper understanding of the qualitative features of the electron energy versus wave number dispersion relations. This method is used as a useful adjunct of first-principles band calculations.

The energy band structure of chromium is computed at few high symmetry points in the 1/48 part of the BZ by first-principle method (Green's function method) by S. Asano and J. Yamashita[1]. The Green function method has merits of yielding quantitatively accurate results. To obtain energy

versus wave-vector dispersion relation at any point in the BZ, a more promising approach is to use interpolation scheme. In light of this, the main objective of this project is to interpolate and extrapolate the energy band structures of chromium in the whole Brillouin zone by Slater-Koster interpolation scheme.

Within this frame work one has to derive the matrix elements of the Hamiltonian between nine localized wave-functions in tight-binding formalism. The symmetry adapted wave-functions are formed by group theory methods for symmetry points and lines of particular symmetry in the BZ, The secular equations for the symmetry points and lines are derived using the symmetrized wave-functions as basis set of the representation. The secular determinant which is in general 9x9 and complex is obtained in its reduced form.

The interaction integrals involved in the matrix elements of the Hamiltonian are related to one another by judicious use of symmetry argument and physical insight. And the matrix elements, thereby the secular equations are expressed in terms of the independent interaction integrals. These independent integrals are treated as disposable constants and are fitted to the first-principle energy band structures of Cr via the Slater-Koster interpolation scheme.

These results may be directly used for computation of the complex energy band structure at any point in the Brillouin

zone, for the study of magnetism and to calculate density of states of Cr. Also in studying optical properties, related to transitions between the energy bands.

CHAPTER 1

ENERGY BAND STRUCTURE.

The motion of an electron in a solid is governed by Schroedinger equation of the form,

$$\frac{-h^2}{2m} \nabla^2 \Psi + V(\vec{r})\ \Psi = \varepsilon \Psi \quad , \qquad (1)$$

where the potential $V(\vec{r})$, is periodic which arises from the periodic arrangement of the lattice particles[2].

In principle the problem of electrons in a solid is a many-electron problem, for the full Hamiltonian of the solid contains not only the one-electron potentials describing the interactions of the electrons with the massive-atomic nuclei, but also pair potentials describing the electron-electron interactions. In the independent-electron-approximation these interactions are represented by an effective one-electron potential $V(\vec{r})$. The problem of how best to choose this effective potential is a complicated one[3].

The wave-function that is solution of eq.(1) is of Bloch-form

$$\Psi(\vec{r}) = U(\vec{r})\ \ e^{i\vec{k}.\vec{r}} \qquad (2)$$

where U(r) has periodicity of the potential.

And $$e^{i\vec{k}.\vec{R}} = 1 \qquad (3)$$

where $\vec{R}$ is the lattice vector and $\vec{k}$ the wave vector which is a good quantum number.

Hence, it is obvious from eq.(3) that not all energy values are possible but only certain values E_n are possible for a given $\vec{k}$. As $\vec{k}$ runs through all values, the permissible energy values belong to real wave vectors.

As a consequence of the translational symmetry of the lattice there exist energy gaps that is forbidden region and allowed region energy bands.

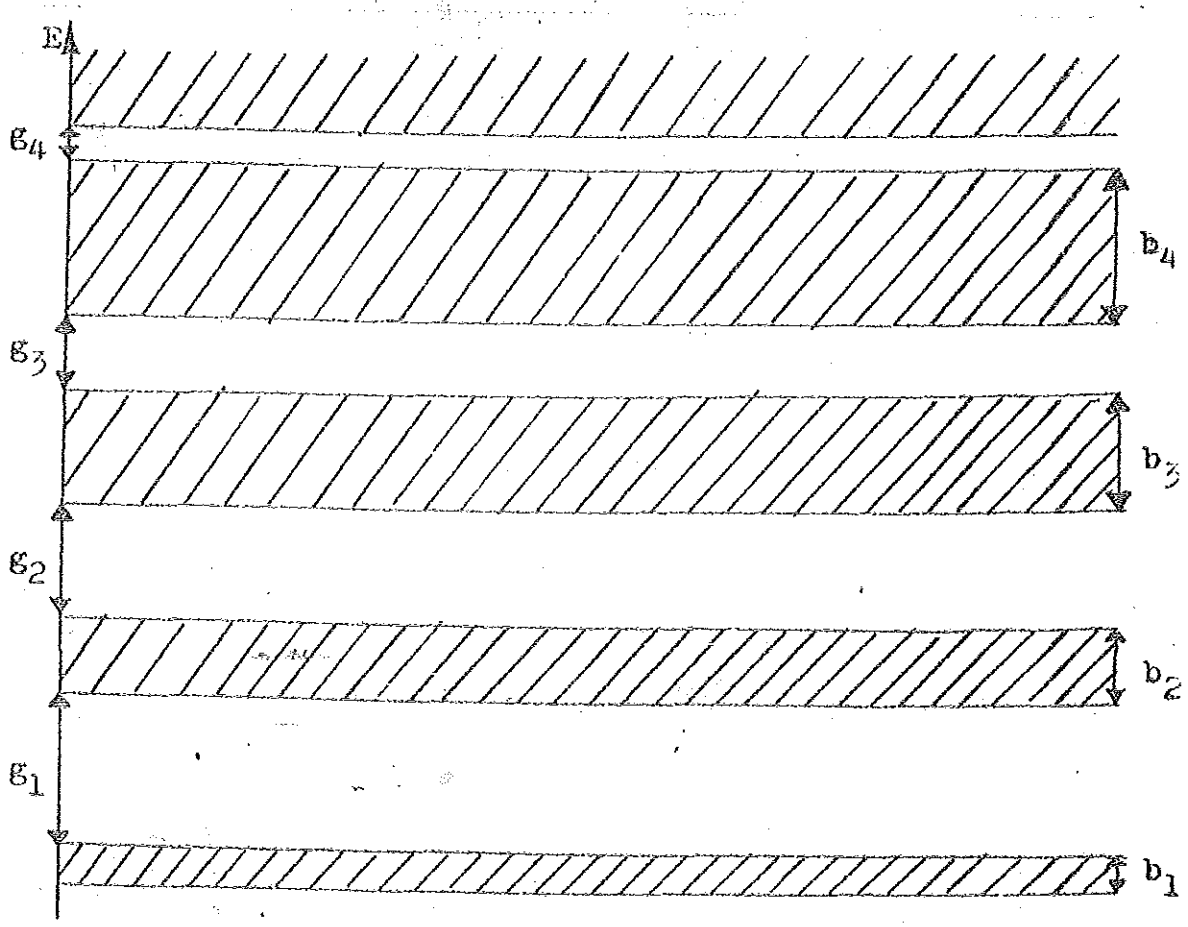

Fig. 1 Energy bands of a crystalline solid.

The energy band structure of a crystalline solids form a complicated physical system. And the problem of calculating band structure is a many-body problem.

First principle methods used in band calculation consist of formulating the form of the crystal potential by inspection and proceed to solve Schrödinger equation. These methods of calculating energy levels have a reasonable claim of exactness in that the expansions employed will, in principle, converge to the state of interest as more functions are added[4]. At the same time the calculations are generally quite difficult to perform except at points of high symmetry in the BZ.

On the other hand there is a more powerful method which provides a reasonably simple technique of approximating the energy of states at general points of the zone. This method is known as the tight-binding approximation or linear combination of atomic orbitals (LCAO).

CHAPTER 2

THE TIGHT-BINDING APPROXIMATION

and

THE SLATER-KOSTER INTERPOLATION SCHEME

The tight-binding approximation deals with the case in which the overlap of atomic wave-functions is enough to require correction to the picture of isolated atoms[5].

The principal assumption in this approximation is that in the vicinity of each lattice point the full periodic crystal Hamiltonian can be approximated by the Hamiltonian of a single atom $\hat{H}_{at}$ at the lattice point.

$$\hat{H}_{at} = \hat{H}_{kin} + U_{at}(\vec{r}) \qquad (4)$$

Also the bound levels of the atomic Hamiltonian are well localized, that is

$$\hat{H}_{at}\ \phi_n^a(\vec{r}) = E_n\ \phi_n^a(\vec{r}) \qquad (5)$$

then we require ϕ_n^a to be very small for $\vec{r}$ that exceed the lattice constant termed as "range of ϕ_n^a" and we can proceed by calculating corrections to the Hamiltonian to this extreme case. The index n in eq.(5) represents a set of quantum numbers.

On the other hand one can formulate the full crystal Hamiltonian and proceed until the necessity for approximation arises[6], The crystal Hamiltonian contains a sum of potentials centered on each atom.

$$\hat{H} = \hat{H}_{at} + \sum_{\nu} V(\vec{r}-\vec{R}_{\nu}) \qquad (6)$$

where $\vec{R}_{\nu}$ is a primitive lattice vector.

We further assume that the motion of electrons in the lattice is determined by the potential of the ion at which vicinity an electron is present at a given moment.

The crystal potential which is regarded as the sum of atomic potential is periodic for the crystal possess translation symmetry. Consequently the eigenfunctions of the full crystal Hamiltonian preserve the Bloch form

$$\psi_{\vec{k}}(\vec{r}) = \sum_{\nu} \exp(i\vec{k}\cdot\vec{R}_{\nu})\ \phi\ (\vec{r}-\vec{R}_{\nu}) \qquad (7)$$

where the function $\phi(\vec{r})$ is not necessarily an exact atomic stationary-state wave-function, however for $\sum_{\nu} V(\vec{r}-\vec{R}_{\nu})\ \phi_n^a(\vec{r})$ very small the function $\phi\ (\vec{r})$ approaches the atomic wave-function $\phi_n^a(\vec{r})$, or to wave-functions with which $\phi_n^a(\vec{r})$ is degenerate. Based on this expectation, one seeks a $\phi(\vec{r})$ such that,

$$\phi(\vec{r}) = \sum_{n} b_n\ \phi_n^a(\vec{r}) \ . \qquad (8)$$

The major problem of the tight-binding approximation is the accurate evaluation of Bloch sums, eq.(7). The approximation consists of neglecting the overlap between the functions on non-neighbouring sites, but it makes a reasonable approximation if the overlap is not small.

The tight-binding approximation is most suitable for

electrons which are tightly bound to their atoms in the bands built from inner electrons or from d-electrons whose orbits have relatively small radii[7] , but very bad for valence and excited states, whence the corresponding Bloch sums converge very slowly.

The tight-binding method demonstrates an important principle. Suppose we take N atoms, and keep them far apart. On each atom there will be different atomic levels; in the whole assembly these will be N-fold degenerate states for a single electron[8].

But when we bring the atoms together, the orbitals overlap and we find that the N-fold degeneracy is split into a band of states. There will be a complete band, of N states, arising from each atomic level. So that we can refer to the 3s-band, 4p-band, etc., arising from the corresponding atomic states. This classification is particularly apt in the case of transition metals, where the d-state of the atom are rather compact within each core, so that they combine to form a relatively narrow and well defined d-band. From eq.(7) and eq.(8)

$$\Psi_{\vec{k}}(\vec{r}) = \sum_{\nu,n} \exp(i\vec{k}\cdot\vec{R}_\nu) b_n \phi_n^a(\vec{r}-\vec{R}_\nu) \qquad (9)$$

This function looks like a series of strongly localized atomic orbitals, multiplied by a wavy phase factor $\exp(i\vec{k}\cdot\vec{R})$. Within each atom the local orbital predominates, and should be a good solution to the local Schroedinger equation.

This suggest that our wave function is a linear combination of atomic orbitals. For this reason this method is also known as Linear Combination of Atomic Orbitals (LCAO).

We can now form the matrix component of the energy between two Bloch sums, eq.(9), but besides running into computing difficulties with three-center integrals the Bloch sums are not orthogonal to each other. We can remove this difficulty by setting up new atomic orbitals, linear combinations of the original ones, which are orthogonal to each other. This can be done most symmetrically by the method of Löwdin[9]We shall assume that this is done, and shall call the resulting orbitals Ψ_n . These Löwdin functions Ψ_n show symmetry properties like those of the atomic orbitals ϕ_n^a from which they were derived[9], From these Löwdin functions, we can now construct Bloch sums,

$$N^{-\frac{1}{2}} \sum_i \exp(i\vec{k}\cdot\vec{R}_i)\ \Psi_n(\vec{r}-\vec{R}_i) \qquad (10)$$

where $\vec{R}_i$ is the vector position of the atom on which the orbital is located, these Bloch sums are normalized and orthogonal to each other. We are assuming periodic boundary conditions, and the number of unit cells in the repeating region is N ; the normalization is over this repeating region. The sum is over primitive unit cells.

The matrix component of energy between two Bloch sums. If $\hat{H}$ is the Hamiltonian

$$N^{-1} \sum_{i,j} \exp(i\vec{k}\cdot(\vec{R}_j-\vec{R}_i)) \int \Psi_n^*(\vec{r}-\vec{R}_i)\hat{H}\Psi_m(\vec{r}-\vec{R}_j)dV \qquad (11)$$

The sum is over the N unit cells. And the position vectors $\vec{R}_i$ and $\vec{R}_j$ ranges over the positions of atoms on which orbitals Ψ_n and Ψ_m are located respectively. One summation of the above double sum can be eliminated, for it merely amounts to multiplication by "N"

$$\sum_j \exp(i\vec{k}\cdot(\vec{R}_j-\vec{R}_i)) \int \Psi_n^*(\vec{r}-\vec{R}_i)\hat{H}\Psi_m(\vec{r}-\vec{R}_j)dV \qquad (12)$$

$(\vec{R}_j-\vec{R}_i)$ is the vector displacement from the atom on which the orbitals Ψ_n is located, to one of its neighbours on which an orbital Ψ_m is located.

The actual calculation of the integrals in, eq.(12) the matrix component of the energy, is extremely difficult. First we must find the orthogonalized Löwdin functions, from the atomic orbitals, and this is a very considerable task. When this is done, each Ψ_n in eq.(12) is a combination of atomic orbitals of many nearby atoms. Thus, the integral in eq.(12) can be made up as a linear combination of many integrals of the form of

$$\int \phi_n^*(\vec{r}-\vec{R}_i)\hat{H}\ \phi_m(\vec{r}-\vec{R}_j)dV \qquad (13)$$

This is three-center integral whose calculation is very difficult. All these complications add up to make the rigorous calculation of the matrix components of energy an almost impossible task, not only because the individual terms are difficult to work out, but also because there are so many of them, combined in complicated ways.

In the Slater-Koster interpolation scheme some simplifications are introduced converting the method from a rigorous one to a rather simple interpolation scheme. We merely use the form in eq.(12) for the matrix components of energy, but replace the integrals by disposable constants, which we choose to fit accurate determination of energies at particular $\vec{k}$ values. We wish only a finite number of arbitrary constants, for we have to fit only a finite number of accurate calculations of energy. To choose a finite number, we proceed as follows. The integral in eq.(12) will get smaller numerically as the atoms in question get further apart. The presence of the orthogonalized Lowdin functions in the Bloch sum, eq.(10), will amplify the above process. Hence, a first natural simplification is to assume arbitrarily that all integrals are to be disregarded except those for neighbours lying closer than a certain minimum distance. We can use only nearest, second nearest and third nearest according to how many disposable constants we wish to use.

There is one thing to be noticed about the integrals in eq.(12). Many of them must be related, through demands of crystal symmetry. Thus, if symmetry operations of rotation and inversion about the atom at position $\vec{R}_i$, where the orbital ψ_n is located, will carry the atom at $\vec{R}_j$ into another unit cell, then there will be relations between the integrals between the orbital and orbitals of type on these various atoms, which clearly must all be at the same distance from the first atom.

This can be systematically handled by the group theory, decreasing greatly the number of independent integrals.

The convenient feature which we can observe from eq.(12) is the very simple way in which each term depends on the propagation constant $\vec{K}$. For each $\vec{K}$ value, the energy levels can be related to the irreducible representations of the group of wave vector, the wave-functions in the crystal are the bases of such irreducible representations. Any series of wave-functions can form the basis of what is in general reducible representation of the group. By judious use of group theory one can build up a set of basic functions for the irreducible representation of the group of wave functions[10]. Such an analysis short circuit many of the calculational complexities inherent in the Slater-Koster interpolation scheme.

The Slater-Koster interpolation scheme is simply a method of interpolating between energy eigenvalues calculated at points of high symmetry in the BZ and thereby obtaining electron dispersion relations that are valid for all $\vec{K}$.

This method of interpolation is advantageous for the parameters of the scheme may be adjusted to bring the energy bands and Fermi surfaces into better agreement with experiment[11]. As is well known, the various approximations made in first-principles band calculations can lead to substantial errors.

The philosophical outlook concerning the utility and significance of interpolation scheme in relation to first principle

band calculations is that these two quite different approaches should be regarded as complementary rather than competitive. Indeed, as it is done here it is possible to combine the best features of both approaches.

In conclusion Slater-Koster interpolation scheme is a useful adjunct to first-principle calculations along the lines just described and its most basic use is to be found in the determination of the band structure and density of states.

CHAPTER 3

GROUP THEORY

3.1 Symmetry - Group Operators

The Schroedinger equation is usually too complicated to be solved analytically or even numerically without making gross approximations. The real importance of symmetry arguments in such situations lies in the fact that for systems of interest, the symmetry properties of the equation may be relatively simple, and more than that they do not involve approximation[12].

One investigates a certain symmetry property of any physical system (represented in the usual formalism by its Hamiltonian) by "rotating" the appropriate coordinate and checking to see if the Hamiltonian still looks the same from the new point of view.

The tool needed to carry out this procedure is the set of operators which change certain parameters of coordinates of the system by a specified amount. The entire set of such operators on a certain coordinate conveniently forms a mathematical group of operators, called a symmetry group which is subject matter of group theory.

The principal reasons group theory has been useful in physics are, it enables to classify and lable the eigenstates of a quantum mechanical system and to understand the degenerate energy eigenstates of the system in terms of the

symmetry properties possessed by its interactions. It produces from these symmetry properties a complete set of commuting observables, whose eigenvalues serve to lable the degenerate levels uniquely. These same commuting observables identify conservation laws obeyed by the system, and so establish selection rules for transitions decay schemes and reactions[13]. The other fundamental use of group theory is revealed in connection with the periodic potential problem is to show how to set up the symmetrized functions.

3.2 Space Groups

The groups of operations with which we are concerned in crystal problems are of a rather specialized nature called space groups. They are a special case of more general groups of linear coordinate transformations which preserve lengths[14]. Such operations leave the lattice invariant and commute with the Hamiltonian and are important in classifying the electron states.

An operator of a space group contains a part which is either a proper or improper rotation, α , and a translation part, t, and is denoted by $\{\alpha/t\}$.

$$\underline{x}' = \underline{\alpha}\,\underline{x} + \underline{t} \tag{14}$$

$$\begin{pmatrix} x_1' \\ x_2' \\ x_3' \end{pmatrix} = \begin{pmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} \\ \alpha_{31} & \alpha_{32} & \alpha_{32} \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} + \begin{pmatrix} t_1 \\ t_2 \\ t_3 \end{pmatrix} \tag{15}$$

Two such operators : $\{\alpha/t\}$ and $\{\beta/t'\}$ multiply in the following way:

$$\{\beta/t'\}\{\alpha/t\} = \{\beta\alpha/\beta t + t'\} \tag{16}$$

The unit operator is represented by $\{\epsilon/0\}$ and the inverse of the operator $\{\alpha/t\}$ is

$$\{\alpha/t\}^{-1} = \{\alpha^{-1} / -\alpha^{-1}t\} \tag{17}$$

Space groups are characterized by the fact that they possess an invariant subgroup of translations of particular form (known as primitive translation) $\{\epsilon/\vec{R}_n\}$. Where $\vec{R}_n$ is the lattice vector given by

$$\vec{R}_n = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3 \tag{18}$$

$\vec{a}_i$'s are primitive translations and n_i 's are integers.

All properties of the space groups can be derived from the fact that they contain an invariant subgroup of primitive translations.

1) Whenever $\vec{R}_n$ is a primitive translation $\hat{\alpha}\vec{R}_n$ also is if $\{\hat{\alpha}/\vec{t}\}$ is a member of the space group.

2) Space groups are finite in number in a space of given dimension. There are 230 in three dimension, 17 in two dimension and 2 in one dimension.

3) Only certain proper rotations can be present, namely rotations about well defined axes through integral

multiples 60^0 and 90^0 about specified axes, and improper rotations (that is, products of these restricted rotations with the inversion).

In enumerating the possible groups which the rotational parts of the operators in the space group can form, it is found that only 32 are possible in three dimensions. These are known as the 32 point groups or 32 crystal classes.

The lattice generated by the primitive translations of a space group must be invariant under the operations of the point group.

The full cubic group O_h is an element of 32 point groups, it consists of 48 operations which leave a cube invariant.

3.3 Matrix Representation of a Group

Matrix representation of a group consists of group of matrices with the same multiplication properties as the group it represents. In practice representations always arise through transformation properties of some functions [15].

To see this in a general way consider a linearly independent set of functions ϕ_1 , ϕ_2 , ... , ϕ_n and a group G of linear transformations of which a typical one is $\hat{T}$. If the functions and transformations are such that $\hat{T}\phi_i$ can

in every case be expressed as a linear combination of the set $\phi_1 , \phi_2 , \ldots , \phi_n$ that is

$$\hat{T}\phi_j = D_{ij}(\hat{T})\phi_i \qquad (19)$$

then we have immediately the set of matrices $D_{ij}(\hat{T})$, Furtheremore, these matrices form a representation of G, for if $\hat{C} = \hat{S}\hat{P}$, then

$$D_{ij}(\hat{C}) = D_{ik}(\hat{S})\, D_{kj}(\hat{P}) \ . \qquad (20)$$

The functions $\phi_1 , \phi_2 , \ldots , \phi_n$ are said to form a basis for the representation $D_{ij}(\hat{T})$. An alternative wording is to say that the functions $\phi_1 , \phi_2 , \ldots , \phi_n$ transform according to the representation $D_{ij}(\hat{T})$ of G.

A representation $D_{ij}(\hat{T})$ of a group G is reducible into the representations D^1, D^2 , ... , D^s if a transformation of the type $D'(\hat{T}) = P^{-1}D(\hat{T})P$ exists which brings every matrix $D_{ij}(\hat{T})$ of the representation into the form

$$\left|\begin{array}{c:c:c:c} D^1_{ij}(\hat{T}) & 0 & 0 & 0 \\ \hdashline 0 & D^2_{ij}(\hat{T}) & 0 & 0 \\ \hdashline 0 & 0 & D^3_{ij}(\hat{T}) & 0 \\ \hdashline 0 & 0 & 0 & \ddots \end{array}\right| \qquad (21)$$

with smaller matrices $D^i(\hat{T})$ along the diagonal and zeros elsewhere. This is written in direct summation

$$D = D^1 \dot{+} D^2 \dot{+} D^3 \dot{+} \ldots \dot{+} D^s \qquad (22)$$

A representation that cannot be reduced is termed irreducible. If a representation D is reduced into irreducible components, the reduction is unique apart from equivalence.

Consider a vector space $R(\phi_1 , \phi_2 , \ldots , \phi_n)$ of which the base vectors ϕ_i transform according to the reducible representation $D_{ij}(\hat{T})$. Since the representation $D_{ij}(\hat{T})$ is reducible there exist by definition some transformation which brings the matrices of D into the reduced form. Such a transformation is equivalent to choosing new base vectors ϕ_i' in R , and these ϕ_i' therefore transform according to the reduced matrices D^k.

Let R^1 be the space spanned by the first n_1 vectors ϕ_i where n_1 is the dimension of the representation D^1 . Hence, R^1 transforms according to the representation D^1 , and similarly successive sets of vectors span spaces R^i transforming according to the representation D^i. Thus, it follows directly from the reducibility of the representation $D_{ij}(T)$ that the vector space R can be split up or reduced into a series of invariant subspaces R^i transforming according to the representation D^i.

Since the ϕ_i' span the whole space R, any function in the space R can be written as the sum of functions, one from each subspace R^i . This is written in symbols

$$R = R^1 \dot{+} R^2 \dot{+} \ldots \dot{+} R^s \qquad (23)$$

Physically this corresponds to the fact that if the functions of a Hamiltonian are considered as one big vec space (Hilbert Space) R, then the functions belonging to different invariant subspaces R^i are in general associated with different energy levels.

The reduction of R has the further important property that the subspaces R^i can always be made orthogonal to one another, that is any function from one R^i is orthogonal to any function from any other R^j.

3.4 Group Character and Class

Let $D_{ij}(\hat{T})$ be any representation of a group of transformations $\hat{T}$. The sum of the diagonal elements of $D_{ij}(\hat{T})$ is called the character X of $\hat{T}$ in this representation[16].

$$X(\hat{T}) = \sum_i D_{ii}(\hat{T}) \qquad (24)$$

Definition: A class is a set of elements out of a group, such that if $\hat{T}$ is one element of the class, then $S\hat{T}S^{-1}$ also belongs to that class for all group elements S.

It can be easily shown that the character is the same for the matrices representing all the operations of the same class.

Theorem 1: The number of irreducible representations equals the number of classes.

From the above discussion it is clear that the set of character is a very useful way of distinguishing a given representation from all inequivalent ones. Moreover, the number of classes in a group is considerably smaller than the number of elements, and hence so is the number of different characters. In particular the irreducible representations of a group can be tabulated easily in this way.

The identity element E always forms a class of its own and $\chi(E)$ is the dimension of the representation.

There is one more general theorem pertaining to the irreducible representation of a finite group.

Theorem 2: The sum of the squares of the dimensions of the representations equals the number of elements of the group.

3.5 Projection Operator Method and Symmetry Adapted Wave-Functions

If one knows the representation matrices of the group, there is then a very powerful theorem which allows us to start with any arbitrary function and produce from it a function of the symmetry of one of the basis functions for one of the irreducible representation of the group. This is the method of projection operators.

Suppose a representation D is reducible into irreducible components $D^{\alpha} \dot{+} D^{\beta} \dot{+} \ldots \dot{+} D^{\varepsilon}$ then one can bring D

into reduced form by a transformation $P^{-1}D(\hat{T})P$, and hence the characters are

$$X(T) = X^{\alpha}(T) + X^{\beta}(T) + \ldots + X^{\varepsilon}(T) \qquad (25)$$

$$X(T) = \sum_{\lambda} C_{\lambda} X^{\lambda}(T) \qquad (26)$$

where the coefficient "C_{λ}" is the number of times the irreducible component D^{λ} occurs in the reduction of D.

To express the projection operator explicitly it is noteworthy to state the fundamental orthogonality relation of the first kind for irreducible representations [17].

Theorem 3: If $D^{\lambda}_{\alpha\beta}(\hat{T})$ be the (α,β) matrix element of the λ^{th} irreducible representation of the group element $\hat{T}$. The number of the elements in the group h is the range of the group element $\hat{T}$. And the range of λ will be the number of inequivalent irreducible representations. The range of α and β will be the dimension, n_{λ} of the λ^{th} irreducible representation. Then

$$\sum_{\hat{T}} D^{\lambda *}_{\alpha\beta}(\hat{T})\, D^{\mu}_{ij}(\hat{T}) = \frac{h}{n_{\lambda}} \delta_{\alpha i} \delta_{\beta j} \delta_{\lambda\mu} \qquad (27)$$

By putting $i = j$, $\alpha = \beta$ and summing, we obtain the orthogonality relation of second type for the characters

$$\sum_{\hat{T}} X^{\lambda}(\hat{T})\, X^{\mu}(\hat{T}) = h\delta_{\lambda\mu} \qquad (28)$$

Multiplying eqn.(26) by $X^{*}(\hat{T})$ and summing we get

$$C_{\lambda} = \frac{1}{h} \sum_{\hat{T}} X^{\lambda *}(\hat{T}) X(\hat{T}) \qquad (29)$$

The uniqueness of the reduction shows that two representations with the same characters are reducible into the same irreducible components and hence are equivalent.

Let R be a vector space transforming according to a representation which can be reduced into irreducible componets by eqn.(29). Let $D^{\lambda}_{ij}(\hat{T})$ be one of the irreducible component representation and ϕ any vector of R. Then, the vectors in R transforming according to the particular irreducible representation $D^{\lambda}_{ij}(\hat{T})$ is given by

$$\phi^{\lambda}_{i} = \sum_{\hat{T}} D^{\lambda *}_{ij}(\hat{T}) \hat{T} \phi \qquad (30)$$

for any fixed value of j. Putting $i = j$ in eqn.(30) and summing, we have

$$\phi^{\lambda} = \sum_{\hat{T}} X^{\lambda *}(\hat{T}) \hat{T} \phi \qquad (31)$$

which belongs to an irreducible subspace transforming according to D^{λ}.

Therefore, the term

$$\hat{p}^{\lambda} = \sum_{\hat{T}} X^{\lambda}(\hat{T}) \hat{T} \qquad (32)$$

is the projection operator for it projects any vector ϕ in the reducible vector space R to another vector ϕ^{λ} which belongs to an irreducible subspace transforming according to

the irreducible representation D^{λ} . The ϕ^{λ} thus obtained are termed as symmetry adapted wave functions.

If the basis of the space group representation D^{λ} are a group of wave vectors, then any operation involves translation t_n only through the simple factor $\exp(i\vec{k}_o \cdot \vec{t}_n)$. That is, we have

$$D^{\lambda}_{ab}\{\hat{\alpha}|\vec{t}_n\} = D^{\lambda}_{ab}\{\hat{\alpha}|0\} \exp(i\vec{k}_o \cdot \vec{t}_n)$$

In setting up the projection operator, the complex conjugate of this matrix is used and is summed over $\vec{t}_n$ (as well as over $\hat{\alpha}$). If the basis functions are atomic wave-functions this summation of atomic orbitals displaced by the amount $-t_n$, multiplied by the factor $\exp(-i\vec{k}_o \cdot \vec{t}_n)$ is simply an ordinary Bloch sum, showing that the procedure of using Bloch sums is a direct result of the translation symmetry of the space group[18].

If we start with an atomic orbital function of arbitrary type at this site, and use the projection operator, we shall remove everything except that part of the orbital which has the correct symmetry. The problem can be simplified, however, if we start from the begining with atomic orbitals of the correct symmetry type. We thus, have for our study of symmetry orbitals the machinery for setting up linear combinations of atomic orbitals of any desired symmetry.

The lattice translations, subgroup of space groups, since it

is abelian group, all irreducible representations are (one-dimensional matrices) $\exp(i\vec{k}\cdot\vec{t}_n)$, where $\vec{k}$ lies inside or on the surface of the Brillouin Zone. At a general point in the Brillouin Zone, it is sufficient that the wave function have the Bloch form in order that it be an acceptable basis function for an irreducible representation of the space group.

If there are n operators in the point group, (n-1) other functions may be obtained in this way, which are characterized by wave vectors $\alpha\vec{k}$. The figure of these $\vec{k}$ vectors is refered to as a "star". It exhibits all of the rotational and reflectional symmetry of the lattice.

The Bloch functions characterized by $\vec{k}$ vectors in the star are bais functions for an n-dimensional irreducible representation of the space group. In this representation, the matrices representing lattice translations are diagonal, with elements $\exp(i\vec{k}'\cdot\vec{t}_n)$ where $\vec{k}'$ runs over all the vectors of the star.

3.6 Brillouin Zone of the Body Centered Cubic Lattice

It is desirable to construct a unit cell in the reciprocal lattice that has the full symmetry of this lattice[19]. This is done by applying the same procedure used in constructing Wigner-Seitz Cell, a unit cell in the direct lattice, in the reciprocal space.

All the electron states in the periodic potential can be

characterized by $\vec{k}$ vectors lying in the interior or on the surface of the Brillouin zone. The energy of these states may be regarded as a function of the $\vec{k}$ vector. This function will be multivalued: there will be many different energies for a single $\vec{k}$. For values of $\vec{k}$ lying inside the zone, the energy will be a continuous function of $\vec{k}$. A single continuous manifold is referred to as an energy band. Discontinuities in the energy may occur only on the surface of the zone.

In the body-centered cubic (bcc) lattice, possible choices for the three translation vectors in the direct lattice are given by

$$\begin{aligned} \vec{a}_1 &= \frac{a}{2}(\hat{i} + \hat{j} + \hat{k}) \\ \vec{a}_2 &= \frac{a}{2}(\hat{i} + \hat{j} - \hat{k}) \\ \vec{a}_3 &= \frac{a}{2}(\hat{i} - \hat{j} + \hat{k}) \end{aligned} \tag{33}$$

where "a" is the lattice parameter and $(\hat{i}, \hat{j}, \hat{k})$ are the cartesian unit vectors along the x, y and z axes respectively.

Then the reciprocal lattice can be generated by the three primitive vectors.

$$\vec{b}_\ell = 2\pi \frac{\vec{a}_m \times \vec{a}_n}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \tag{34}$$

in which ℓ, m and n are the different even permutation of 1, 2 and 3.

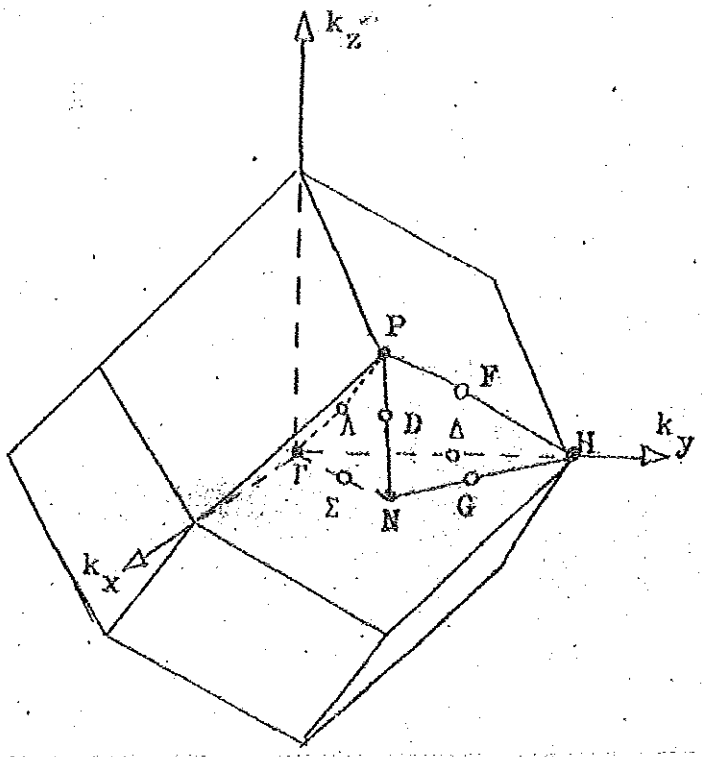

Fig.(2): Brillouin Zone for Body Centered Cubic Lattice

The center of the zone is designated by Γ , The (010) , (111) and (110) axes are labeled by Δ , Λ and Σ , respectively. The principal "symmetry points" of the zone are Γ , H , P and N . The last three points are intersections of the Δ , Λ and Σ axes (respectively) with the faces of the zone.

The coordinates of points Γ , H , P and N are (0,0,0), $\frac{2\pi}{a}(0,1,0)$, $\frac{2\pi}{a}(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and $\frac{2\pi}{a}(\frac{1}{2},\frac{1}{2},0)$ respectively. All the equivalent points can be generated by adding the reciprocal lattice vector to the corresponding points.

3.7 Projection Operator Method Applied to a Typical Symmetry Direction in the Brillouin Zone of bcc Lattice

Example: For Σ direction in the Brillouin zone of the body - centered cubic cell.

For Σ direction $K_x=K_y$ and $K_z=0$, $K_x\in(0,\pi/2a)$. The operators of point group $C_{2v}(2mm)$ leave the Σ direction invariant. Hence, C_{2v} group operators are symmetry operators of the Σ direction. The operators of the C_{2v} group are

$$\{E,\ C_2\ ,\ JC_4^2\ ,\ JC_2\} \tag{35}$$

where,

$E=(x,y,z)$, $C_2=(y,x,-z)$, $JC_4^2=(x,y,-z)$ and $JC_2=(y,x,z)$.

Let us now choose nine atomic functions (s, p_x, p_y, p_z, dxy, dxz, dyz, $d_{x^2-y^2}$, $d_{3z^2-r^2}$) as basis of the group C_{2v}. By operating on these atomic wave-functions by the operators of the group C_{2v} , one can obtain the characters of the representation matrices of these operators. The characters are

$$X(E)=9\ ;\ X(C_2)=1\ ,\ X(JC_4^2)=3\ ,\ X(JC_2)=3 \tag{36}$$

Table 1 ; Character Table, Group of Σ, C_{2v} [20]

Representation	E	C_2	JC_4^2	JC_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

The coefficients C_λ , from eqn.(29), are

$$C_{\Sigma 1} = 4 \ , \ C_{\Sigma 2} = 1 \ , \ C_{\Sigma 3} = 2 \ , \ C_{\Sigma 4} = 2$$

Hence, the dimensions of the irreducible representation Σ_i's are given by the above coefficients

$$D = 4\Sigma_1 + \Sigma_2 + 2\Sigma_3 + 2\Sigma_4$$

The projection operators

$$\hat{P}_\lambda = \Sigma \ X^{\lambda *} \ (\hat{T}) \hat{T}$$

are given by

$$\begin{aligned}
\hat{P}_{\Sigma 1} &= E + C_2 + JC_4^2 + JC_2 \\
\hat{P}_{\Sigma 2} &= E + C_2 - JC_4^2 - JC_2 \\
\hat{P}_{\Sigma 3} &= E - C_2 - JC_4^2 + JC_2 \\
\hat{P}_{\Sigma 4} &= E - C_2 + JC_4^2 - JC_2 \ .
\end{aligned} \tag{37}$$

By applying these operators on the atomic wave-functions one can form symmetry adapted wave functions of the different irreducible representations. The independent and normalized symmetry adapted wave functions are

$$\begin{aligned}
\Sigma_1 &\sim \{ \ |s\rangle \ , \frac{1}{\sqrt{2}} \ (|p_x\rangle + |p_y\rangle \ ) \ , \ |d_{xy}\rangle \ , \ |d_{3z-r^2}\rangle \} \\
\Sigma_2 &\sim \{ \ \frac{1}{\sqrt{2}} \ (|d_{yz}\rangle - |d_{xz}\rangle) \} \\
\Sigma_3 &\sim \{ \ |p_z\rangle \ , \ \frac{1}{\sqrt{2}} \ (|d_{yz}\rangle + |d_{xz}\rangle) \} \\
\Sigma_4 &\sim \{ \ \frac{1}{\sqrt{2}} \ (|p_x\rangle - |p_y\rangle) \ , \ |d_{x^2-y^2}\rangle \}
\end{aligned} \tag{38}$$

CHAPTER 4

ENERGY BANDS IN CHROMIUM VIA THE GREEN'S - FUNCTION METHOD

Among the many methods that have been proposed for the calculation of electronic energy band structure along lines of high symmetry in $\vec{k}$ - space for a given periodic potential, the Green's - function method has proved to be outstandingly succesful for its ability to yield quantitatively accurate results and rapid convergence. The Green's-function method developed by Korringa (1947) and by Kohn and Rostoker (1954) (often, therefore, also called the KKR method).

To calculate the band structure corresponding to a periodic potential $V(\vec{r})$, we seek solutions of Schroedinger equation, eq.(1), such that the Bloch condition, eq.(2), holds. The aim being to calculate the energy values $E(\vec{k})$ as a function of arbitrary $\vec{k}$ lying within the first BZ in the reciprocal lattice space.

In developing the Green's-function method one starts from the integral form of the Schroedinger equation, which is equivalent formulation of eq.(1).

$$\psi(\vec{r}) = \int_V G(\vec{r}, \vec{r}')V(\vec{r}')\psi(\vec{r}')dV \qquad (39)$$

where the integral is over a unit cell of volume V and the Green's-function $G(\vec{r}, \vec{r}')$ is given by

$$G(\vec{r}, \vec{r}') = -\frac{1}{V}\sum_n \frac{\exp[i(\vec{K}_n+\vec{k})\cdot(\vec{r}-\vec{r}')]}{(\vec{K}_n+\vec{k})^2 - E} \qquad (40)$$

The summation in eq.(40) is over all reciprocal lattice vectors $\vec{K}_n$. For $\vec{r}$ and $\vec{r}'$ lying within the unit cell, $G(\vec{r}, \vec{r}')$ satisfies the differential equation

$$(\nabla^2+E)\ G(\vec{r}, \vec{r}')= \delta(\vec{r}-\vec{r}') \qquad (41)$$

In the paper of S. Asano and J. Yamashita [1] the band structure of paramagnetic Cr is evaluated by the Green's-function method. And the crystal potential is set up by the self-consistent field (SCF) procedure, which is beyound the restriction set by Hartree - Fock SCF or Hartree - Fock - Slater SCF. To start with an effective potential, $V_{eff}(\vec{r})$, is written as

$$V_{eff}(\vec{r}) = V_c(\vec{r})+V_{ex}(\vec{r})+V_{corr}(\vec{r}) \qquad (42)$$

Here, $V_c(\vec{r})$ is the Coulomb potential and it is evaluated from the total charge distribution $\rho(\vec{r})$. The exchange potential, $V_{ex}(\vec{r})$, is also evaluated from $\rho(\vec{r})$ by the Slater approximation

$$V_{ex}(\vec{r}) = -2.95(\rho(\vec{r}))^{1/3} \qquad (43)$$

The correlation part of the effective potential, V_{corr} is assumed to be

$$V_{corr}(\vec{r})= V^o_{3d}(\vec{r})-(V^o_c(\vec{r})+V^o_{ex}(\vec{r})) \qquad (44)$$

where, the Coulomb potential $V^o_c(\vec{r})$ and the exchange potential $V^o_{ex}(\vec{r})$ are evaluated from the total charge distribution $\rho_o(\vec{r})$ of a

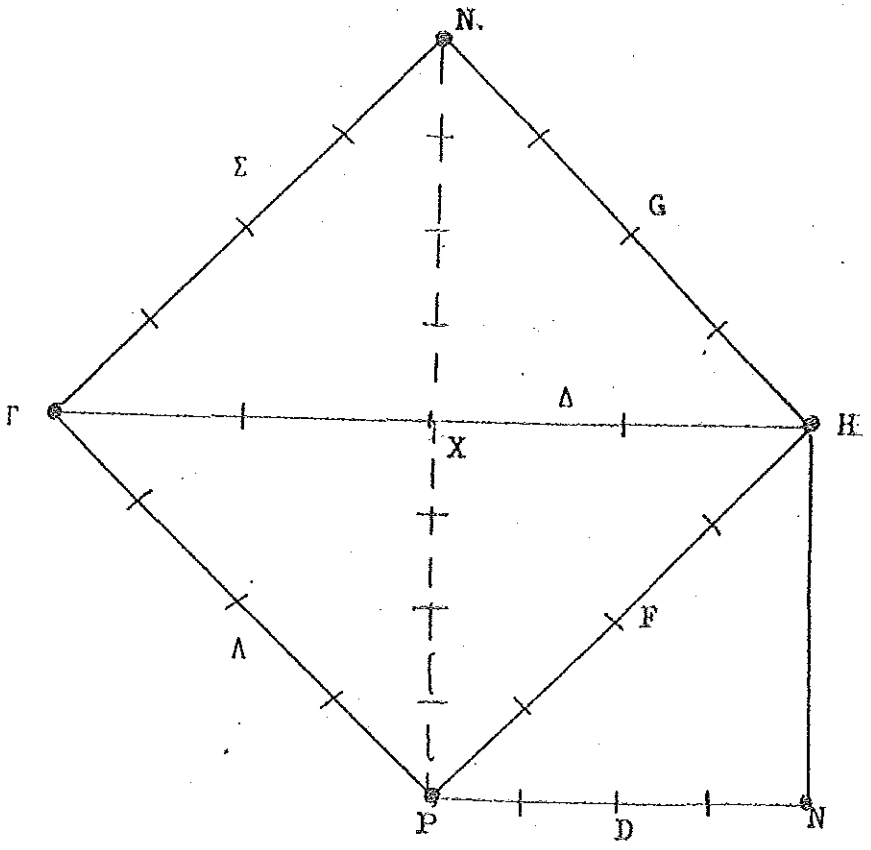

Fig.3. The 1/48 part of Brillouin zone faces showing the points at which $E(\vec{k})$-values are computed by Green's -function method.

Table 2. The calculated $E(k)$-values for paramagnetic Cr. The energies are given in *rydberg* units and the symbols following the energies are irreducible representation labels defined by B.S.W.†

$\Gamma(0\,0\,0)$	−.76453 1	−.31928 25′	−.31928 25′	−.31928 25′	−.18604 12	−.18604 12
$\Delta(\frac{2}{4}\,0\,0)$	−.67118 1	−.31715 5	−.31715 5	−.28614 2′	−.24634 2	−.16098 1
$\Delta(\frac{4}{4}\,0\,0)$	−.50175 1	−.38723 2	−.27707 5	−.27707 5	−.20445 2′	−.06181 1
$\Delta(\frac{6}{4}\,0\,0)$	−.51859 2	−.51716 1	−.16938 5	−.16938 5	−.12051 2′	
$H(\frac{8}{4}\,0\,0)$	−.57001 12	−.57001 12	−.08518 25′	−.08518 25′	−.08518 25′	
$\Delta(\frac{2}{4}\,\frac{2}{4}\,\frac{2}{4})$	−.69332 1	−.34037 3	−.34037 3	−.25988 1	−.19296 3	−.19296 3
$\Delta(\frac{4}{4}\,\frac{4}{4}\,\frac{4}{4})$	−.52718 1	−.39551 3	−.39551 3	−.18303 3	−.18303 3	−.09326 1
$\Delta(\frac{6}{4}\,\frac{6}{4}\,\frac{6}{4})$	−.42558 3	−.42558 3	−.39484 1	−.16405 3	−.16405 3	
$P(\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4})$	−.40717 4	−.40717 4	−.40717 4	−.15666 3	−.15666 3	
$\Sigma(\frac{2}{4}\,\frac{2}{4}\,0)$	−.71623 1	−.33637 2	−.32244 1	−.28584 3	−.20111 1	−.18384 4
$\Sigma(\frac{4}{4}\,\frac{4}{4}\,0)$	−.60372 1	−.37577 2	−.33073 1	−.20514 1	−.19940 3	−.17649 4
$\Sigma(\frac{6}{4}\,\frac{6}{4}\,0)$	−.55354 1	−.41283 2	−.23483 1	−.18271 1	−.16601 4	−.10227 3
$N(\frac{3}{4}\,\frac{3}{4}\,0)$	−.56023 1	−.42758 2	−.18073 1	−.16067 4	−.10758 1′	−.05775 3
$F(\frac{2}{4}\,\frac{2}{4}\,\frac{6}{4})$	−.52844 3	−.52844 3	−.20644 1	−.10660 3	−.10660 3	
$F(\frac{4}{4}\,\frac{4}{4}\,\frac{6}{4})$	−.43730 3	−.43730 3	−.39073 1	−.14620 3	−.14620 3	
$F(\frac{6}{4}\,\frac{6}{4}\,\frac{6}{4})$	−.45729 1	−.38650 3	−.38650 3	−.16051 3	−.16051 3	
$G(\frac{2}{4}\,0\,\frac{6}{4})$	−.54446 1	−.53930 4	−.15341 3	−.13596 1	−.08119 2	
$G(\frac{4}{4}\,0\,\frac{6}{4})$	−.50443 1	−.45054 4	−.28356 3	−.22015 1	−.07154 2	
$G(\frac{6}{4}\,0\,\frac{6}{4})$	−.53137 1	−.38853 3	−.31055 4	−.21078 1	−.06180 2	
$(\frac{1}{4}\,\frac{1}{4}\,\frac{5}{4})$	−.49139 +	−.40489 −	−.32727 +	−.24424 −	−.14703 +	−.03831 +
$(\frac{3}{4}\,\frac{3}{4}\,\frac{5}{4})$	−.47339 +	−.41902 −	−.35305 +	−.19397 −	−.14592 +	.08554 +
$(\frac{5}{4}\,\frac{5}{4}\,\frac{5}{4})$	−.44858 +	−.41381 −	−.36750 +	−.16408 −	−.15739 +	
$(\frac{2}{4}\,0\,\frac{5}{4})$	−.50053 +	−.38933 +	−.31968 −	−.25250 +	−.16234 −	−.05720 +
$(\frac{4}{4}\,0\,\frac{5}{4})$	−.52146 +	−.37533 −	−.34056 +	−.21405 +	−.10799 −	−.05022 +
$(\frac{6}{4}\,0\,\frac{5}{4})$	−.54916 +	−.41393 −	−.24350 +	−.18818 +	−.07079 −	−.06424 +
$D(\frac{1}{4}\,\frac{1}{4}\,\frac{3}{4})$	−.54040 1	−.42994 4	−.20093 3	−.17731 1	−.16007 2	
$D(\frac{3}{4}\,\frac{3}{4}\,\frac{3}{4})$	−.48933 1	−.43323 4	−.29347 3	−.16899 1	−.15866 2	
$D(\frac{5}{4}\,\frac{5}{4}\,\frac{3}{4})$	−.43270 1	−.42865 4	−.36280 3	−.16036 1	−.15724 2	

†B.S.W = Brillouin, Smoluchowski, Wigner notation (Ref.14).

CHAPTER 5

INTERPOLATION AND EXTRAPOLATION OF THE ENERGY BANDS IN CHROMIUM

5.1 Energy Band Structure of Cr by the Slater - Koster Interpolation Scheme.

The central problem of this project being determination of the electronic energy band structure of Cr, we are now in a position to extrapolate the energy band structure in the whole BZ. This is achieved by using the values of E(K) computed by the ab - initio method (the Green's function method) at few points in the 1/48 part of the BZ.

Chromium located in the fourth row and 6B column of the periodic table is a transition metal. The stable room temperature form of Cr is body centered Cubic (bcc) Bravais lattice. The electronic configuration of Cr is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$, its atomic number is 24 and has lattice parameter of length 3.21 A^o.

Each atom in the bcc structure has eight nearest neighbours only along the body diagonal directions $<111>$, six second nearest neighbours along $<100>$ directions and twelve third nearest neighbours along the face diagonal directions $<110>$.

The schroedinger equation for the electrons in Cr can be written as:

$$\hat{H} \Psi_{K,n} = E^n_{K,n} \Psi_{K,n} \qquad (47)$$

Multiplying both sides of eq.(47) from the left by the complex conjugate of another wave function $\Psi^*_{K,n}$ in the biorthonormal set give rise to a secular equation:

$$| H_{nm} - E S_{nm} | = 0 \qquad (48)$$

Here, H_{nm} is the matrix element of the Hamiltonian in the n^{th} row and m^{th} colum. Hence, H_{nm} simply represents the expression in eq. (12)

$$H_{nm} = \sum_j \exp(i\vec{k}.(\vec{R}_j - \vec{R}_i)) \int \psi_n^* (\vec{r} - \vec{R}_i)\, \hat{H}(\vec{r})\, \psi_m(\vec{r} - \vec{R}_j)\, dv \qquad (49)$$

To get a more convenient expression in eq. (49) fix $\vec{R}_i$ at the origin consequently reducing the three - center integral to two - center integral.

$$H_{nm} = \sum_j \exp(i\vec{k}.\vec{R}_j) \int \psi_n^* (\vec{r})\, \hat{H}(\vec{r})\, \psi_m(\vec{r} - \vec{R}_j)\, dv \qquad (50)$$

Now the wave - functions ψ_n's can be chosen to be orthonormalized atomic orbitals.

For our purpose the atomic wave - functions in the integral of eq. (50) are the non-degenerate s-orbital, the triply degenerate p-orbital and the five - fold degenerate d-type atomic orbital.

The s-type atomic orbital is spherically symmetrical, so that the charge - cloud density is a function only of r.

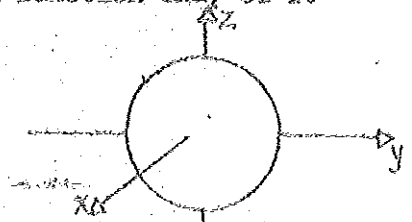

Fig (4) The s-type atomic orbital.

The 3p - type atomic orbital in which the boundary surface consists of two regions together resembling a "dumb - bell". These functions will have transformation properties like the sets x,y,z.

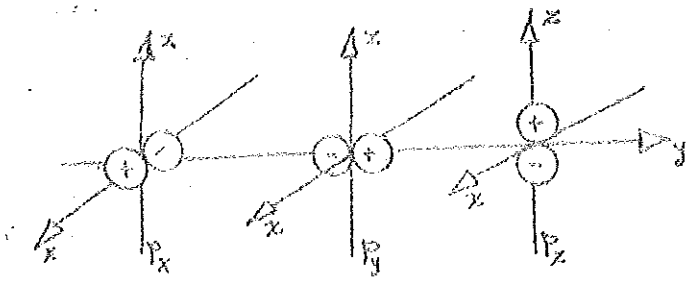

Fig (5) The 3p - type atomic orbitals p_x , p_y and p_z.

There is a marked directional character in these orbitals, which is exhibited by means of a suffix p_x, p_y, p_z. The other important characteristic of these atomic orbitals is that the regions where the wave - function is of opposite sign are separated by a "nodal plane", over which the wave - function is zero.

The five - fold degenerate atomic orbitals have transformation properties like the sets xy, yz, zx, $x^2 - y^2$, $3z^2 - r^2$.

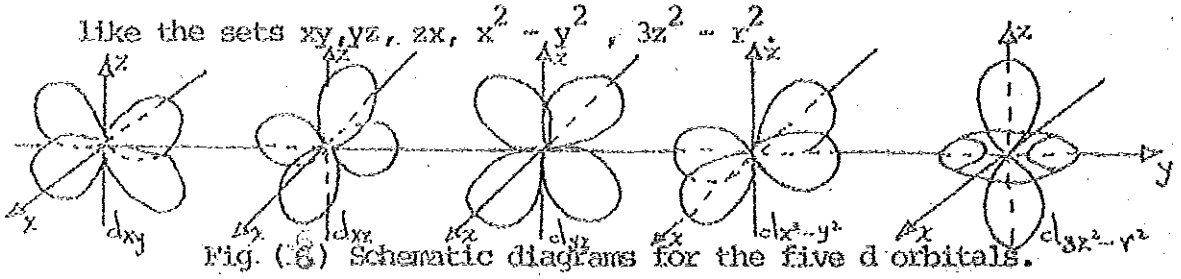

Fig. (6) Schematic diagrams for the five d orbitals.

We have now nine atomic wave - function which can be used as the basis of the reducible representation. In the foregoing discussion the following abbreviations will be employed

$$\psi_s = |1\rangle \ , \ \psi_{px} = |2\rangle, \ \psi_{py} = |3\rangle, \ \psi_{pz} = |4\rangle, \ \psi_{dxy} = |5\rangle \quad (51)$$

$$\psi_{dxz} = |6\rangle \ , \ \psi_{dyz} = |7\rangle, \ \psi_{dx^2-y^2} = |8\rangle, \ \psi_{d3z^2-r} = |9\rangle$$

We let the atoms to be located at the vector positions

$$\vec{R}_j = \alpha_1 a \hat{i} + \alpha_2 a \hat{j} + \alpha_3 a \hat{k} \quad (52)$$

Here, α_1, α_2, α_3 are integers, 2a is the lattice parameter and $\hat{i}$, $\hat{j}$, $\hat{k}$ are unit vectors along the x, y, z axis respectively. Let the subscripts n, m refer to two out of the set of atomic wave - functions used as the basis of the reducible representation. Then we shall denote our integrals in eq. (50) by the expression:

$$E_{nm}(\alpha_1 \alpha_2 \alpha_3) = \int \psi_n^{*}(\vec{r})\, \hat{H}(\vec{r})\, \psi_m(\vec{r}-\alpha_1 a\hat{i}-\alpha_2 a\hat{j}-\alpha_3 a\hat{k})\, dv \qquad (53)$$

Then the matrix components of energy between the Bloch sums in terms of the newly defined parameters $E_{nm}(\alpha_1 \alpha_2 \alpha_3)$ is given by

$$H_{nm} = \sum_{|\alpha_1|=0,1,2} \exp i(\alpha_1 k_x a + \alpha_2 k_y a + \alpha_3 k_z a)\, E_{nm}(\alpha_1 \alpha_2 \alpha_3) \qquad (54)$$

We now wish to express our matrix components of energy in terms of the smallest set of integrals which are given by eq. (53) that is possible. This is done by making use of all relations between these integrals which symmetry permits. So that the various E's in the matrix component of the energy are all independent. This is crucial for we treat them all as disposable constants in the Slater - Koster interpolation scheme.

Taking contribution from the nearest, first nearest and second nearest neighbours amongst the nine atomic wave - functions in the integral equation to eq. (54) there will be 2106 types of integrals but most of them are dependent. By judious use of symmetry arguments only 45 E's are found out to be independent. These independent parameters are given in Table 4.

The matrix components of energy between the Bloch sums of the nine atomic orbitals can now be constructed using the thirty - one independent E's. There are 81 matrix components, but by virtue of the fact that the Hamiltonian operator is Hermitian the matrix elements above and below the diagonal are related by

$$H_{mn} = H_{nm}^{*} \qquad (55)$$

Hence, it is sufficient to derive the upper triangular matrix elements. And these forty-five matrix elements are given in Table 3. And the abbreviation $\alpha = ak_x$, $\beta = ak_y$ and $\delta = ak_z$ is employed. Furthermore new notation is adapted to denote the matrix elements

$$(n \mid M) = H_{nm} \qquad (56)$$

Some matrix elements of energy for simple cubic crystals are given in the paper of J.C. Slater and G.F. Koster (Table 2 of ref. 9). These elements are sufficent to derive the rest and can be adapted to the body centered cubic structure case by applying the required symmetry transformation.

To compute the energy band structure we have to solve a set of secular equations given by eq. (48). This is done most systematically along the six lines of particular symmetry, at the four special points of symmetry and along low symmetry direction in the 1/48 part of the BZ which is depicted in fig.2.

The secular matrix for each line and point of symmetry will be 9 x 9 and complex. The numerical solution of such an equathn is tedious. But, by using the symmetry adapted wave - functions as basis functions rather than the simple atomic orbitals, the secular equations can be reduced to the simplified irreducible form. The symmetry adapted basis functions are constructed by the method of projection operator discussed in chapter 4. These symmetry adapted wave functions together with the secular equations in irreducible form for all symmetry points, lines as well as for general direction are given in Appendix A.

As a foregoing example let's construct the secular equation for the symmetry direction Σ . The symmetry adapted wave functions for this case have already been constructed in Chapter 4.

For Σ direction $k_x = k_y \in (0, \pi/2a)$ and $k_z = 0$, hence $\alpha = \beta \in (0, \pi/2)$ and $\delta = 0$. The symmetry adapted wave - functions given in eq. (38) employing the new notation are as follows:

$$\Sigma \sim \{ |1), |2'), |5), |9) \}$$
$$\Sigma_2 \sim \{ |6') \}$$
$$\Sigma_3 \sim \{ |4), |7') \}$$

$$\Sigma_4 \sim \{|3'\rangle, |8\rangle\} \tag{57}$$

where, $|2'\rangle = \frac{1}{\sqrt{2}}(|2\rangle + |3\rangle)$

$|6'\rangle = \frac{1}{\sqrt{2}}(|6\rangle - |7\rangle)$

$|7'\rangle = \frac{1}{\sqrt{2}}(|6\rangle + |7\rangle)$

$|3'\rangle = \frac{1}{\sqrt{2}}(|2\rangle - |3\rangle)$

The secular matrix for Σ - direction is constructed using the preceeding symmetrized wave - functions for this direction. Consequently, the resulting equation have the reduced form eq. (21). The irreducible representations of Σ are Σ_1, Σ_2, Σ_3 and Σ_4. Thus we have

$$\Sigma = 4\Sigma_1 + \Sigma_2 + 2\Sigma_3 + 2\Sigma_4 \tag{58}$$

Here, each Σ_i correspond to different energy level and the coefficient of Σ_i indicates order of degeneracy of the level. The secular matrix in irreducible form is

$$\begin{vmatrix} & & & & 0 & 0 & 0 & 0 & 0 \\ & & & & 0 & 0 & 0 & 0 & 0 \\ & A & & & 0 & 0 & 0 & 0 & 0 \\ & & & & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & B & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & & C & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & & & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & D & \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & & \end{vmatrix} = 0 \tag{59}$$

Where

$$/A/ = \begin{vmatrix} (1/1) - E(\Sigma_1) & (1/2') & (1/5) & (1/9) \\ (2'/1) & (2'/2') - E(\Sigma_1) & (2'/5) & (2'/9) \\ (5/1) & (5/2') & (5/5) - E(\Sigma_1) & (5/9) \\ (9/1) & (9/2') & (9/5) & (9/9) - E(\Sigma_1) \end{vmatrix} = 0$$

$$/B/ = (6'/6') - E(\Sigma_2) = 0 .$$

$$/C/ = \begin{vmatrix} (4/4) - E(\Sigma_3) & (4/7') \\ (7/4') & (7'/7') - E(\Sigma_3) \end{vmatrix} = 0$$

$$/D/ = \begin{vmatrix} (3'/3') - E(\Sigma_4) & (3'/8) \\ (8/3') & (8/8 - E(\Sigma_4) \end{vmatrix} = 0$$

For a given joint in the Σ - direction, that is for fixed value of k_x, k_y and k_z all the above matrix elements in the secular equation are expressed as a function of the thirty one independent E's. The value of the energies which are eigenvalues of the above equations is given in Table 2.

From the secular equations for the symmetry points and lines 129 linear and non-linear equations can be obtained from the available data of energy values in Table 2.

In the final analysis the task of extrapolating the whole BZ is reduced to solving a set of 129 linear and non-linear equations in 31 independent parameters.

Table 3. Matrix elements of the Hamiltonian.

$(1|1) = E_{11}(000) + 8E_{11}(111)\mathrm{Cos}\alpha\mathrm{Cos}\beta\mathrm{Cos}\delta + 2E_{11}(200)(\mathrm{Cos}2\alpha + \mathrm{Cos}2\beta + \mathrm{Cos}2\delta) + 4E_{11}(220)(\mathrm{Cos}2\alpha\mathrm{Cos}2\beta + \mathrm{Cos}2\alpha\mathrm{Cos}2\delta + \mathrm{Cos}2\beta\mathrm{Cos}2\delta)$

$(1|2) = 8iE_{12}(111)\ \mathrm{Sin}\alpha\mathrm{Cos}\beta\mathrm{Cos}\delta + 2iE_{12}(200)\mathrm{Sin}2\alpha + 4iE_{12}(220)(\mathrm{Sin}2\alpha\mathrm{Cos}2\beta + \mathrm{Sin}2\alpha\mathrm{Cos}2\delta)$

$(1|3) = 8iE_{12}(111)\mathrm{Cos}\alpha\mathrm{Sin}\beta\mathrm{Cos}\delta + 2iE_{12}(200)\mathrm{Sin}2\beta + 4iE_{12}(220)\mathrm{Sin}2\beta(\mathrm{Cos}2\delta + \mathrm{Cos}2\alpha)$

$(1|4) = 8iE_{12}(111)\mathrm{Cos}\alpha\mathrm{Cos}\beta\,\mathrm{Sin}\delta + 2iE_{12}(200)\mathrm{Sin}2\delta + 4iE_{12}(220)\mathrm{Sin}2\delta(\mathrm{Cos}2\alpha + \mathrm{Cos}2\beta)$

$(1|5) = -8E_{15}(111)\mathrm{Sin}\alpha\mathrm{Sin}\beta\mathrm{Cos}\delta - 4E_{15}(220)\mathrm{Sin}2\alpha\mathrm{Sin}2\beta$

$(1|6) = -8E_{15}(111)\mathrm{Sin}\alpha\mathrm{Cos}\beta\,\mathrm{Sin}\delta - 4E_{15}(220)\mathrm{Sin}2\alpha\mathrm{Sin}2\delta$

$(1|7) = -8E_{15}(111)\mathrm{Cos}\alpha\mathrm{Sin}\beta\,\mathrm{Sin}\delta - 4E_{15}(220)\mathrm{Sin}2\alpha\mathrm{Sin}2\delta$

$(1|8) = \sqrt{3}\,E_{19}(002)(\mathrm{Cos}2\alpha - \mathrm{Cos}2\beta) + 2\sqrt{3}\,E_{19}(220)(-\mathrm{Cos}2\alpha\mathrm{Cos}2\delta + \mathrm{Cos}2\beta\mathrm{Cos}2\delta)$

$(1|9) = E_{19}(002)(-\mathrm{Cos}2\alpha - \mathrm{Cos}2\beta + 2\mathrm{Cos}2\delta) - 2E_{19}(220)(-2\mathrm{Cos}2\alpha\mathrm{Cos}2\beta + \mathrm{Cos}2\alpha\mathrm{Cos}2\delta + \mathrm{Cos}2\beta\mathrm{Cos}2\delta)$

$(2|2) = E_{22}(000) + 8E_{22}(111)\mathrm{Cos}\alpha\mathrm{Cos}\beta\mathrm{Cos}\delta + 2E(200)\mathrm{Cos}2\alpha + 2E_{33}(200)(\mathrm{Cos}2\beta + \mathrm{Cos}2\delta) + 4E_{22}(220)(\mathrm{Cos}2\alpha\mathrm{Cos}2\beta + \mathrm{Cos}2\alpha\mathrm{Cos}2\delta) + 4E_{22}(022)\mathrm{Cos}2\beta\mathrm{Cos}2\delta$

$(2|3) = -8E_{23}(111)\mathrm{Sin}\alpha\mathrm{Sin}\beta\mathrm{Cos}\delta - 4E_{23}(220)\ \mathrm{Sin}2\alpha\mathrm{Sin}2\beta$

$(2|4) = -8E_{23}(111)\mathrm{Sin}\alpha\mathrm{Cos}\beta\,\mathrm{Sin}\delta - 4E_{23}(220)\ \mathrm{Sin}2\delta\,\mathrm{Sin}2\beta$

$(2|5) = -8iE_{25}(111)\mathrm{Cos}\alpha\mathrm{Sin}\beta\mathrm{Cos}\delta + 2iE_{25}(020)\mathrm{Sin}2\beta + 4iE_{25}(220)\mathrm{Cos}2\alpha\mathrm{Sin}2\beta + 4iE_{25}(022)\ \mathrm{Sin}2\beta\mathrm{Cos}2\delta$

$(2|6) = 8iE_{25}(111)\mathrm{Cos}\alpha\mathrm{Cos}\beta\,\mathrm{Sin}\delta + 2iE_{25}(020)\mathrm{Sin}2\delta + 4iE_{25}(220)\mathrm{Cos}2\alpha\mathrm{Sin}2\delta + 4iE_{25}(022)\mathrm{Sin}2\delta\,\mathrm{Cos}2\beta$

$(2|7) = -8iE_{27}(111)\ Sin\alpha Sin\beta Sin\delta$

$(2|8) = 8iE_{28}(111)\ Sin\alpha Cos\beta Cos\delta + \sqrt{3}iE_{49}(002)\ Sin2\alpha$

$(2|9) = -\frac{8}{\sqrt{3}}iE_{28}(111)\ Sin\alpha Cos\beta Cos\delta - iE_{49}(002)\ Sin2\alpha - 2iE_{49}(022)$
$(Sin2\alpha Cos2\beta + Sin2\alpha Cos2\delta) + 2\sqrt{3}iE_{49}(022)(Sin2\alpha Cos2\beta -$
$Sin2\alpha Cos2\delta)$

$(3|3) = E_{22}(000) + 8E_{22}(111)\ Cos\alpha Cos\beta Cos\delta + 2E_{22}(200)Cos2\beta + 2E_{33}(200)$
$(Cos2\alpha + Cos2\delta) + 4E_{22}(022)Cos2\alpha Cos2\delta + 4E_{22}(220)Cos2\beta\ (Cos2\alpha + Cos2\delta)$

$(3|4) = -8E_{23}(111)Cos\alpha Sin\beta Sin\delta - 4E_{23}(220)Sin2\alpha Sin2\beta$

$(3|5) = 8iE_{25}(111)Sin\alpha Cos\beta Cos\delta + 2iE_{25}(020)Sin2\alpha + 4iE_{25}(020)Sin2\alpha Cos2\delta +$
$4iE_{25}(022)\ Sin2\alpha\ Cos2\delta$

$(3|6) = -8iE_{27}(111)Sin\alpha\ Sin\beta\ Sin\delta$

$(3|7) = 8iE_{25}(111)Cos\alpha Cos\beta Sin\delta + 2iE_{25}(020)Sin2\delta + 4iE_{25}(220)Cos2\beta Sin2\delta +$
$4iE_{25}(022)Sin2\delta Cos2\alpha$

$(3|8) = -8iE_{25}(111)Cos\alpha Sin\beta Cos\delta - \sqrt{3}iE_{49}(002)Sin2\beta -$
$2\sqrt{3}iE_{49}(022)Sin2\beta\ (Cos2\delta + Cos2\alpha) + 2iE_{49}(022)Sin2\beta\ (Cos2\delta - Cos2\alpha)$

$(3|9) = -8/\sqrt{3}iE_{28}(111)Cos\alpha Sin\beta Cos\delta - iE_{49}(002)Sin2\beta -$
$2iE_{49}(022)Sin2\beta\ (Cos2\alpha + Cos2\delta) + 2\sqrt{3}iE_{48}(022)Sin2\beta\ (Cos2\alpha - Cos2\delta)$

$(4|4) = E_{22}(000) + 8E_{22}(111)Cos\alpha Cos\beta Cos\delta + 2E_{22}(200)Cos\delta + 2E_{33}(200)$
$(Cos2\alpha + Cos2\beta) + 4E_{22}(022)Cos2\alpha Cos2\beta + 4E_{22}(220)Cos2\delta\ (Cos2\alpha + Cos2\beta)$

$(4|5) = -8iE_{27}(111)Sin\alpha Sin\beta Sin\delta$

$(4|6) = 8iE_{25}(111)Sin\alpha Cos\beta Cos\delta + 2iE_{25}(020)Sin2\alpha + 4iE_{25}(220)Cos2\delta Sin2\alpha +$
$4iE_{25}(022)Sin2\alpha Cos2\beta$

$(4|7) = 8iE_{25}(111)Cos\alpha Sin\beta Cos\delta + 2iE_{25}(020)Sin2\beta + 4iE_{25}(220)Sin2\beta Cos2\delta +$
$4iE_{25}(022)Cos2\alpha Sin2\beta$

$(4|8) = 0$

$$(4|9) = \frac{16}{\sqrt{3}} iE_{28}(111)\mathrm{Cos}\alpha\mathrm{Cos}\beta\,\mathrm{Sin}\delta + 2iE_{49}(002)\mathrm{Sin}2\delta + 4iE_{49}(022)$$
$$(\mathrm{Cos}2\alpha\mathrm{Sin}2\delta + \mathrm{Cos}2\beta\,\mathrm{Sin}2\delta)$$

$$(5|5) = E_{55}(000) + 8E_{55}(111)\mathrm{Cos}\alpha\mathrm{Cos}\beta\,\mathrm{Cos}\delta + 2E_{55}(200)(\mathrm{Cos}2\alpha + \mathrm{Cos}2\beta) +$$
$$2E_{55}(002)\mathrm{Cos}2\delta + 4E_{55}(220)\mathrm{Cos}2\alpha\mathrm{Cos}2\beta + 4E_{55}(022)(\mathrm{Cos}2\alpha\mathrm{Cos}2\delta +$$
$$\mathrm{Cos}2\beta\,\mathrm{Cos}2\delta)$$

$$(5|6) = -8E_{56}(111)\mathrm{Cos}\alpha\mathrm{Sin}\beta\,\mathrm{Sin}\delta - 4E_{56}(022)\mathrm{Sin}2\beta\,\mathrm{Sin}2\delta$$

$$(5|7) = -8E_{56}(111)\mathrm{Sin}\alpha\mathrm{Cos}\beta\,\mathrm{Sin}\delta - 4E_{56}(022)\mathrm{Sin}2\beta\,\mathrm{Sin}2\delta$$

$$(5|8) = 0$$

$$(5|9) = -8E_{59}(111)\mathrm{Sin}\alpha\mathrm{Sin}\beta\,\mathrm{Cos}\delta - 4E_{59}(220)\mathrm{Sin}2\alpha\mathrm{Sin}2\beta$$

$$(6|6) = E_{55}(000) + 8E_{55}(111)\mathrm{Cos}\alpha\mathrm{Cos}\beta\,\mathrm{Cos}\delta + 2E_{55}(200)(\mathrm{Cos}2\alpha + \mathrm{Cos}2\delta) +$$
$$2E_{55}(002)\mathrm{Cos}2\beta + 4E_{55}(220)\mathrm{Cos}2\beta\,(\mathrm{Cos}2\alpha + \mathrm{Cos}2\delta)$$

$$(6|7) = -8E_{56}(111)\mathrm{Sin}\alpha\mathrm{Sin}\beta\,\mathrm{Cos}\delta - 4E_{56}(022)\mathrm{Sin}2\alpha\mathrm{Sin}2\beta$$

$$(6|8) = 4\sqrt{3}E_{59}(111)\mathrm{Sin}\alpha\mathrm{Cos}\beta\,\mathrm{Sin}\delta + 2\sqrt{3}E_{59}(220)\mathrm{Sin}2\alpha\mathrm{Sin}2\delta$$

$$(6|9) = 4E_{59}(111)\mathrm{Sin}\alpha\mathrm{Cos}\beta\,\mathrm{Sin}\delta + 2E_{59}(220)\mathrm{Sin}2\alpha\mathrm{Sin}2\delta$$

$$(7|7) = E_{55}(000) + 8E_{55}(111)\mathrm{Cos}\alpha\mathrm{Cos}\beta\,\mathrm{Cos}\delta + 2E_{55}(200)(\mathrm{Cos}2\beta + \mathrm{Cos}2\delta) +$$
$$2E_{55}(002)\mathrm{Cos}2\alpha + 4E_{55}(220)\mathrm{Cos}2\beta\,\mathrm{Cos}2\delta + 4E_{55}(022)\mathrm{Cos}2\alpha\,(\mathrm{Cos}2\beta + \mathrm{Cos}2\delta$$

$$(7|8) = -4\sqrt{3}E_{59}(111)\mathrm{Cos}\alpha\mathrm{Sin}\beta\,\mathrm{Sin}\delta - 2\sqrt{3}E_{59}(220)\mathrm{Sin}2\beta\,\mathrm{Sin}2\delta$$

$$(7|9) = 4E_{59}(111)\mathrm{Cos}\alpha\mathrm{Sin}\beta\,\mathrm{Sin}\delta + 2E_{59}(220)\mathrm{Sin}2\beta\,\mathrm{Sin}2\delta$$

$$(8|8) = E_{99}(000) + 8E_{99}(111)\mathrm{Cos}\alpha\mathrm{Cos}\beta\,\mathrm{Cos}\delta + \frac{3}{2}E_{99}(002)(\mathrm{Cos}2\alpha + \mathrm{Cos}2\beta) +$$
$$2E_{88}(002)(\tfrac{1}{4}\mathrm{Cos}2\alpha + \tfrac{1}{4}\mathrm{Cos}2\beta + \mathrm{Cos}2\delta) + 3E_{99}(220)(\mathrm{Cos}2\alpha\mathrm{Cos}2\delta +$$
$$\mathrm{Cos}2\beta\,\mathrm{Cos}2\delta) + 4E_{88}(220)(\mathrm{Cos}2\alpha\mathrm{Cos}2\beta + \tfrac{1}{4}\mathrm{Cos}2\alpha\mathrm{Cos}2\delta + \tfrac{1}{4}\mathrm{Cos}2\beta\,\mathrm{Cos}2\delta)$$

$$(8|9) = \sqrt{\tfrac{3}{2}}\,E_{99}(002)(-\mathrm{Cos}2\alpha + \mathrm{Cos}2\beta) - \sqrt{\tfrac{3}{2}}\,E_{88}(002)(-\mathrm{Cos}2\alpha + \mathrm{Cos}2\beta) +$$
$$\sqrt{3}\,E_{99}(220)(\mathrm{Cos}2\alpha\mathrm{Cos}2\delta - \mathrm{Cos}2\beta\,\mathrm{Cos}2\delta) - \sqrt{3}E_{88}(220)$$
$$(\mathrm{Cos}2\alpha\mathrm{Cos}2\delta - \mathrm{Cos}2\beta\,\mathrm{Cos}2\delta)$$

$$(9|9) = E_{99}(000) + 8E_{99}(111)\cos\alpha\cos\beta\cos\delta + 2E_{99}(002)\left(\frac{1}{4}\cos 2\alpha + \frac{1}{4}\cos 2\beta + \cos 2\alpha\right) + \frac{3}{2}E_{88}(002)(\cos 2\alpha + \cos 2\beta) + 4E_{99}(220)(\cos 2\alpha\cos 2\beta + \frac{1}{4}\cos 2\alpha\cos 2\delta + \frac{1}{4}\cos 2\beta\cos 2\delta) + 3E_{88}(220)(\cos 2\alpha\cos 2\delta + \cos 2\beta\cos 2\delta)$$

$E_{12}(220), E_{19}(220), E_{22}(220), E_{22}(022), E_{23}(220), E_{25}(220), E_{25}(022), E_{49}(022), E_{48}(022), E_{55}(022), E_{56}(022), E_{55}(022), E_{99}(220), E_{88}(220)$ are taken to have zero value.

5.2 Numerical Analysis and Computer Programming to Evaluate the Parameters.

As it is well known from the theory of simultaneous equations, one can expect a unique set of solutions if and only if the number of unknowns matches the number of equations. In our case the number of equations by far exceeds the number of unknowns. Mathematically the existence of unique solution is doubtfull. But based on physical ground we know that there exist a unique set of solutions. As a matter of fact, the 129 equations should be redundant or nearly redundant. Indentifying redundancy amongst the non-linear equations is a cumbersome task, so we resorte to other possibility to accomplish the primary purpose of determining the parameters.

Solving the linear set only six parameters can be obtained. These parameters are comparable with iron parameters [20]. Comparison of the band structure of Cr with that of iron calculated by Augmented plane wave method [21] shows that the band structures of Cr and Fe have the same shape except for some shift.

From this point of view it is reasonable to use the iron parameters as crude starting values and to refine them till they satisfy the 129 equations, there by reproducing the band structure along the symmetry lines of the BZ computed by first - principle method.

As can be seen explicitly in eq. (53) the parameters depend solely on the overlap of the orbitals. The parameters in absolute value will be greater for overlapping orbitals on the same center than for overlapping orbitals between nearest neighbours and this in turn is greater than the overlap between second nearest neighbours and so on. Based on this fact the thirty-one parameters can catagorized into four groups:-

1. $E_{11}(000)$, $E_{22}(000)$, $E_{55}(000)$, $E_{99}(000)$
2. $E_{11}(111)$, $E_{12}(111)$, $E_{15}(111)$, $E_{22}(111)$, $E_{23}(111)$, $E_{25}(111)$

   $E_{27}(111), E_{28}(111), E_{55}(111), E_{56}(111), E_{59}(111), E_{99}(111).$

3. $E_{11}(200)$, $E_{12}(200)$, $E_{19}(002)$, $E_{22}(200)$, $E_{33}(200)$
$E_{25}(020)$, $E_{49}(002)$, $E_{55}(200)$, $E_{66}(002)$, $E_{88}(002)$
$E_{99}(002)$ (60)

4. $E_{11}(220$, $E_{15}(220)$, $E_{55}(220)$, $E_{59}(220)$

Now using the iron parameters in table 4 as starting values the four parameters in group one are varied on an interval of length of one Ry with steps of 0.01 Ry. First $E_{11}(000)$ is varied fixing all other parameters. The value of $E_{11}(000)$ which yields the minimum absolute error in the process of solving the secular equations is taken as starting value for $E_{11}(000)$. Next $E_{22}(000)$ is varied in the same manner and its value which minimizes the absolute error in solving the secular equations is taken as starting value and the procedure continued for $E_{55}(000)$ and $E_{99}(000)$. The order of the parameters is cyclically interchanged, that is we start with $E_{22}(000)$ and after fixing it we continue varying $E_{55}(000)$, $E_{99}(000)$ and $E_{11}(000)$. This is also done starting with $E_{55}(000)$ and after fixing it the other three parameters are varied in the order shown in Table 5.

Had it not been for the tremendous computation time the programme consumes this process can be done for all sixteen permutation of the four parameters. The energy values of Cr for symmetry point Γ and symmetry line Σ are computed using the different values of the first four parameters in Table 5 is given in Table 6. These values of the energy are compared with those computed by using iron parameters in Fig 7. A satisfactory improvement is seen in reproducing the energy values computed by the KKR method. As expected amongst the new values of the first four parameters the best agreement is seen in the bands constructed using those parameters which minimized the error most in solving the secular equations.

The second part of this process uses the values of the first four parameters obtained by the first process and iron parameters for the rest. And all the 31 parameters are varied on an interval of length 0.1 Ry with steps 0.01 Ry. The sum of the absolute error in solving the secular equations decreased by one - half in the process of varying the parameters in the aforementioned interval. And above all the new values of all the thirty - one parameters lie with in the open interval. This suggests that to get better values the only requirement is to shrink the interval and refine the steps of variation. In this process the new values were varied on an interval of length 0.01 Ry with increment 0.001 Ry. In this case some of the newly obtained values lie on the edge of the interval. This is a doubtful situation for the best values may lie outside the interval. This was remedied by varying all of them on the same interval with the same increment but using the new values as starting ones. And the outcome highly reduced the error and all the thirty - one parameters lie in the open interval. And refining the widty of the interval and the steps further the variation continued in an interval of width 0.001 Ry and with an increment of 0.0001 Ry. The error kept on decreasing but not appreciably as before and finally varying in the same interval and with the same steps the error is found to strike the same value. This suggest to refine the interval and the increment but this is not acceptable for the initial values, that is the iron parameters were given to four decimal accuracy. The iteration which is strictly converging process was terminated at this point. The programme used in this method is given in flowchart form and in Fortran language in Appendix B.

Table 4. Values of the Interaction Integrals for Iron in Rydberg Units

$E_{11}(000) = 0.4041$	$E_{11}(200) = -0.0291$
$E_{22}(000) = 0.9815$	$E_{12}(200) = 0.0828$
$E_{55}(000) = -0.1103$	$E_{19}(002) = -0.0210$
$E_{99}(000) = -0.1188$	$E_{22}(200) = 00.2148$
$E_{11}(111) = -0.1341$	$E_{23}(200) = 0.0110$
$E_{12}(111) = 0.0876$	$E_{25}(020) = 0.0184$
$E_{15}(111) = -0.0363$	$E_{49}(002) = -0.0371$
$E_{22}(111) = 0.1036$	$E_{55}(200) = 0.0154$
$E_{23}(111) = 0.0765$	$E_{55}(002) = 0.0013$
$E_{25}(111) = -0.0310$	$E_{88}(002) = -0.0010$
$E_{27}(111) = -0.0305$	$E_{99}(002) = -0.0329$
$E_{28}(111) = 0.0251$	$E_{11}(220) = 0.0119$
$E_{55}(111) = -0.0131$	$E_{15}(220) = -0.0041$
$E_{56}(111) = -0.0208$	$E_{55}(220) = -0.0039$
$E_{59}(111) = -0.0182$	$E_{59}(220) = 0.0010$
$E_{99}(111) = 0.0218$	

Table 5. Values of the First Four Interaction Integrals Obtained by the First Process in Rydberg Units.

$E_{11}(000)$	0.3041	$E_{44}(000)$	0.4816	$E_{33}(000)$	-0.2703
$E_{22}(000)$	0.4815	$E_{55}(000)$	-0.2503	$E_{99}(000)$	-0.2588
$E_{55}(000)$	-0.2503	$E_{99}(000)$	-0.2588	$E_{11}(000)$	0.3241
$E_{99}(000)$	-0.2588	$E_{11}(000)$	0.3441	$E_{44}(000)$	0.7219

Table 6. The Calculated $E(\vec{K})$-Values in Rydberg Units for Cr.

a) Using the interaction integrals of iron.

$\Gamma(000)$	-0.70050 1	-0.16650 25	-0.16650 25	-0.16650 25	-0.04610 12	-0.04610 12
$\sum(\frac{\pi}{a}\frac{\pi}{a}0)$	—	-0.18063 2	—	-0.07778 3	—	—
$\sum(\frac{\pi}{a}\frac{\pi}{a}0)$	—	-0.21510 2	—	—	-0.07046 3	—
$\sum(\frac{3\pi}{a}\frac{3\pi}{a}0)$	—	-0.24750 2	—	—	—	-0.08343 3

b) Using the first four interaction integrals in the first column of Table(5).

$\Gamma(000)$	-0.80950 1	-0.30650 25	-0.30650 25	-0.30650 25	-0.18610 12	-0.18610 12
$\sum(\frac{\pi}{a}\frac{\pi}{a}0)$	—	-0.32063 2	—	-0.21778 3	—	—
$\sum(\frac{\pi}{a}\frac{\pi}{a}0)$	—	-0.35910 2	—	—	-0.23046 3	—
$\sum(\frac{3\pi}{a}\frac{3\pi}{a}0)$	—	-0.38749 2	—	—	—	-0.19447 3

c) Using the first four interaction integrals in the second column of Table(5).

$\Gamma(000)$	-0.76050 1	-0.30650 25	-0.30650 25	-0.30650 25	-0.2510 12	-0.21610 12
$\sum(\frac{\pi}{a}\frac{\pi}{a}0)$	—	-0.33620 2	—	-0.22977 3	—	—
$\sum(\frac{\pi}{a}\frac{\pi}{a}0)$	—	-0.38010 2	—	—	-0.24333 3	—
$\sum(\frac{3\pi}{a}\frac{3\pi}{a}0)$	—	-0.41732 2	—	—	—	-0.17030 3

d) Using the first four interaction integrals in the third column of Table(5).

$\Gamma(000)$	-0.77150 1	-0.32750 25	-0.32750 25	-0.32750 25	-0.17510 12	-0.17510 12
$\sum(\frac{\pi}{a}\frac{\pi}{a}0)$	—	-0.35602 2	—	-0.24641 3	—	—
$\sum(\frac{\pi}{a}\frac{\pi}{a}0)$	—	-0.40010 2	—	—	-0.21864 3	—
$\sum(\frac{3\pi}{a}\frac{3\pi}{a}0)$	—	-0.43732 2	—	—	—	-0.15107 3

Table 7. Values of the Interaction Integrals for Chromium in Rydberg Units

$E_{11}(000) = 0.3401$
$E_{22}(000) = 0.5240$
$E_{55}(000) = -0.2548$
$E_{99}(000) = -0.2536$
$E_{11}(111) = -0.1341E$
$E_{12}(111) = 0.9665$
$E_{15}(111) = -0.0387$
$E_{22}(111) = 0.0941$
$E_{23}(111) = 0.0365$
$E_{25}(111) = 0.0154$
$E_{27}(111) = -0.0224$
$E_{28}(111) = 0.0256$
$E_{55}(111) = -0.0151$
$E_{56}(111) = -0.0229$
$E_{59}(111) = -0.0201$
$E_{99}(111) = 0.0238$
$E_{11}(200) = -0.0291$
$E_{12}(200) = 0.1128$
$E_{19}(002) = -0.0169$
$E_{22}(200) = 0.1698$
$E_{33}(200) = 0.0315$
$E_{25}(020) = 0.0193$
$E_{49}(002) = -0.0296$
$E_{55}(200) = 0.0154$
$E_{55}(002) = 0.0030$
$E_{88}(002) = -0.0009$
$E_{99}(002) = -0.0418$
$E_{11}(220) = 0.0119$
$E_{15}(220) = -0.0061$
$E_{55}(220) = -0.0040$
$E_{59}(220) = 0.0005$

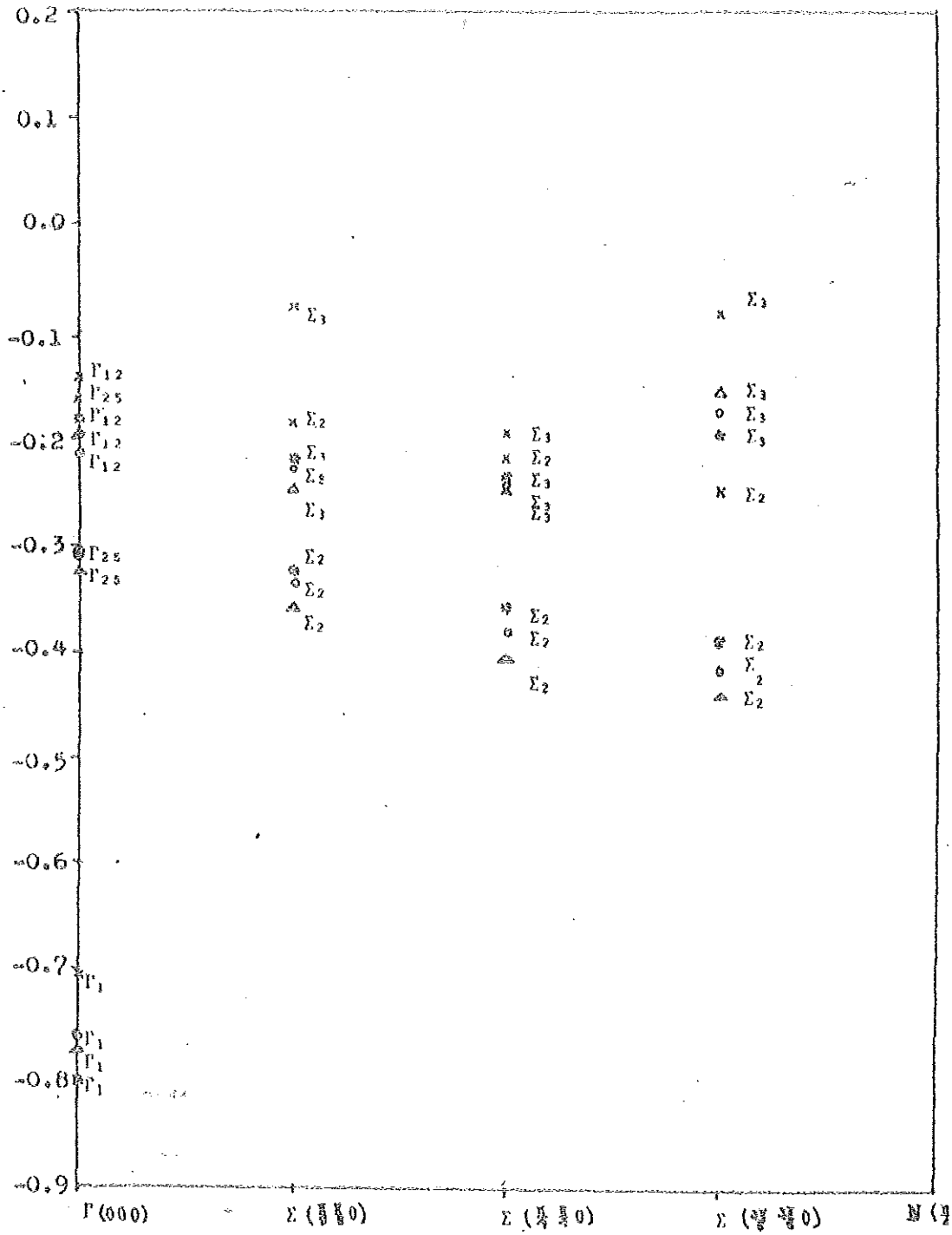

Fig. 7. $E(\vec{k})$-values in units of rydberg according to table 6. "x" stands for E(k)-values in part A of table 6., "*" in part B, "o" in part C and "Δ" in part D of table 6.

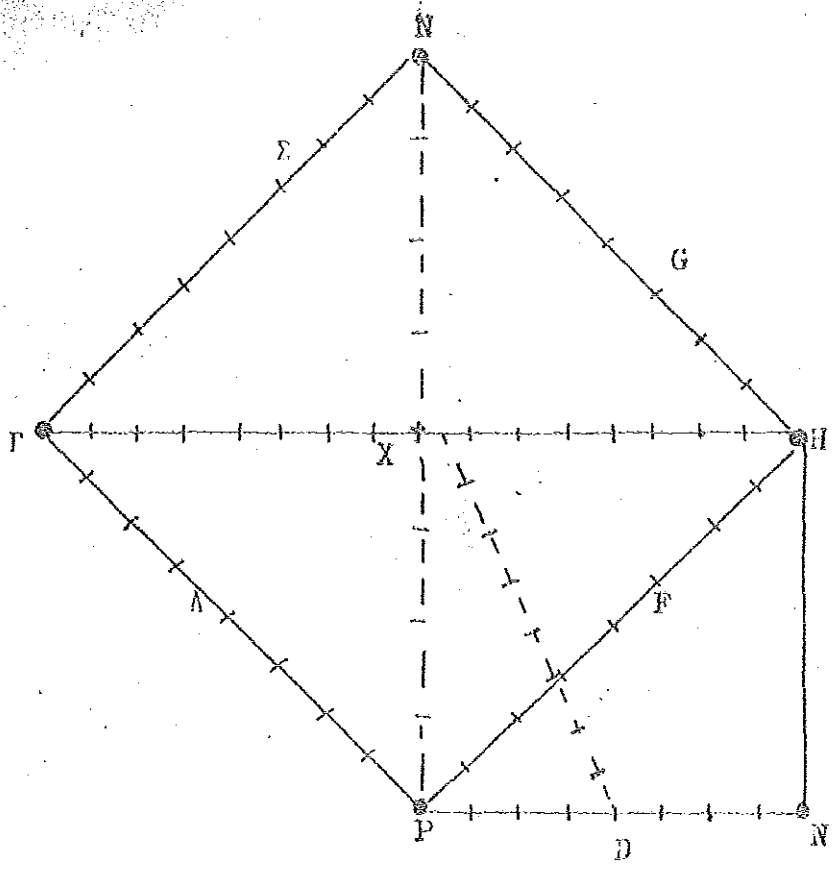

Fig. 8 . The 1/48 part of BZ faces showing the points at which $E(\vec{k})$ is computed by the Slater-Koster interpolation scheme.

Table 8. Energy-values Computed by the Slater-Foster Interpolation Scheme

$\Gamma'(000)$	−0.76450 1	−0.32377 4	−0.32377 2	−0.32377 2	−0.17127 12	−0.17129 12	1.74244 15	1.74244 15	1.74244 15
$\Delta(\frac{\pi}{16}00)$	−0.73171 1	−0.32281 5	−0.32281 5	−0.32214 2	−0.17858 1	−0.17482 2	1.70208 1	1.72314 5	1.72314 5
$\Delta(\frac{\pi}{8}00)$	−0.70861 1	−0.31914 5	−0.31914 5	−0.31656 2	−0.20526 2	−0.17112 1	1.68663 1	1.66664 5	1.66664 5
$\Delta(\frac{3\pi}{16}00)$	−0.68175 1	−0.31278 5	−0.31276 5	−0.30739 2	−0.22227 2	−0.15077 1	1.40589 1	1.57664 5	1.57664 5
$\Delta(\frac{\pi}{4}00)$	−0.64077 1	−0.30549 5	−0.30549 5	−0.29462 2	−0.24527 2	−0.16778 1	1.45231 1	1.45671 5	1.45671 5
$\Delta(\frac{5\pi}{16}00)$	−0.50037 1	−0.27078 5	−0.29078 5	−0.27861 2	−0.27343 2	−0.15883 1	0.93527 1	1.32072 5	1.32072 5
$\Delta(\frac{3\pi}{8}00)$	−0.47347 1	−0.30576 2	−0.27469 5	−0.27469 5	−0.25967 2	−0.11806 1	0.67775 1	1.17014 5	1.17014 5
$\Delta(\frac{7\pi}{16}00)$	−0.45211 1	−0.34107 2	−0.25524 5	−0.25524 5	−0.23831 2	−0.08121 1	0.48312 1	1.01526 5	1.01526 5
$\Delta(\frac{\pi}{2}00)$	−0.43446 1	−0.37810 2	−0.23280 5	−0.23280 5	−0.21520 2	−0.06426 1	0.31040 1	0.86360 5	0.86360 5
$\Delta(\frac{9\pi}{16}00)$	−0.44315 1	−0.41558 2	−0.20811 5	−0.20811 5	−0.19115 2	−0.01739 1	0.45235 1	0.72154 5	0.72154 5
$\Delta(\frac{5\pi}{8}00)$	−0.46628 1	−0.45147 2	−0.18224 5	−0.18224 5	−0.16722 2	0.01178 1	0.54397 5	0.81397 5	0.65107 1
$\Delta(\frac{11\pi}{16}00)$	−0.47386 1	−0.48497 2	−0.15655 5	−0.15655 5	−0.14438 2	0.00181 1	0.48426 5	0.48426 5	0.85493 1
$\Delta(\frac{3\pi}{4}00)$	−0.51453 2	−0.61351 1	−0.13258 5	−0.13258 5	−0.12378 2	0.01769 1	0.31429 5	0.39427 5	1.03066 1
$\Delta(\frac{13\pi}{16}00)$	−0.53890 2	−0.53101 1	−0.11110 5	−0.11110 5	−0.10646 2	0.05403 1	0.32478 5	0.32478 5	1.17771 1
$\Delta(\frac{7\pi}{8}00)$	−0.55708 2	−0.55402 1	−0.01593 5	−0.01593 5	−0.01335 2	0.07468 1	0.27565 5	0.27565 5	1.28864 1
$\Delta(\frac{15\pi}{16}00)$	−0.56830 2	−0.56808 1	−0.08585 5	−0.08585 5	−0.08518 2	0.13541 1	0.24647 5	0.24647 5	1.35762 1
$H(\pi00)$	−0.57201 12	−0.57201 12	−0.08240 25	−0.08240 25	−0.08240 25	0.23680 15	0.23680 15	0.23680 15	1.38110 1
$\Lambda(\frac{\pi}{16}\frac{\pi}{16}\frac{\pi}{16})$	−0.71146 1	−0.35413 3	−0.35413 3	−0.30544 1	−0.17246 3	−0.17246 3	1.61715 3	1.61715 3	3.00236 1
$\Lambda(\frac{3\pi}{8}\frac{3\pi}{8}\frac{3\pi}{8})$	−0.65715 1	−0.34322 3	−0.34322 3	−0.25527 1	−0.17432 3	−0.17432 3	1.51072 3	1.51072 3	3.00879 1
$\Lambda(\frac{3\pi}{16}\frac{3\pi}{16}\frac{3\pi}{16})$	−0.62248 1	−0.37761 3	−0.37761 3	−0.17845 3	−0.17845 3	−0.15332 1	1.25992 3	1.25992 3	3.37907 1
$\Lambda(\frac{\pi}{4}\frac{\pi}{4}\frac{\pi}{4})$	−0.53117 1	−0.39656 3	−0.39656 3	−0.18126 3	−0.18126 3	−0.02572 1	0.97210 3	0.97210 3	14.24147 1
$\Lambda(\frac{5\pi}{16}\frac{5\pi}{16}\frac{5\pi}{16})$	−0.44568 1	−0.41953 3	−0.41953 3	−0.16504 3	−0.16504 3	0.16164 1	0.69218 3	0.69218 3	0.24386 1
$\Lambda(\frac{3\pi}{8}\frac{3\pi}{8}\frac{3\pi}{8})$	−0.47143 1	−0.44775 3	−0.44775 3	−0.16717 3	−0.16717 3	0.39402 1	0.45569 3	0.45569 3	0.51736 1
$\Lambda(\frac{7\pi}{16}\frac{7\pi}{16}\frac{7\pi}{16})$	−0.58844 1	−0.49500 3	−0.49500 3	−0.13241 3	−0.13241 3	0.14681 1	0.27595 3	0.27595 3	0.61533 1
$P(\frac{\pi}{2}\frac{\pi}{2}\frac{\pi}{2})$	−0.40817 4	−0.40817 4	−0.40817 4	−0.12660 3	−0.12660 3	0.05840 4	0.05840 4	0.05840 4	0.65750 1

$\Sigma(\frac{\pi}{16}\ \frac{\pi}{16}\ 0)$	-0.72103	1	-0.32716	2	-0.32143	1	-0.31401	3	-0.17517	1	-0.18573	4	1.67421	4	1.70420	3	1.76905	1
$\Sigma(\frac{\pi}{8}\ \frac{\pi}{8}\ 0)$	-0.71601	1	-0.33923	2	-0.32160	1	-0.28657	3	-0.20477	1	-0.13217	4	1.55700	4	1.57650	3	1.85816	1
$\Sigma(\frac{3\pi}{16}\ \frac{3\pi}{16}\ 0)$	-0.65011	1	-0.35610	2	-0.31143	1	-0.24301	3	-0.20403	1	-0.18210	4	1.35164	4	1.43226	3	2.06647	1
$\Sigma(\frac{\pi}{4}\ \frac{\pi}{4}\ 0)$	-0.60294	1	-0.37600	2	-0.33316	1	-0.20324	1	-0.17250	3	-0.17020	4	1.10940	4	1.24000	3	2.71658	1
$\Sigma(\frac{5\pi}{16}\ \frac{5\pi}{16}\ 0)$	-0.57341	1	-0.37590	4	-0.24756	1	-0.22566	1	-0.16530	4	-0.14259	3	0.86716	4	1.04774	3	12.54578	1
$\Sigma(\frac{3\pi}{8}\ \frac{3\pi}{8}\ 0)$	-0.55358	1	-0.41277	2	-0.238001	1	-0.18482	1	-0.15521	4	-0.10003	3	0.46358	1	0.66180	4	0.88475	3
$\Sigma(\frac{7\pi}{16}\ \frac{7\pi}{16}\ 0)$	-0.54837	1	-0.42404	2	-0.22242	1	-0.17243	1	-0.13147	4	-0.07159	3	0.30128	1	0.52459	4	0.77584	3
$N(\frac{\pi}{2}\ \frac{\pi}{2}\ 0)$	-0.56026	1	-0.42777	2	-0.17707	1	-0.12710	4	-0.10760	1′	-0.06160	3	0.47015	1	0.47040	4	0.73760	3
$F(\frac{\pi}{8}\ \frac{\pi}{8}\ \frac{7\pi}{8})$	-0.53371	3	-0.53371	3	-0.22170	1	-0.10167	3	-0.10167	3	0.23803	3	0.23803	3	0.33583	1	1.13403	1
$F(\frac{\pi}{4}\ \frac{\pi}{4}\ \frac{3\pi}{4})$	-0.37313	3	-0.37313	3	-0.37610	1	-0.16456	3	-0.16456	3	0.21746	3	0.21746	3	0.43370	1	0.71737	1
$F(\frac{3\pi}{8}\ \frac{3\pi}{8}\ \frac{5\pi}{8})$	-0.50650	1	-0.37111	3	-0.37111	3	-0.15607	3	-0.15607	3	0.16467	3	0.16467	3	0.37410	1	0.57508	1
$G(\frac{\pi}{8}\ 0\ \frac{7\pi}{8})$	-0.53317	1	-0.53273	4	-0.16535	3	-0.15340	1	-0.07135	2	0.18636	4	0.27053	1	0.31014	3	1.20640	1
$G(\frac{\pi}{4}\ 0\ \frac{3\pi}{4})$	-0.50008	1	-0.48167	4	-0.29642	3	-0.22882	1	-0.07735	2	0.06460	4	0.35261	1	0.48720	3	0.81830	1
$G(\frac{3\pi}{8}\ 0\ \frac{5\pi}{8})$	-0.47415	1	-0.31250	3	-0.31912	4	-0.27376	1	-0.06465	2	-0.05716	4	0.43770	1	0.47720	1	0.66426	3
$(\frac{\pi}{16}\ \frac{\pi}{2}\ \frac{\pi}{16})$	-0.54500	+	-0.42567	−	-0.27733	+	-0.23377	−	-0.19314	+	-0.01130	+	0.24344	+	0.84262	−	1.43183	+
$(\frac{\pi}{8}\ \frac{\pi}{2}\ \frac{\pi}{8})$	-0.49070	+	-0.40703	−	-0.32130	+	-0.28121	−	-0.14584	+	-0.03130	−	0.27248	+	0.78247	−	2.00465	+
$(\frac{3\pi}{16}\ \frac{\pi}{2}\ \frac{3\pi}{16})$	-0.48849	+	-0.42772	−	-0.33070	+	-0.22761	−	-0.14716	+	-0.06255	+	0.32427	+	0.69127	−	3.72470	+
$(\frac{\pi}{4}\ \frac{\pi}{2}\ \frac{\pi}{4})$	-0.46207	+	-0.41252	−	-0.35237	+	-0.19866	−	-0.14902	+	-0.06927	+	0.00675	+	0.37830	+	0.58107	−
$(\frac{5\pi}{16}\ \frac{\pi}{2}\ \frac{5\pi}{16})$	-0.45773	+	-0.40703	−	-0.37372	+	-0.18753	−	-0.16072	+	-0.13672	+	0.08073	+	0.46625	−	0.48625	+
$(\frac{3\pi}{8}\ \frac{\pi}{2}\ \frac{3\pi}{8})$	-0.44472	+	-0.42042	−	-0.35753	+	-0.15542	−	-0.15375	+	0.66680	+	0.08469	+	0.36137	−	0.57772	+
$(\frac{7\pi}{16}\ \frac{\pi}{2}\ \frac{7\pi}{16})$	-0.42533	+	-0.40787	−	-0.40469	+	-0.14203	−	0.06734	+	0.06734	+	0.06734	+	0.27905	−	0.63442	+
$(\frac{\pi}{8}\ \frac{\pi}{2}\ 0)$	-0.53978	+	-0.31923	+	-0.31583	−	-0.21583	+	-0.19822	−	-0.10659	+	0.25135	+	0.66285	+	0.84515	−
$(\frac{\pi}{4}\ \frac{\pi}{2}\ 0)$	-0.54105	+	-0.36932	−	-0.34521	+	-0.24557	+	-0.15963	−	-0.04741	+	0.29249	+	0.34997	+	0.80060	−
$(\frac{3\pi}{8}\ \frac{\pi}{2}\ 0)$	-0.57056	+	-0.44610	−	-0.23289	+	-0.18737	+	-0.12256	−	-0.08737	+	0.20760	+	0.33365	+	0.75605	−
$D(\frac{\pi}{2}\ \frac{\pi}{2}\ \frac{\pi}{16})$	-0.55750	1	-0.42892	4	-0.22054	1	-0.15816	2	-0.10678	3	-0.04552	3	0.36238	1	0.46597	4	0.71051	1

$D(\frac{\pi}{2}\ \frac{\pi}{2}\ \frac{\pi}{8})$	−0.54720 1	−0.43167 4	−0.20595 3	−0.20383 1	−0.15857 2	−0.00973 3	0.39563 1	0.43592 4	0.64743 1
$D(\frac{\pi}{2}\ \frac{\pi}{2}\ \frac{3\pi}{16})$	−0.52174 1	−0.43653 4	−0.24725 3	−0.19267 1	−0.15799 2	0.06659 3	0.38830 4	0.44540 1	0.58283 1
$D(\frac{\pi}{2}\ \frac{\pi}{2}\ \frac{\pi}{4})$	−0.48145 1	−0.44482 4	−0.28508 3	−0.17287 1	−0.15730 2	0.15917 3	0.32788 4	0.50410 1	0.53717 1
$D(\frac{\pi}{2}\ \frac{\pi}{2}\ \frac{5\pi}{16})$	−0.47606 1	−0.46097 4	−0.29444 3	−0.16438 1	−0.15661 2	0.31740 3	0.25952 4	0.50948 1	0.56250 1
$D(\frac{\pi}{2}\ \frac{\pi}{2}\ \frac{3\pi}{8})$	−0.43897 1	−0.41617 4	−0.33427 3	−0.15911 1	−0.15603 2	0.18860 4	0.18860 4	0.48642 1	0.61257 1
$D(\frac{\pi}{2}\ \frac{\pi}{2}\ \frac{7\pi}{16})$	−0.41824 1	−0.41625 4	−0.34672 3	−0.13703 1	−0.15564 2	0.00623 3	0.12016 4	0.45271 1	0.64582 1
$(0\ \frac{2644\pi}{512}\ 0)$	−0.62513	−0.28544	−0.24625	−0.23957	−0.21731	−0.20924	0.28712	0.82697	1.25576
$(\frac{\pi}{16}\ \frac{2632\pi}{512}\ \frac{\pi}{16})$	−0.65236	−0.24657	−0.24249	−0.22263	−0.20442	0.06482	0.28500	0.78169	1.38934
$(\frac{\pi}{8}\ \frac{2628\pi}{512}\ \frac{\pi}{16})$	−0.66469	−0.28203	−0.25080	−0.23303	−0.20932	−0.18752	0.29267	0.65528	1.44359
$(\frac{3\pi}{16}\ \frac{3610\pi}{512}\ \frac{2\pi}{31})$	−0.64659	−0.26286	−0.25346	−0.22309	−0.17771	−0.15573	0.3017	0.49686	1.40403
$(\frac{\pi}{4}\ \frac{2608\pi}{512}\ \frac{\pi}{8})$	−0.57668	−0.24901	−0.23754	−0.22154	−0.12787	−0.10341	0.34066	0.35524	1.26570
$(\frac{5\pi}{16}\ \frac{2598\pi}{512}\ \frac{5\pi}{32})$	−0.45813	−0.24669	−0.23690	−0.23169	−0.01916	0.17596	0.25258	0.37953	1.04673
$(\frac{3\pi}{8}\ \frac{2586\pi}{512}\ \frac{3\pi}{16})$	−0.33136	−0.33420	−0.20183	−0.20120	−0.19059	0.11049	0.18574	0.42391	0.77375
$(\frac{7\pi}{16}\ \frac{2570\pi}{512}\ \frac{7\pi}{32})$	−0.48752	−0.25957	−0.18479	−0.16598	−0.13847	0.14382	0.28083	0.46781	0.56553
$(\frac{\pi}{2}\ \frac{2556\pi}{512}\ \frac{\pi}{4})$	−0.53145	−0.22997	−0.17288	−0.14283	−0.12730	0.12140	0.49593	0.50410	0.53717

CHAPTER 6

RESULTS AND DISCUSSION

The principal result of this work is obtaining the values of the interaction integrals for paramagnetic Cr which were treated as simple parameters. Their values can be used to obtain many valuable physical properties of the crystal such as energy band structure.

Once the interaction integrals are obtained computation of the energy values is a simple task of diagonalizing the different secular equations. The energy values are nothing else but eigen-values of the complex matrices. The energy values at the symmetry points and at many points along lines of particular symmetry in the 1/48 part of the BZ are computed by diagonalizing the secular equations listed in Appendix A. Such computation has been carried out along the high symmetry lines Δ , Λ , Σ , D and along the low symmetry line from symmetry point P to point X in the BZ.

The energy bands at the symmetry points are connected with the compatible energy bands along the symmetry lines [22].

The energy band structure computed by Slater-Koster inter-polation scheme contain higher energy levels that are not given by the first - principle method. This is basically one of the advantages of the Slater-Koster method which makes it an extra-polation scheme. The other important achievement of this method pertains to the interpolation of the energy band structure along any general direction in the BZ which is not computed by the first - principle method. As an illustration energy bands

along a general direction are shown in Appendix D, Fig(j). This involves solving 9x9 complex secular equations at all points along this direction for it lacks symmetry the secular determinant does not have reduced form (Appendix A, No.13). The only operator which leaves this general direction invariant is the identity operator.

The energy band structure of Cr interpolated along symmetry lines by the Slater-Koster method is shown in Figures (f to j) of Appendix D together with E(k)-values computed by Green's function method |1|. The computation by the interpolation scheme is carried out at more dense points than it is in the first - principle calculation of Asano and Yamashita |1|. This is the other advantage of using the interpolation scheme in conjunction to the first principle band calculation methods.

In Fig.(15) the higher bands along Λ - direction Λ_1 at $\vec{k} = (\frac{\pi}{8a}\ \frac{\pi}{8a}\ \frac{\pi}{8a})$ along Σ - direction Σ_1 at $\vec{k} = (\frac{\pi}{4a}\ \frac{\pi}{4a}\ 0)$ show some anomally. There is also sharp peak in the energy band along D - direction D_3 at $\vec{k} = (\frac{\pi}{2a}\ \frac{\pi}{2a}\ \frac{3\pi}{8a})$ (Figure 16) and the higher band along the low symmetry direction D^+ show some anomally at $\vec{k} = (\frac{\pi}{16a}\ \frac{\pi}{2a}\ \frac{3\pi}{16a})$.

The unexpected peaks occuring in the higher bands may be accounted to be due to the fact that the energy values for higher bands is not calculated by the KKR method. So, in the processes of improving the values of the parameters by our search method, the secular equations for higher bands were disregarded due to the deficient available data and this produces an abnormal behavior in the higher bands. The other most important reason that accounts for

the observed anomally is the neglect of some of the interaction integrals between second nearest neighbours.

Some discrepancy is also seen in the inter calculated bands. The maximum error, that is the maximum difference between energy values calculated by the first - principle method and the interpolation scheme is 0.08459 Ry and it is along the Λ - direction Λ_1 - band , The error along a given direction is maximum except in some cases in the relatively higher bands.

The discrepancies reflect shortcomings of the method when it is used as a quantitative method of determining energy bands. The reason for this is not far to seek. The Slater-Koster interpolation scheme which is basically LCAO method regarded as a mathematical method of obtaining approximate solutions of the Schroedinger equation, it is most successful when the interatomic distance of nearest neighbours is large compared with the spread of the atomic wave-functions.

Since the K-vector along the Λ - direction intersects perpendicularly the <111> plane on which the number of atoms is relatively less and therefore the interatomic distance is shorter compared to the spread of atomic wave-functions, the maximum discrepancy is observed between energy values along the Λ - direction for the LCAO method met its limitation along this direction.

The absolute mean difference between the interpolated energy values and those values of the energy computed by the first - principle method along Λ - direction is 0.0212218 Ry, along Δ - direction 0.0170921 Ry, along low-symmetry direction P-X 0.00828 Ry and along the Σ - direction 0.002471 Ry.

The Slater-Koster interpolation scheme which is basically LCAO method is at its best along the Σ - direction. The $\vec{k}$ - vector along Σ - direction intersects perpendicularly the <110> plane which is the most dense plane in bcc lattice. The separation between planes along this direction is relatively long to preserve the number of particles in a primitive unit cell of the Bravais lattice. Hence, the LCAO method is most successful along this direction for the inter-atomic distance of nearest neighbours is large compared with the spread of the atomic wave-functions.

At the symmetry points in the BZ the absolute mean difference between the interpolated and those values of energy computed by the first principle method are: at symmetry point Γ 0.00333 Ry, at symmetry point H 0.00243 Ry, at symmetry point P 0.01608 Ry and at symmetry point N it is 0.00625 Ry.

Iron and chromium are both transition metals and their stable room temperature form is body centered cubic (bcc) Bravais lattice. Mass number of Fe is 25 and of Cr is 24. The Lattice constant of Fe is 2.87A and of Cr is 2.88 A. Hence, it is reasonable to expect that the band structure of Fe and Cr have some similarity.

The interaction integrals of Cr are evaluated using Fe interaction integrals as rough starting values. These interaction integrals which are treated as disposable constants (parameters) in the Slater-Koster interpolation scheme are varied on an interval of physically acceptable range. The computation is carried

out by NCR computer. The programme in flowchart form and in FORTRAN language is given in Appendix B.

The shape of the band structure is influenced most by the interaction integrals between Bloch wave-functions on the same center. This is revealed by the fact that these integrals varied most from their initial value than the rest.

The interaction integral $E_{11}(111)$ remained unaltered throughout the variation processes. This integral depends on the structure of the lattice. For Iron and Chromium have the same lattice structure the interaction integrals which depend on the structure factor varied negligibly or remain unaltered. Only those integrals which depend on the potential varied appreciably. Amongst the 31 interaction integrals $E_{22}(000)$ varied most from its initial value. The difference between $E_{22}(000)$ of Iron and Chromium is 0.4575 Ry.

CONCLUSION

The Slater-Koster interpolation scheme, which short circuit many of the calculational complexities inherent in energy band calculation by the judicious use of symmetry arguments and group theory methods thereby leading to a deeper understanding of the qualitative features of the electron energy versus wave number dispersion relations is used here as a useful adjunct of ab-initio calculation (Green's functions method). Knowledge of $E(\vec{k})$ over a sufficiently broad range of energies would permit the determination of the crystal potential (by use of techniques developed in Nuclear Physics). It would then be possible to determine wave-functions which could be used to calculate wave-function dependent properties.

Moreover, the results obtained can be directly used to calculate density of states and the complex energy band structure of Cr. These give us valuable information for the study of electrical conductivity, magnetism, optical properties related to transition between energy bands, charge and spin densities as observed in diffraction experiments and other related properties.

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Appendix A. Symmetrized wave-functions and secular equations.

1. Point $\Gamma(000)$ $\alpha = \beta = \delta = 0$

The whole cubic group O_h leaves this point invariant.

$$D = \Gamma_1 + 3\Gamma_{15} + 3\Gamma_{25'} + 2\Gamma_{12}$$

$$\Gamma_1 \sim \{|1)\}$$

$$\Gamma_{15} \sim \{|2) , |3) , |4)\}$$

$$\Gamma_{25'} \sim \{|5) , |6) , |7)\}$$

$$\Gamma_{12} \sim \{|8) , |9)\}$$

$$(1|1) = E(\Gamma_1)$$

$$\begin{vmatrix} (2|2) - E(\Gamma_{15}) & (2|3) & (2|4) \\ (3|2) & (3|3) - E(\Gamma_{15}) & (3|4) \\ (4|2) & (4|3) & (4|4) - E(\Gamma_{15}) \end{vmatrix} = 0$$

$$\begin{vmatrix} (5|5) - E(\Gamma_{25'}) & (5|6) & (5|7) \\ (5|6) & (6|6) - E(\Gamma_{25'}) & (6|7) \\ (5|7) & (6|7) & (7|7) - E(\Gamma_{25'}) \end{vmatrix} = 0$$

$$\begin{vmatrix} (8|8) - E(\Gamma_{12}) & (8|9) \\ (9|8) & (9|9) - E(\Gamma_{12}) \end{vmatrix} = 0$$

2. Point $H(0\ ,\ \pi/a\ ,\ 0)$ $\quad \alpha = \delta = 0 \quad \beta = \pi$

The whole cubic group O_h leaves it invariant.

$$D = H_1 + H_{15} + H_{25'} + H_{12}$$

$$H_1 \sim \{|1)\}$$

$$H_{15} \sim \{|2)\ ,\ |3)\ ,\ |4)\}$$

$$H_{25'} \sim \{|5)\ ,\ |6)\ ,\ |7)\}$$

$$H_{12} \sim \{|8\ ,\ |9)\}$$

$$(1|1) = E(H_1)$$

$$\begin{vmatrix} (2|2) - E(H_{15}) & (2|3) & (2|4) \\ (3|2) & (3|3) - E(H_{15}) & (3|4) \\ (4|2) & (4|3) & (4|4) - E(H_{15}) \end{vmatrix} = 0$$

$$\begin{vmatrix} (5|5) - E(H_{25'}) & (5|6) & (5|7) \\ (5|6) & (6|6) - E(H_{25'}) & (6|7) \\ (5|7) & (6|7) & (7|7) - E(H_{25'}) \end{vmatrix} = 0$$

$$\begin{vmatrix} (8|8) - E(H_{12}) & (8|9) \\ (9|8) & (9|9) - E(H_{12}) \end{vmatrix} = 0$$

3. Point $P(\frac{\pi}{2a}, \frac{\pi}{2a}, \frac{\pi}{2a})$ $\alpha = \beta = \delta = \pi/2$

The group $T_d = (E, C_2, C_3, JC_4, JC_2)$ leaves it invariant.

$D = P_1 + P_3 + 2P_4$

$P_1 \sim \{|1)\}$

$P_3 \sim \{|8), |9)\}$

$P_4 \sim \{|2), |3), |4), |5), |6), |7)\}$

$(1|1) = E(P_1)$

$$\begin{vmatrix} (8|8) - E(P_3) & (8|9) \\ (9|8) & (9|9) - E(P_3) \end{vmatrix} = 0$$

$$\begin{vmatrix} (2|2)-E(P_4) & (2|3) & (2|4) & (2|5) & (2|6) & (2|7) \\ (3|2) & (3|3)-E(P_4) & (3|4) & (3|5) & (3|6) & (3|7) \\ (4|2) & (4|3) & (4|4)-E(P_4) & (4|5) & (4|6) & (4|7) \\ (5|2) & (5|3) & (5|4) & (5|5)-E(P_4) & (5|6) & (5|7) \\ (6|2) & (6|3) & (6|4) & (6|5) & (6|6)-E(P_4) & (6|7) \\ (7\ 2) & (7|3) & (7|4) & (7|5) & (7|6) & (7|7)-E(P_4) \end{vmatrix} =$$

4. Point $N(\frac{\pi}{2a}, \frac{\pi}{2a}, 0)$ $\alpha = \beta = \pi/2$, $\delta = 0$

The group $D_{2h} = \{E, C_2^3, C_2'^1, C_2'^3, J, JC_2^3, JC_2'^1, JC_2'^4\}$ leaves it invariant.

$$D = 3N_1 + N_2 + N_3 + N_4 + N_1' + N_3' + N_4'$$

$$N_1 \sim \{|1), |5), |9)\}$$
$$N_2 \sim \{\tfrac{1}{\sqrt{2}}(|6) - |7))\}$$
$$N_3 \sim \{\tfrac{1}{\sqrt{2}}(|6) + |7))\}$$
$$N_4 \sim \{|8)\}$$
$$N_1' \sim \{\tfrac{1}{\sqrt{2}}(|2) + |3))\}$$
$$N_3' \sim \{|4)\}$$
$$N_4' \sim \{\tfrac{1}{\sqrt{2}}(|2) - |3))\}$$

$$\begin{vmatrix} (1|1) - E(N_1) & (1|5) & (1|9) \\ (5|1) & (5|5) - E(N_1) & (5|9) \\ (9|1) & (9|5) & (9|9) - E(N_1) \end{vmatrix} = 0$$

$$\tfrac{1}{2}\{(7|7) + (6|6) - (6|7) - (7|6)\} = E(N_2)$$
$$\tfrac{1}{2}\{(7|7) + (6|6) + (6|7) + (7|6)\} = E(N_3)$$
$$(8|8) = E(N_4)$$
$$\tfrac{1}{2}\{(2|2) + (3|3) + (2|3) + (3|2)\} = E(N_1')$$
$$(4|4) = E(N_3')$$
$$\tfrac{1}{2}\{(2|2) + (3|3) - (2|3) - (3|2)\} = E(N_4')$$

5. Direction $\Delta(\alpha = \delta = 0\ ,\ \beta \in (0,\pi)$

There are 8 operations which leave the Δ direction invariant, they are $\{E,\ C_4^3,\ C_4^4,\ C_2^2,\ JC_2^1,\ JC_2^3,\ JC_2'^2,\ JC_2'^5\}$. This is the group C_{4v}, it is a group of plane operations which sends a square into itself. It contains a fourfold rational axis and four reflection planes.

$$D = 3\Delta_1 + \Delta_2 + \Delta_2' + 2\Delta_5$$

$$\Delta_1 \sim \{|1)\ ,\ |3)\ ,\ \tfrac{1}{2}(\sqrt{3}|8) + |9))\}$$
$$\Delta_2 \sim \{\tfrac{1}{2}(\sqrt{3}|9) - |8))\}$$
$$\Delta_2' \sim \{|6)\}$$
$$\Delta_5 \sim \{|2)\ ,\ |4)\ ,\ |5)\ ,\ |7)\}$$

let $|8') = \tfrac{1}{2}(\sqrt{3}|8) + |9))$

$|9') = \tfrac{1}{2}(\sqrt{3}|9) - |8))$

$$\begin{vmatrix} (1|1) - E(\Delta_1) & (1|3) & (1|8') \\ (3|1) & (3|3) - E(\Delta_1) & (3|8') \\ (8'|1) & (8'|3) & (8'|8') - E(\Delta_1) \end{vmatrix} = 0$$

$$\tfrac{1}{4}\{3(9|9) + (8|8) - \sqrt{3}(8|9) - \sqrt{3}(9|8)\} = E(\Delta_2)$$
$$(6|6) = E(\Delta_2,)$$

$$\begin{vmatrix} (2|2) - E(\Delta_5) & (2|4) & (2|5) & (2|7) \\ (4|2) & (4|4) - E(\Delta_5) & (4|5) & (4|7) \\ (5|2) & (5|4) & (5|5) - E(\Delta_5) & (5|7) \\ (6|2) & (6|4) & (6|5) & (7|7) - E(\Delta_5) \end{vmatrix} = 0$$

6. Direction $\Lambda(\alpha = \beta = \delta \quad , \quad \alpha \in (0 \, , \, \pi/2))$

Group C_{3v} leaves Λ direction in Brillouin zone invariant.

There are 12 operators in C_{3v}

$C_{3v} \sim \{E, \, 2C_3, \, 3JC_2, \, J, \, 2JC_3, \, 3C_2\}$

$D = 3\Lambda_1 + 6\Lambda_3$

$\Lambda_1 = \{|1), \, \frac{1}{\sqrt{3}}(|2) + |3) + |4) \quad , \, \frac{1}{\sqrt{3}}(|5)+|6)+|7))\}$

$\Lambda_3 = \{\frac{1}{\sqrt{6}}(2|2)-|3)-|4)) \, , \, \frac{1}{\sqrt{2}}(|3)-|4)) \, , \, \frac{1}{\sqrt{6}}(2|5)-|5)-|7)),$

$\frac{1}{\sqrt{2}}(|6)-|7)), \, |8), |9)\}$

let $|2') = \frac{1}{\sqrt{3}}(|2)+|3)+|4))$

$|3') = \frac{1}{\sqrt{3}}(|5)+|6)+|7))$

$|4') = \frac{1}{\sqrt{6}}(2|2)-|3)-|4))$

$|5') = \frac{1}{\sqrt{2}}(|3)-|4))$

$|6') = \frac{1}{\sqrt{6}}(2|5)-|6)-|7))$

$|7') = \frac{1}{\sqrt{2}}(|6)-|7))$

$$\begin{vmatrix} (1|1)-E(\Lambda_1) & (1|2') & (1'|3') \\ (2'|1) & (2'|2')-E(\Lambda_1) & (2|3') \\ (3'|1) & (3'|2') & (3'|3')-E(\Lambda_1) \end{vmatrix} = 0$$

$$\begin{vmatrix} (4'|4')-E(\Lambda_3) & (4'|5') & (4'|6') & (4'|7') & (4'|8') & (4'|9) \\ (5'|4') & (5'|5')-E(\Lambda_3) & (5'|6') & (5'|7') & (5'|8) & (5'|9) \\ (6'|4') & (6'|5') & (6'|6')-E(\Lambda_3) & (6'|7') & (6'|8) & (6'|9) \\ (7'|4') & (7'|5') & (7'|6') & (7'|7')-E(\Lambda_3) & (7'|8) & (7'|9) \\ (8|4') & (8|5') & (8|6') & (8|7') & (8|8)-E(\Lambda_3) & (8|9) \\ (9|4') & (9|5') & (9|6') & (9|7') & (9|8) & (9|9)-E(\Lambda_3) \end{vmatrix} = 0$$

7. Direction $F(\alpha = \delta\ ,\ \beta = \pi - \alpha \qquad \alpha \in (0,\ \pi/2))$

Group $C_{3v} \sim (E,\ C_3^7,\ C_3^8,\ JC_2'^5,\ JC_2'^3,\ JC_2'^1)$

$D = 3F_1 + 3F_3$

$$F_1 \sim \{|1),\ \tfrac{1}{\sqrt{3}}(|2)+|4)-|3)),\ \tfrac{1}{\sqrt{3}}(|6)-|5)-|7))\}$$

$$F_3 \sim \{\tfrac{1}{\sqrt{2}}(|2)+|3)),\ \tfrac{1}{\sqrt{6}}(2|4)+|3)-|2)),\ \tfrac{1}{\sqrt{2}}(|7)-|5)),\ \tfrac{1}{\sqrt{2}}(2|6)+|5)+|7))\ ;\ |8),\ |9)\}$$

let
$$|2') = \tfrac{1}{\sqrt{3}}(|2)+|4)-|3))$$
$$|3') = \tfrac{1}{\sqrt{3}}(|6)-|5)-|7))$$
$$|4') = \tfrac{1}{\sqrt{2}}(|2)+|3))$$
$$|5') = \tfrac{1}{\sqrt{6}}(2|4)+|3)-|2))$$
$$|6') = \tfrac{1}{\sqrt{2}}(|7)-|5))$$
$$|7') = \tfrac{1}{\sqrt{2}}(2|6)+|5)+|7))$$

$$\begin{vmatrix} (1|1) - E(F_1) & (1|2') & (1|3') \\ (2'|1) & (2'|2') - E(F_1) & (2'|3') \\ (3'|1) & (3'|2') & (3'|3') - E(F_1) \end{vmatrix} = 0$$

$$\begin{vmatrix} (4'|4') - E(F_3) & (4'|5') & (4'|6') & (4'|7') & (4'|8) & (4'|9) \\ (5'|4') & (5'|5') - E(F_3) & (5'|6') & (5'|7') & (5'|8) & (5'|9) \\ (6'|4') & (6'|5') & (6'|6') - E(F_3) & (6'|7') & (6'|8) & (6'|9) \\ (7'|4') & (7'|5') & (7'|6') & (7'|7') - E(F_3) & (7'|8) & (7'|9) \\ (8|4') & (8|5') & (8|6') & (8|7') & (8|8) - E(F_3) & (8|9) \\ (9|4') & (9|5') & (9|6') & (9|7') & (9|8) & (9|9) - E(F_3) \end{vmatrix}$$

8. Direction $\Sigma(\alpha = \beta, \ \delta = 0, \quad \alpha \in (0, \pi/2))$

Group $C_{2v} \sim (E, C_2, C_4^2, JC_2)$

$D = 4\Sigma_1 + \Sigma_2 + 2\Sigma_3 + 2\Sigma_4$

$\Sigma_1 \sim \{|1), \frac{1}{\sqrt{2}}(|2)+|3)), |5), |9))$

$\Sigma_2 \sim \{\frac{1}{\sqrt{2}}(|7)-|6))$

$\Sigma_3 \sim \{|4), \frac{1}{\sqrt{2}}(|7)+|6))\}$

$\Sigma_4 \sim \frac{1}{\sqrt{2}}(|2)-|3)), |8)\}$

let $|2') = \frac{1}{\sqrt{2}}(|2)+|3))$

$|6') = \frac{1}{\sqrt{2}}(|7)-|6))$

$|7') = \frac{1}{\sqrt{2}}(|7)+|6))$

$|3') = \frac{1}{\sqrt{2}}(|2)-|3))$

$$\begin{vmatrix} (1|1)-E(\Sigma_1) & (1|2') & (1|5) & (1|9) \\ (2'|1) & (2'|2')-E(\Sigma_1) & (2'|5) & (2|9) \\ (5|1) & (5|2') & (5|5)-E(\Sigma_1) & (3|9) \\ (9|1) & (9|2') & (9|5) & (9|9)-E(\Sigma_1) \end{vmatrix} = 0$$

$$\tfrac{1}{2}\{(6|6)+(7|7)-(6|7)-(7|6)\} = E(\Sigma_2)$$

$$\begin{vmatrix} (4|4)-E(\Sigma_3) & (4|7') \\ (7'|4) & (7'|7')-E(\Sigma_3) \end{vmatrix} = 0$$

$$\begin{vmatrix} (3'|3')-E(\Sigma_4) & (3'|8) \\ (8|3') & (8|8)-E(\Sigma_4) \end{vmatrix} = 0$$

9. Direction $D(\alpha = \beta = \pi/2 \ , \ \delta \in (0 \ , \pi/2))$

Group $C_{2v} \sim (E, C_2^3, JC_2'^4, JC_2'^1)$ leaves direction D invariant.

$D \doteq 4D_1 + D_2 + 2D_3 + 2D_4$

$D_1 \sim \{|1), |4), |5), |9)\}$

$D_2 \sim \{|8)\}$

$D_3 \sim \{\frac{1}{\sqrt{2}}(|2)+|3)) \ , \ \frac{1}{\sqrt{2}}(|6)+|7))\}$

$D_4 \sim \{\frac{1}{\sqrt{2}}(|2)-|3)) \ , \ \frac{1}{\sqrt{2}}(|6)-|7))\}$

let $|2') = \frac{1}{\sqrt{2}}(|2)+|3))$

$|6') = \frac{1}{\sqrt{2}}(|6)+|7))$

$|3') = \frac{1}{\sqrt{2}}(|2)-|3))$

$|7') = \frac{1}{\sqrt{2}}(|6)-|7))$

$$\begin{vmatrix} (1|1) - E(D_1) & (1|4) & (1|5) & (1|9) \\ (4|1) & (4|4) - E(D_1) & (4|5) & (4|9) \\ (5|1) & (5|4) & (5|5) - E(D_1) & (5|9) \\ (9|1) & (9|4) & (9|5) & (9|9) - E(D_1) \end{vmatrix} = 0$$

$(8|8) = E(D_2)$

$$\begin{vmatrix} (2'|2') - E(D_3) & (2'|6') \\ (6'|2') & (6'|6') - E(D_3) \end{vmatrix} = 0$$

$$\begin{vmatrix} (3'|3') - E(D_4) & (3'|7') \\ (7'|3') & (7'|7') - E(D_4) \end{vmatrix} = 0$$

10. Direction $G(\beta = \pi - \alpha\ ,\ \delta = 0\ ,\ \alpha \in (0\ ,\ \pi/2))$

Group C_{2v} leaves direction G invariant.

$C_{2v} \sim \{E,\ C_2'^4\ ,\ JC_2'^1,\ JC_2^3\}$

$D = 4G_1 + G_2 + 2G_3 + 2G_4$

$G_1 \sim \{|1),\ \frac{1}{\sqrt{2}}(|2)-|3)),\ |5),\ |9)\}$

$G_2 \sim \{\frac{1}{\sqrt{2}}(|6)+|7))\}$

$G_3 \sim \{|4),\ \frac{1}{\sqrt{2}}(|6)-|7))\}$

$G_4 \sim \{\frac{1}{\sqrt{2}}(|2)+|3)),\ |8)\}$

let $\quad |2') = \frac{1}{\sqrt{2}}(|2)+|3))$

$\quad |6') = \frac{1}{\sqrt{2}}(|6)+|7))$

$\quad |3') = \frac{1}{\sqrt{2}}(|2)-|3))$

$\quad |7') = \frac{1}{\sqrt{2}}(|6)-|7))$

$$\begin{vmatrix} (1|1)-E(G_1) & (1|3') & (1|5) & (1|9) \\ (3'|1) & (3'|3')-E(G_1) & (3'|5) & (3'|9) \\ (5|1) & (5|3') & (5|5)-E(G_1) & (5|9) \\ (9|1) & (9|3') & (9|5) & (9|9)-E(G_1) \end{vmatrix} = 0$$

$$\tfrac{1}{2}\{(6|6)+(7|7)+(6|7)+(7|6)\} = E(G_2)$$

$$\begin{vmatrix} (4|4)-E(G_3) & (4|7') \\ (7'|4) & (7'|7')-E(G_3) \end{vmatrix} = 0$$

$$\begin{vmatrix} (2'|2')-E(G_4) & (2'|8) \\ (8|2') & (8|8)-E(G_4) \end{vmatrix} = 0$$

11. Direction P - X $\alpha = \delta \in (0, \pi/2)$, $\beta = \pi/2$

Group $C_s \sim \{E, \sigma C_2'^S\}$ leaves this direction invariant.

$D = 6D^+ + 3D^-$

$D^+ \sim \{|1), |3), |6), \frac{1}{\sqrt{2}}(|2)+|4)), \frac{1}{\sqrt{2}}(|5)+|7)), (\frac{1}{2}|9)+\sqrt{3}|8))\}$

$D^- \sim \{\frac{1}{\sqrt{2}}(|2)-|4)), \frac{1}{\sqrt{2}}(2|5)-|7)) , (\frac{1}{2}|9)-\sqrt{3}|8))\}$

let $|2') = \frac{1}{\sqrt{2}}(|2)+|4))$

$|5') = \frac{1}{\sqrt{2}}(|5)+|7))$

$|8') = \frac{1}{2}|9)+ \sqrt{3}|8)$

$|4') = \frac{1}{\sqrt{2}}(|2)-|4))$

$|7') = \frac{1}{\sqrt{2}}(2|5)-|7))$

$|9') = \frac{1}{2}|9)- \sqrt{3}|8)$

$$\begin{vmatrix} (1|1)-E(D^+) & (1|3) & (1|6) & (1|2') & (1|5') & (1|8') \\ (3|1) & (3|3)-E(D^+) & (3|6) & (3|2') & (3|5') & (3|8') \\ (6|1) & (6|3) & (6|6)-E(D^+) & (6|2') & (6|5') & (6|8') \\ (2'|1) & (2'|3) & (2'|6) & (2'|2')-E(D^+) & (2'|5') & (2'|8') \\ (5'|1) & (5'|3) & (5'|6) & (5'|2') & (5'|5')-E(D^+) & (5'|8') \\ (8'|1) & (8'|3) & (8'|6) & (8'|2') & (8'|5') & (8'|8')-E(D^+) \end{vmatrix} = 0$$

$$\begin{vmatrix} (4'|4') - E(D^-) & (4'|6') & (4'|9') \\ (6'|4') & (6'|6') - E(D^-) & (6'|9') \\ (9'|4') & (9'|6') & (9'|9') - E(D^-) \end{vmatrix} = 0$$

12. Direction $N-X$ $\alpha \in (0, \pi/2)$, $\beta = \pi/2$, $\delta = 0$

Group $C_s \sim \{E, JC_2^3\}$

$D = 6N^+ + 3N^-$

$N^+ \sim \{|1), |2), |5), |8), |9)\}$

$N^- \sim \{|4), |6), |7)\}$

$$\begin{vmatrix} (1|1)-E(N^+) & (1|2) & (1|3) & (1|5) & (1|8) & (1|9) \\ (2|1) & (2|2)-E(N^+) & (2|3) & (2|5) & (2|8) & (2|9) \\ (3|1) & (3|2) & (3|3)-E(N^+) & (3|5) & (3|8) & (3|9) \\ (5|1) & (5|2) & (5|3) & (5|5)-E(N^+) & (5|8) & (5|9) \\ (8|1) & (8|2) & (8|3) & (8|5) & (8|8)-E(N^+) & (8|9) \\ (9|1) & (9|2) & (9|3) & (9|5) & (9|8) & (9|9)-E(N^+) \end{vmatrix} = 0$$

$$\begin{vmatrix} (4|4) - E(N^-) & (4|6) & (4|7) \\ (6|4) & (6|6) - E(N^-) & (6|7) \\ (7|4) & (7|6) & (7|7) - E(N^-) \end{vmatrix} = 0$$

13. General direction in the BZ. Only the identity operator E leaves this direction invariant.

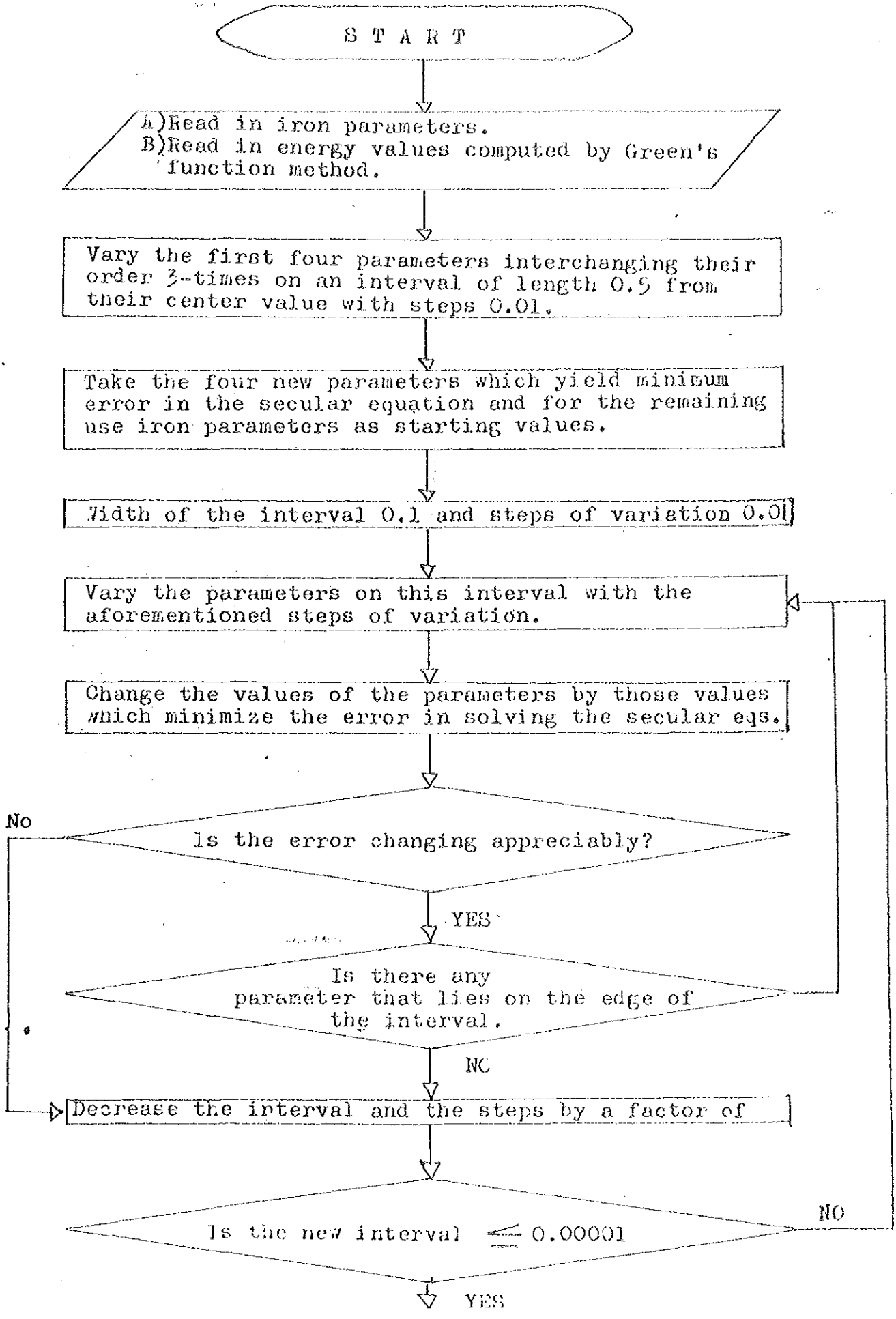
$g \sim \{E\}$

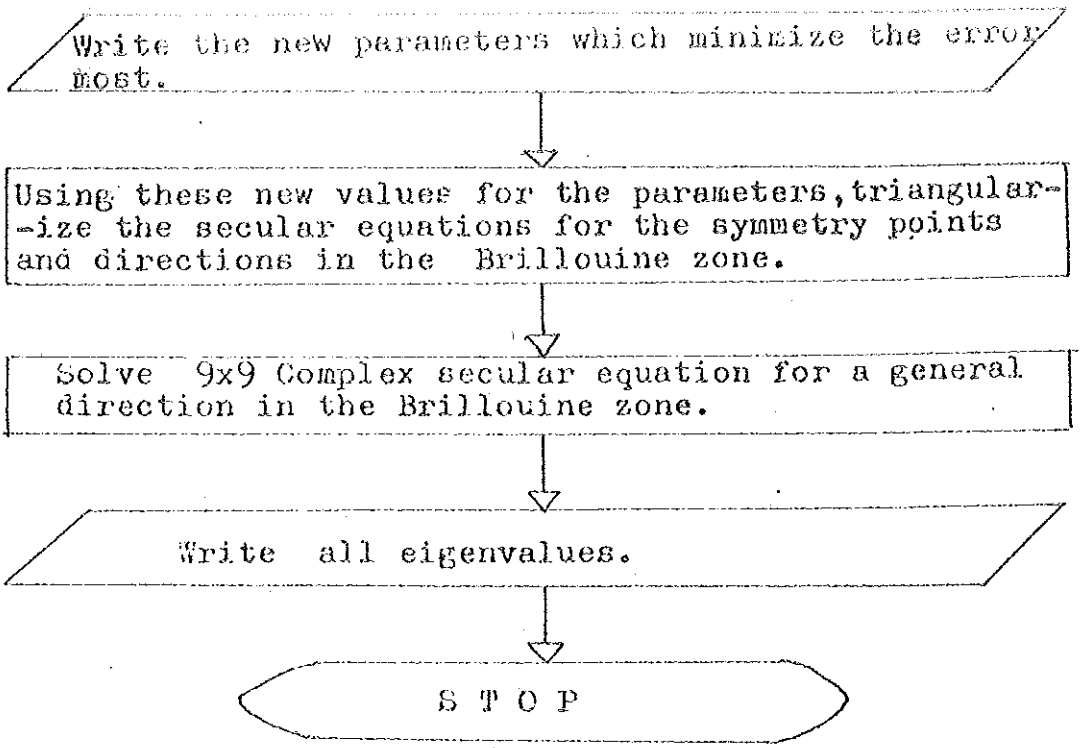
$D = 9g$

$g \sim \{|1), |2), |3), |4), |5), |6), |7), |8), |9)\}$

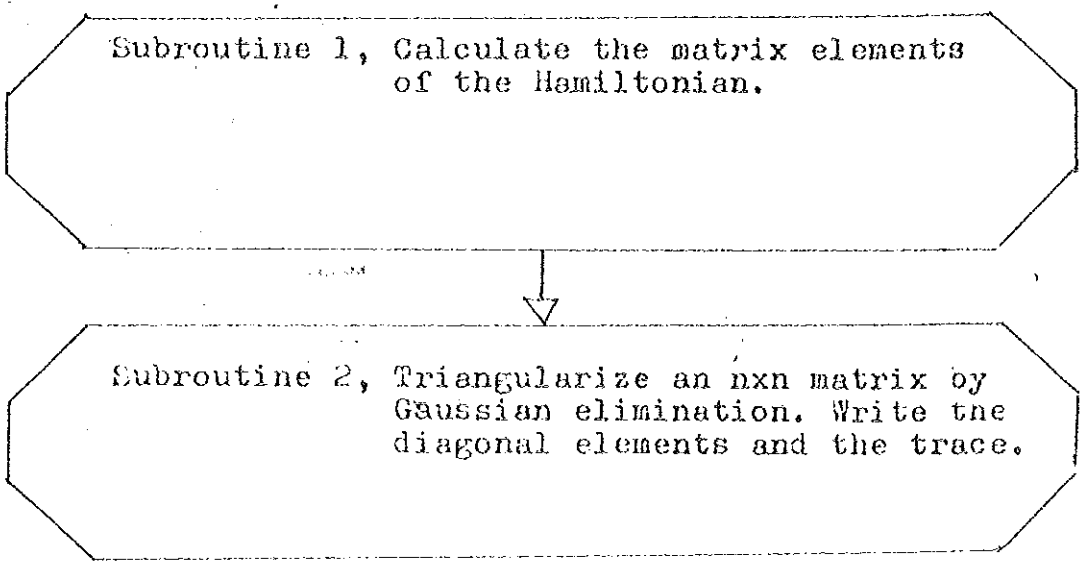
$$\begin{vmatrix}
(1|1)-E(g) & (1|2) & (1|3) & (1|4) & (1|5) & (1|6) & (1|7) & (1|8) & (1|9) \\
(2|1) & (2|2)-E(g) & (2|3) & (2|4) & (2|5) & (2|6) & (2|7) & (2|8) & (2|9) \\
(3|1) & (3|2) & (3|3)-E(g) & (3|4) & (3|5) & (3|6) & (3|7) & (3|8) & (3|9) \\
(4|1) & (4|2) & (4|3) & (4|4)-E(g) & (4|5) & (4|6) & (4|7) & (4|8) & (4|9) \\
(5|1) & (5|2) & (5|3) & (5|4) & (5|5)-E(g) & (5|6) & (5|7) & (5|8) & (5|9) \\
(6|1) & (6|2) & (6|3) & (6|4) & (6|5) & (6|6)-E(g) & (6|7) & (6|8) & (6|9) \\
(7|1) & (7|2) & (7|3) & (7|4) & (7|5) & (7|6) & (7|7)-E(g) & (7|8) & (7|9) \\
(8|1) & (8|2) & (8|3) & (8|4) & (8|5) & (8|6) & (8|7) & (8|8)-E(g) & (8|9) \\
(9|1) & (9|2) & (9|3) & (9|4) & (9|5) & (9|6) & (9|7) & (9|8) & (9|9)-E(g)
\end{vmatrix} = 0$$

Appendix B. Flow chart for the interpolation scheme.





SUBROUTINES THAT ARE USED IN THIS PROGRAMME.



```
      ....+....1....+....2....+....3....+....4....+....5....+....6....+....7..
NCR   C THIS PROGRAMME IS TO EVALUATE THE INTERACTION INTEGRALS WHICH APPEAR
      C IN THE BAND STRUCTURE CALCULATION OF CHROMIUM WHICH ARE SIMPLY TREATE
      C AS DISPOSABLE PARAMETERS IN THE SLATER-KOSTER INTERPOLATION SCHEME. I
      C THIS PROGRAMMETHESE PARAMETERS ARE VARIED ON AN INTERVAL CHOSEN ON PH
      C SICAL GROUND.
            COMPLEX H(45),K(39,3),G1,G2(6,6),G3(6,6),H1(6,6),H2(6,6),P1(6,6),
           1P2(6,6),N1(6,6),N2,N3,N4,N5,D1(6,6),D2,D3,D4(6,6),L1(6,6),L2(6,6),
           2F1(6,6),F2(6,6),S1(6,6),S2,S3(6,6),S4(6,6),D5(6,6),D6,D7(6,6),D8(6
           3,6),G4(6,6),G5,G6(6,6),G7(6,6),Z1(6,6),Z2(6,6),Z3(6,6),Z4(6,6),DET
           4,C2,C3,C4,C6,C8,C12
            DIMENSION EE(31)
            COMMON E(31)
            PI = 3.1415926
            C2 = CMPLX(2.0,0.0)
            C3 = CMPLX(3.0,0.0)
            C4 = CMPLX(4.0,0.0)
            C6 = CMPLX(6.0,0.0)
            C8 = CMPLX(8.0,0.0)
            C12= CMPLX(12.0,0.0)
            READ (2,700) (E(I) , I=1,31)
        700 FORMAT (11F7.4/11F7.4/9F7.4)
            READ (2,705) ((K(I,J),I=1,39), J=1,3)
        705 FORMAT(7(F8.5,F3.1)/7(F8.5,F3.1)/7(F8.5,F3.1)/7(F8.5,F3.1)/7(F8.5,
           1F3.1)/7(F8.5,F3.1)/7(F8.5,F3.1)/7(F8.5,F3.1)/7(F8.5,F3.1)/7(F8.5,F
           23.1)/7(F8.5,F3.1)/7(F8.5,F3.1)/7(F8.5,F3.1)/7(F8.5,F3.1)/7(F8.5,F3
           3.1)/7(F8.5,F3.1)/5(F8.5,F3.1))
            DO 36 I=1,4
         36 EE(I) = E(I)
            DO 35 L=1,16
            DO 15 I=1,4
            EMIN = 2.
            SUMIN = 10**12
            EMAX = E(I) + 0.5
            E(I) = E(I) - 0.5
            DO 25 J=1,50
            SUM = 0.0
            A = 0.0
            B = 0.0
            C = 0.0
            CALL HAMILT (A,B,C,H)
            G1 = H(1) + CMPLX(0.76453,0.0)
            SUM = SUM + CABS(G1)
            G2(1,1) = H(31) + CMPLX(0.31928,0.0)
            G2(1,2) = H(32)
            G2(1,3) = H(33)
            G2(2,1) = H(32)
            G2(2,2) = H(36) + CMPLX(0.31928,0.0)
            G2(2,3) = H(37)
            G2(3,1) = H(33)
            G2(3,2) = H(37)
            G2(3,3) = H(40) + CMPLX(0.31928,0.0)
            CALL GAUSEL (DET,G2,3)
            SUM = SUM + CABS(DET)
            G3(1,1) =H(43) + CMPLX(0.18604,0.0)
            G3(1,2) = H(44)
            G3(2,1) = H(44)
            G3(2,2) = H(45) + CMPLX(0.18604,0.0)
```

```
      Z3(2,3) = H(12)
      Z3(2,4) = H(13)
      Z3(2,5) = H(16)
      Z3(2,6) = H(17)
      Z3(3,1) =-H(3)
      Z3(3,2) = H(11)
      Z3(3,3) = H(18)-K(J+33,I)
      Z3(3,4) = H(20)
      Z3(3,5) = H(23)
      Z3(3,6) = H(24)
      Z3(4,1) = H(5)
      Z3(4,2) =-H(13)
      Z3(4,3) =-H(20)
      Z3(4,4) = H(31)-K(J+33,I)
      Z3(4,5) = H(34)
      Z3(4,6) = H(35)
      Z3(5,1) = H(8)
      Z3(5,2) =-H(16)
      Z3(5,3) =-H(23)
      Z3(5,4) = H(34)
      Z3(5,5) = H(43)-K(J+33,I)
      Z3(5,6) = H(44)
      Z3(6,1) = H(9)
      Z3(6,2) =-H(17)
      Z3(6,3) =-H(24)
      Z3(6,4) = H(35)
      Z3(6,5) = H(44)
      Z3(6,6) = H(45)-K(J+33,I)
      CALL GAUSEL (DET,Z3,6)
      SUM = SUM + CABS(DET)
  145 CONTINUE

      DO 155 J=1,2
      Z4(1,1) = H(25)-K(J+37,I)
      Z4(1,2) = H(27)
      Z4(1,3) =H(28)
      Z4(2,1) = H(27)
      Z4(2,2) = H(36)-K(J+37,I)
      Z4(2,3) = H(37)
      Z4(3,1) = H(28)
      Z4(3,2) = H(37)
      Z4(3,3) = H(40)-K(J+37,2)
      CALL GAUSEL (DET,Z4,3)
      SUM = SUM + CABS(DET)
  155 CONTINUE
      A = A + (PI/8.)
      CALL HAMILT (A,B,G,H)
  130 CONTINUE
      E(I) = E(I) + 0.02
      IF (SUM.GE.SUMIN) GO TO 25
      SUMIN = SUM
      EMIN = E(I)
   25 CONTINUE
      IF (EMIN.EQ.2) GO TO 45
      WRITE (3,500) I,EMIN,SUMIN
  500 FORMAT (1X,I1,F15.5,10X,E10.4)
      GO TO 15
   45 WRITE (3,600) I,((II) , II=1,4)
  600 FORMAT ('WRONG VALUE FOR E(',I2,')',4F15.5)
   15 CONTINUE
      STOP
```

```
      SUBROUTINE HAMILT (A,B,C,H)
      COMMON E(31)
      COMPLEX H(45)
      H(1)=CMPLX(E(1)+(8.*E(10)*COS(A)*COS(B)*COS(C)+(2.*E(20)*(COS(2.*
     1A)*COS(2.*B)+COS(2.*C) ))+(4.*E(28)*(COS(2.*A)*COS(2.*B)+COS(2.*A)
     2*COS(2.*C)+COS(2.*B)*COS(2.*C))),0.0)
      H(2)=CMPLX(0.0,((8.*E(5)*SIN(A)*COS(B)*COS(C))+(2.*E(6)*SIN(2.*A))
     1 ))
      H(3)=CMPLX(0.0,((8.*E(9)*COS(A)*SIN(B)*COS(C))+(2.*E(6)*SIN(2.*B))
     1 ))
      H(4)=CMPLX(0.0,((8.*E(5)*COS(A)*SIN(B)*COS(C))+(2.* E(6)*SIN(2.*C)
     1 )))
      H(5)=CMPLX(((((-8.)*E(7)*SIN(A)*SIN(B)*COS(C))+((-4.)*E(29)*SIN(2.*
     1A)*SIN(2.*B))),0.0)
      H(6)=CMPLX(((((-8.)*E(7)*COS(A)*SIN(B)*SIN(C))-(4.*E(29)*SIN(2.*B)*
     1 SIN(2.*C))),0.0)
      H(7)=CMPLX(((((-8.)*E(7)*SIN(A)*COS(B)*SIN(C))-(4.*E(29)*SIN(2.*A)*
     1 SIN(2.*C))),0.0)
      H(8)=CMPLX(((SQRT(3.))*E(9)*(COS(2.*A)-COS(2.*B))),0.0)
      H(9) = CMPLX((E(9)*(2.*COS(2.*C)-COS(2.*B)-COS(2.*A))),0.0)
      H(10)=CMPLX((E(2)+(8.*E(11)*COS(A)*COS(B)*COS(C))+(2.*E(12)*COS(2.
     1*A))+(2.*E(13)*(COS(2.*B)+COS(2.*C)))),0.0)
      H(11)=CMPLX(((((-8.)*E(14)*SIN(A)*SIN(B)*COS(C))),0.0)
      H(12)=CMPLX(((((-8.)*E(14)*SIN(A)*COS(B)*SIN(C))),0.0)
      H(13)=CMPLX(0.0,((8.*E(15)*COS(A)*SIN(B)*COS(C))+(2.*E(16)*SIN(2.*
     1B))))
      H(14)=CMPLX(0.0,((((-8.)*E(17)*SIN(A)*SIN(B)*SIN(C))))
      H(15)=CMPLX(0.0,((8.*E(15)*COS(A)*COS(B)*SIN(C))+(2.*E(16)*SIN(2.*
     1 C))))
      H(16)=CMPLX(0.0,((8.*E(18)*SIN(A)*COS(B)*COS(C))+((SQRT(3.))*E(19)
     1 *SIN(2.*A))))
      H(17)=CMPLX(0.0,(((((-8.)/(SQRT(3.)))*E(18)*SIN(A)*COS(B)*COS(C))-(
     1 E(19)*SIN(2.*A))))
      H(18)=CMPLX((E(2)+(8.*E(11)*COS(A)*COS(B)*COS(C))+(2.*E(12)*COS(2.
     1*B))+(2.*E(13)*(COS(2.*A)+COS(2.*C)))),0.0)
      H(19)=CMPLX(((-8.)*E(14)*COS(A)*SIN(B)*SIN(C)),0.0)
      H(20)=CMPLX(0.0,((8.*E(15)*SIN(A)*COS(B)*COS(C))+(2.*E(16)*SIN(2.*
     1A))+(4.*E(16)*SIN(2.*A)*COS(2.*C))))
      H(21)=CMPLX(0.0,((8.*E(15)*COS(A)*COS(B)*SIN(C))+(2.*E(16)*SIN(2.*
     1C))))
      H(22)=CMPLX(0.0,(((-8.)*E(17)*SIN(A)*SIN(B)*SIN(C))))
      H(23)=CMPLX(0.0,(((-8.)*E(18)*COS(A)*SIN(B)*COS(C))-((SQRT(3.))*E(
     1 19)*SIN(2.*B))))
      H(24)=CMPLX(0.0,(((((-8.)/(SQRT(3.)))*E(18)*COS(A)*SIN(B)*COS(C))-(
     1 E(19)*SIN(2.*B))))
      H(25)=CMPLX((E(2)+(8.*E(11)*COS(A)*COS(B)*COS(C))+(2.*E(12)*COS(C)
     1 )+(2.*E(13)*(COS(2.*A)+COS(2.*B)))),0.0)
      H(26)=CMPLX(0.0,((-8.)*E(17)*SIN(A)*SIN(B)*SIN(C))))
      H(27)=CMPLX(0.0,((8.*E(15)*COS(A)*SIN(B)*COS(C))+(2.*E(16)*SIN(2.*
     1B))))
      H(28)=CMPLX(0.0,((8.*E(15)*SIN(A)*COS(B)*COS(C))+(2.*E(16)*SIN(2.*
     1A))))
      H(29)=CMPLX(0.0,0.0)
      H(30)=CMPLX(0.0,(((16./(SQRT(3.)))*E(18)*COS(A)*COS(B)*SIN(C))+(2.
     1 *E(19)*SIN(2.*C))))
      H(31)=CMPLX((E(3)+(8.*E(24)*COS(A)*COS(B)*COS(C))+(2.*E(21)*(COS(2
     1.*A)+COS(2.*B)))+(2.*E(22)*COS(2.*C)+(4.*E(30)*COS(2.*A)*COS(2.*B
     2))),0.0)
      H(32)=CMPLX(((-8.)*E(25)*SIN(A)*COS(B)*SIN(C)),0.0)
      H(33)=CMPLX(((-8.)*E(25)*COS(A)*SIN(B)*SIN(C)),0.0)
      H(34)=CMPLX(0.0,0.0)
      H(35)=CMPLX(((((-8.)*E(27)*SIN(A)*SIN(B)*COS(C))-(4.*E(31)*SIN(2.*A
     1 )*SIN(2.*B))),0.0)
      H(36)=CMPLX((E(3)+(8.*E(24)*COS(A)*COS(B)*COS(C))+(2.*E(21)*(COS(2
     1.*B)+COS(2.*C))+(2.*E(22)*COS(2.*A)+(4.*E(30)*COS(2.*B)*COS(2.*C
     2))),0.0)
      H(37)=CMPLX(((((-8.)*E(25)*SIN(A)*SIN(B)*COS(C)),0.0)
      H(38)=CMPLX((((((-4.)*(SQRT(3.)))*E(27)*COS(A)*SIN(B)*SIN(C))-(2.*(
     1SQRT(3.))*E(31)*SIN(2.*B)*SIN(2.*C))),0.0)
      H(39)=CMPLX((((4.*E(27)*COS(A)*SIN(B)*SIN(C))+(2.*E(31)*SIN(2.*B)*S
     1IN(2.*C)))),0.0)
      H(40)=CMPLX((E(3)+(8.*E(24)*COS(A)*COS(B)*COS(C))+(2.*E(21)*(COS(2
     1.*A)+COS(2.*C)))+(2.*E(22)*COS(2.*B))+(4.*E(30)*COS(2.*A)*COS(2.*C
     2))),0.0)
      H(41)=CMPLX(((4.*(SQRT(3.))*E(27)*SIN(A)*COS(B)*SIN(C))+(2.*(SQRT(
     1 3.))*E(31)*SIN(2.*A)*SIN(2.*C))),0.0)
      H(42)=CMPLX(((4.*E(27)*SIN(A)*COS(B)*SIN(C))+(2.*E(31)*SIN(2.*A)*S
     1IN(2.*C))),0.0)
      H(43)=CMPLX((E(4)+(8.*E(8)*COS(A)*COS(B)*COS(C))+((3./2.)*E(23)*(C
     1OS(2.*A)+COS(2.*B)))+(2.*E(26)*(((1./4.)*(COS(2.*A)+COS(2.*B)))+CO
     2S(2.*C)))),0.0)
      H(44)=CMPLX(((SQRT(3.)/2.)*(((E(23)*(COS(2.*B)-COS(2.*A)))-(E(26)*(
     1COS(2.*B)-COS(2.*A))))),0.0)
      H(45)=CMPLX((E(4)+(8.*E(8)*COS(A)*COS(B)*COS(C))+(2.*E(23)*((3./4.
     1)*(COS(2.*A)+COS(2.*B))+COS(2.*C)))+((3./2.)*E(26)*(COS(2.*A)+COS(
     2 2.*B)))),0.0)
      RETURN
      END
```

```
LABEL CONT   ...1....+....2....+....3....+....4....+....5....+....6....+....7...
             SUBROUTINE GAUSEL (PROD,A,N)
             COMPLEX A(6,6),F,TEMP,PROD
             PROD = CMPLX(1.0,0.0)
             N = N-1
             DO 5 I = 1 , N
             XMAX = CABS(A(I,I))
             MAX = I
             DO 10 J = I , N
             IF (XMAX.LT.CABS(A(J,I)))GO TO 9
             GO TO 10
   9         XMAX=CABS(A(J,I))
             MAX = J
  10         CONTINUE
             IF (XMAX.LE.10**(-7)) GO TO 20
             IF (MAX.EQ.I) GO TO 40
             DO 30 J = I , N
             TEMP = A(I,J)
             A(I,J) = A(MAX,J)
  30         A(MAX,J) = TEMP
             PROD =PROD * CMPLX(-1.0,0.0)
  40         L=I+1
             DO 80 J = L , N
             F = A(J,I) / A(I,I)
             DO 50 K = I , N
  50         A(J,K) = A(J,K) - F * A(I,K)
  80         CONTINUE
   5         CONTINUE
             DO 60 I = 1 , N
  60         PROD = PROD * A(I,I)
             GO TO 70
  20         PROD = CMPLX(0.0,0.0)
  70         RETURN
             END
```

APPENDIX C. E(k)-values calculated by the Green's function method.

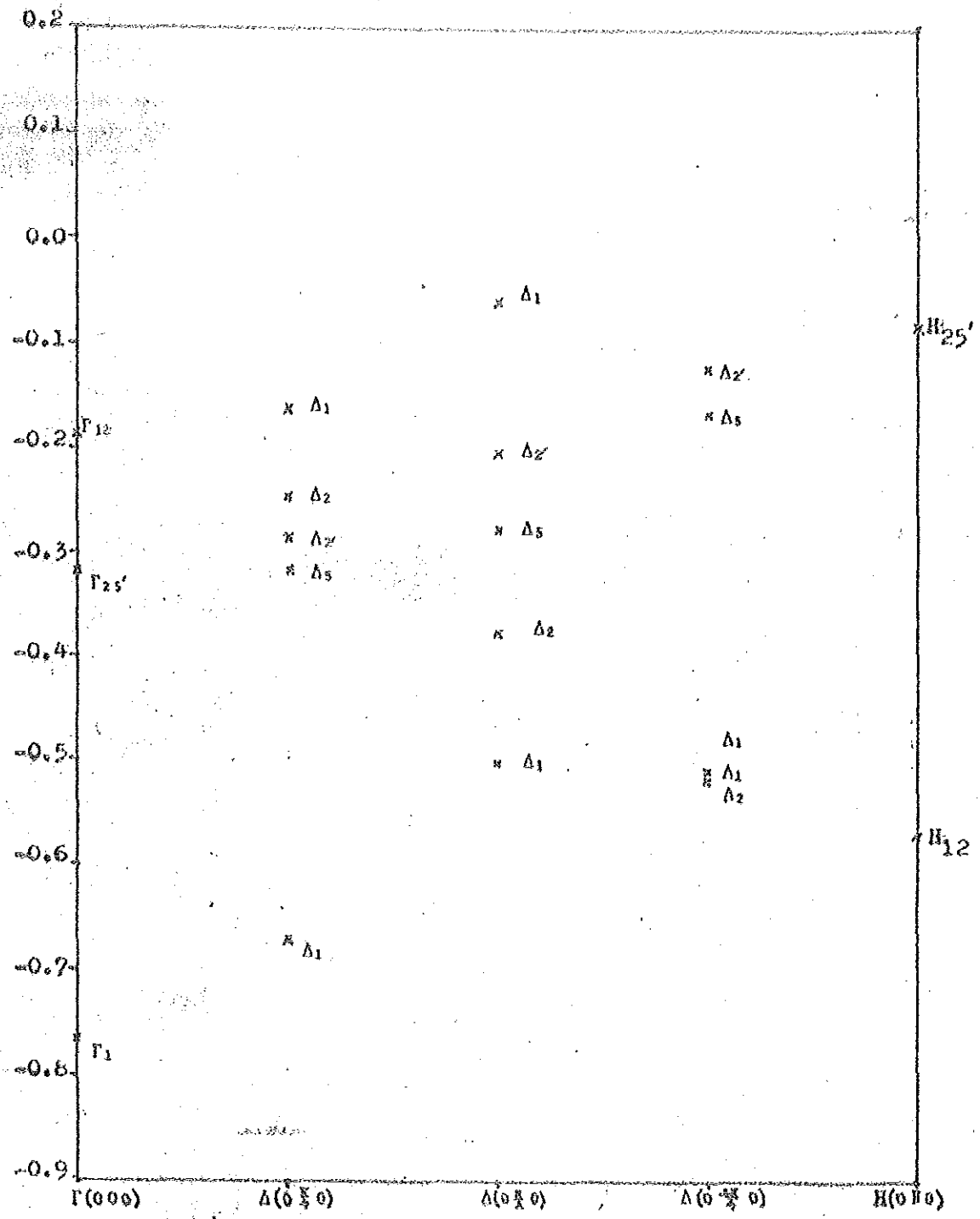


Fig. C. E(k)-values in units of rydberg computed by KKR method along Γ-H(Δ-direction) in BZ.

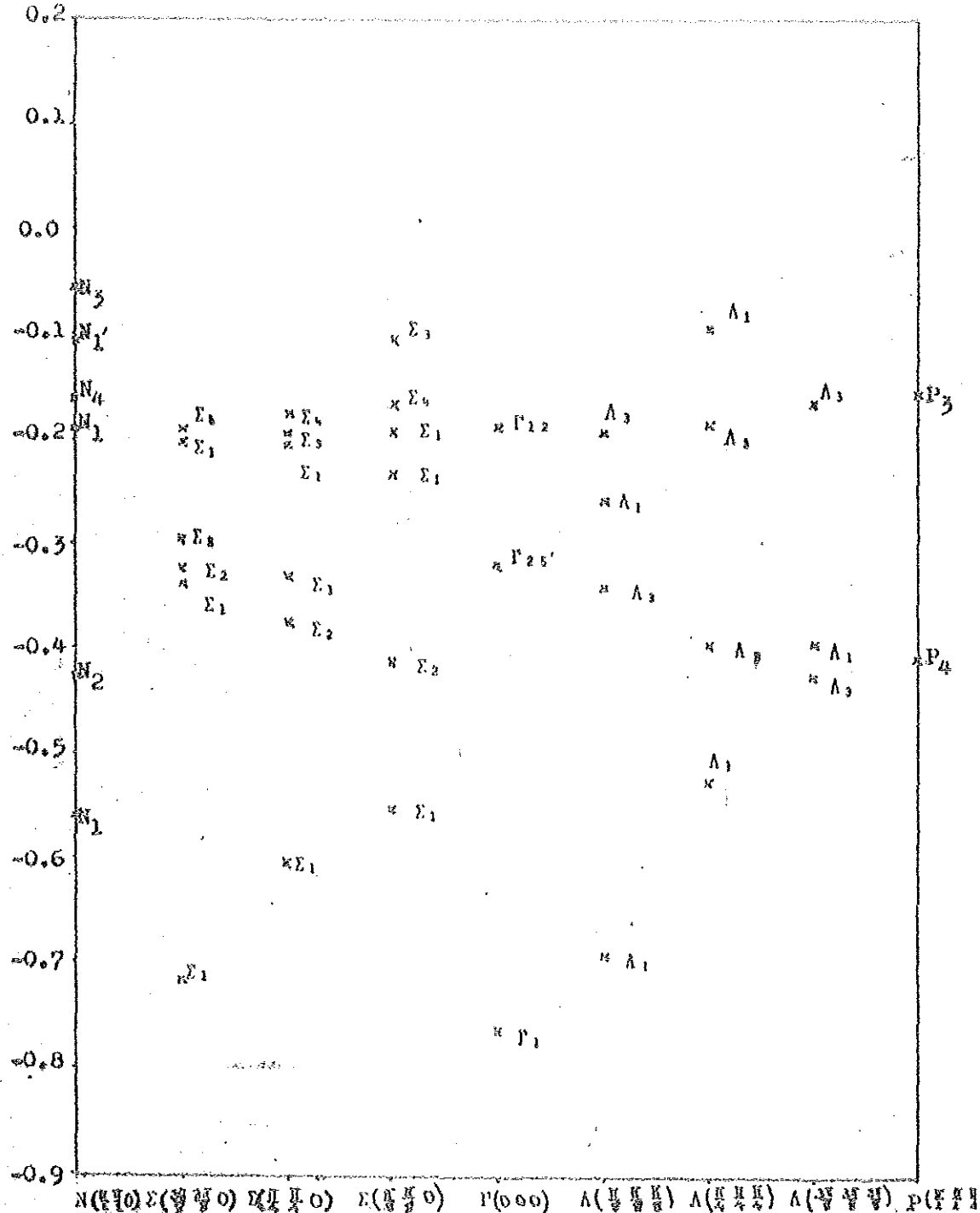


Fig. 4. E(k)-values in units of rydberg computed by KKR method along N- -P(Σ-direction and Λ-direction) in the BZ.

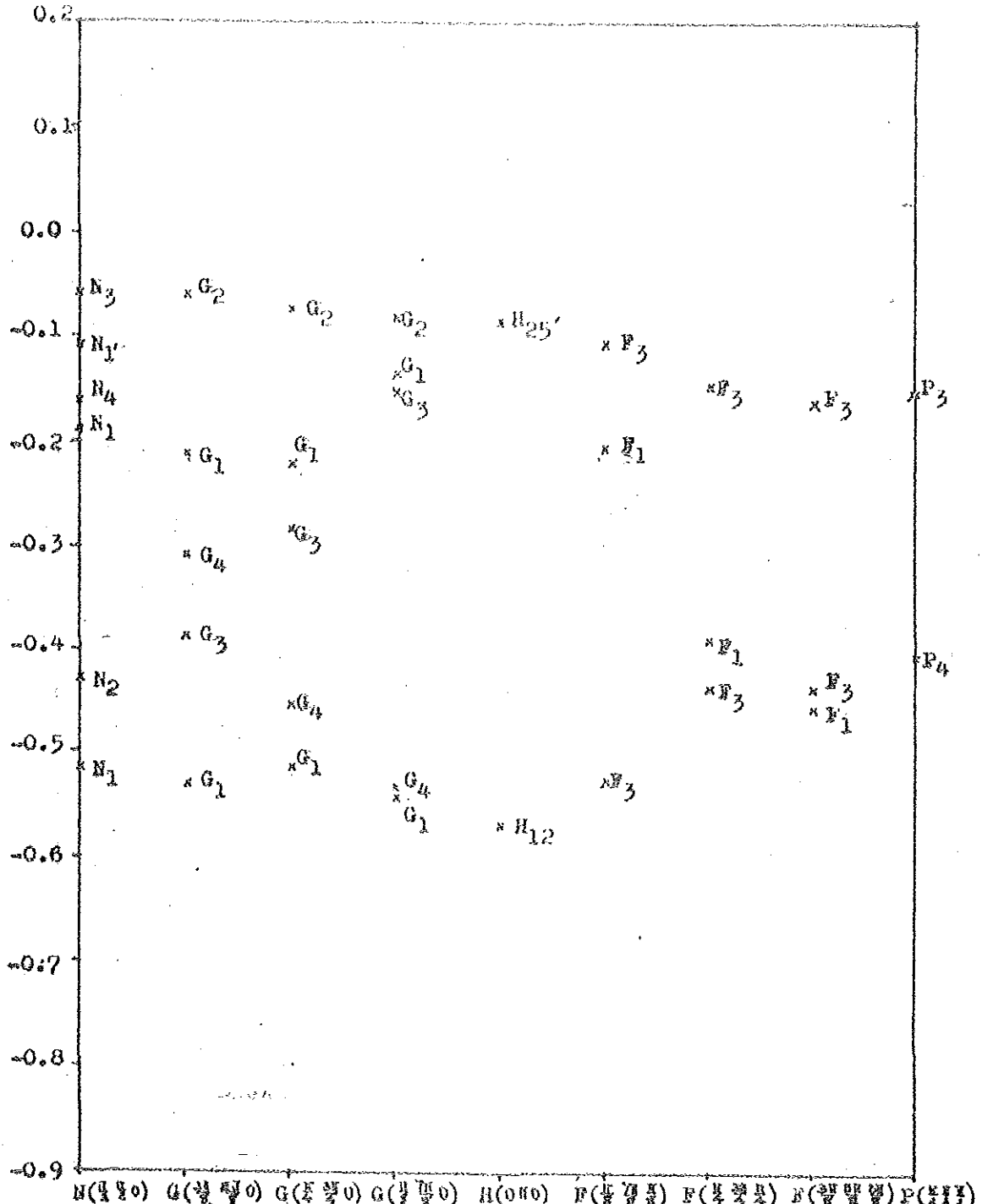


Fig.c. E(k)-values in units of rydberg computed by KKR method along N-H-P (G-direction and F-direction) in BZ.

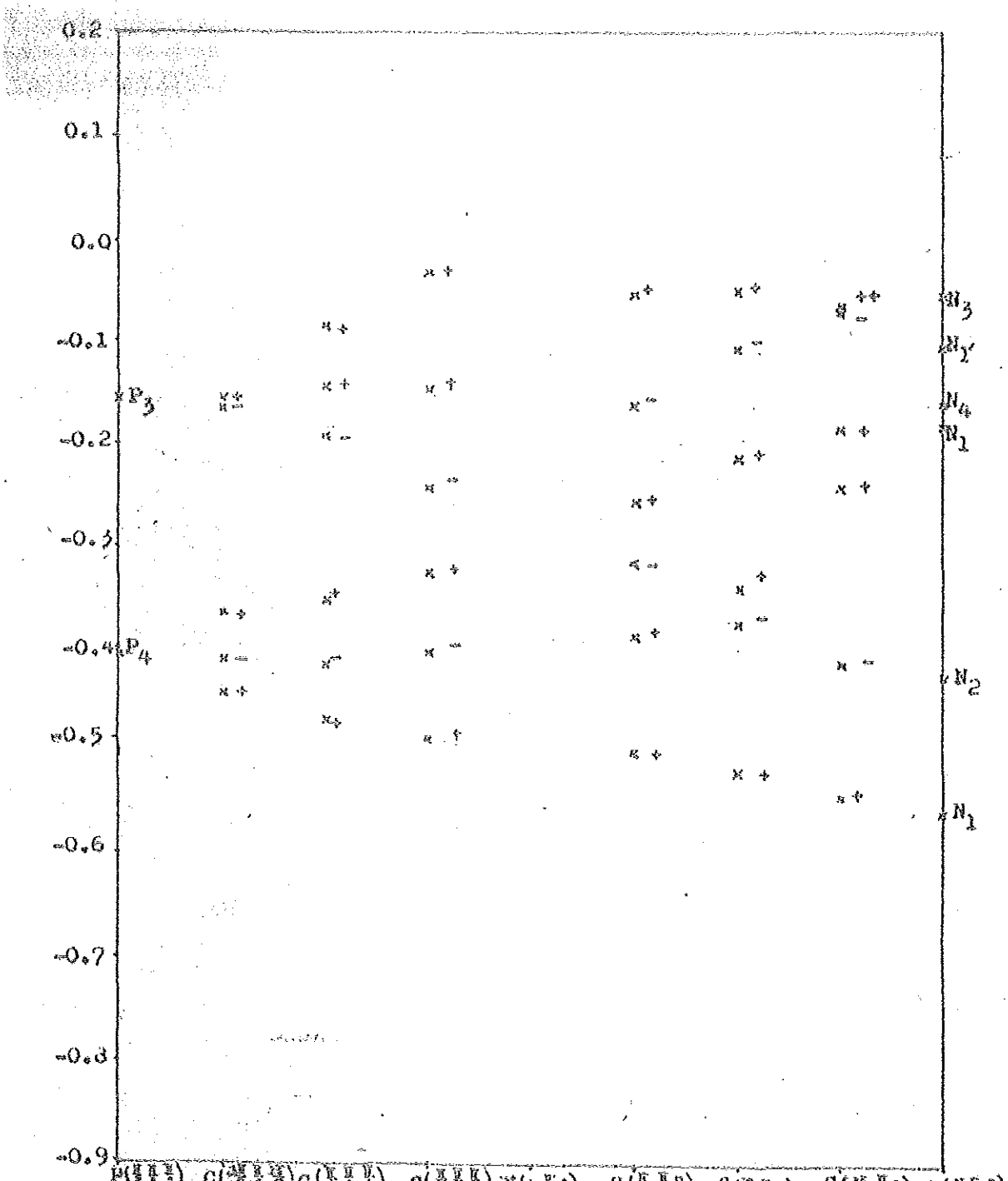


Fig.4. $E(\vec{k})$-values in units of rydberg computed by KKR method along P-X-N (low-symmetry direction) in the BZ.

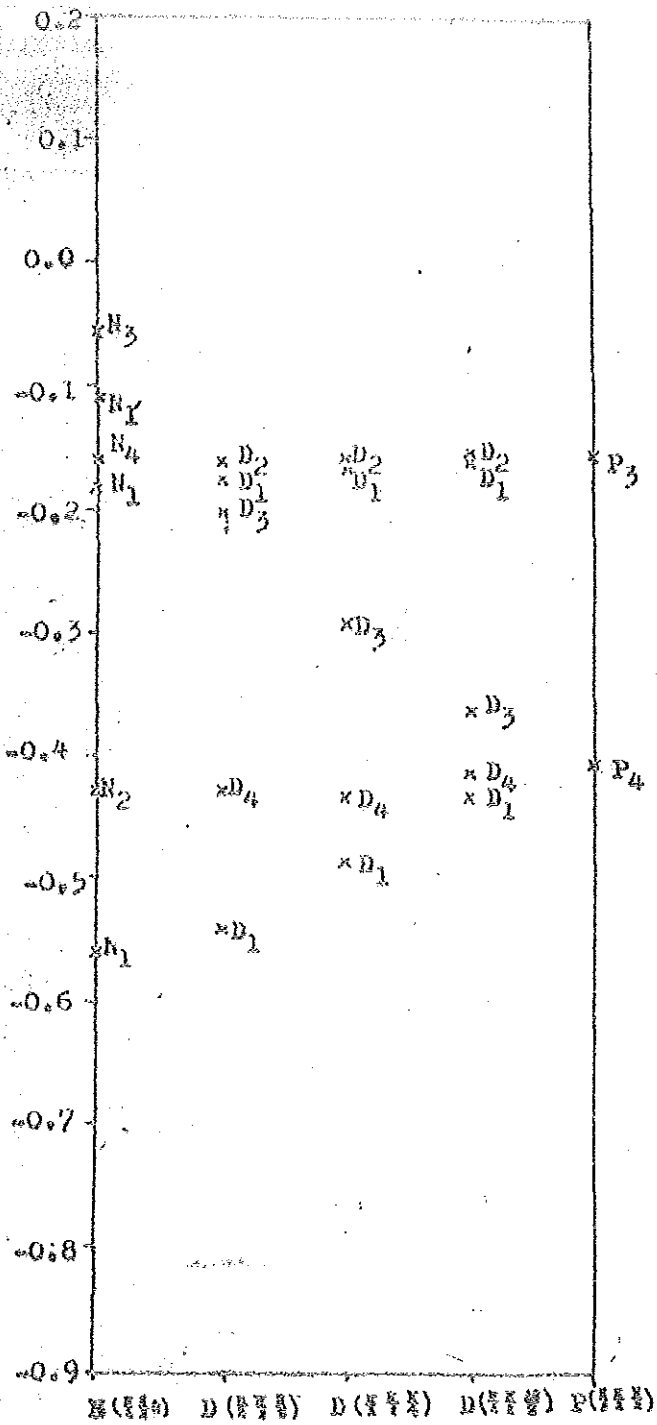


Fig. 8. E(k)-values in units of rydberg computed by KKR method along N-P (D-direction) in BZ.

APPENDIX D. E(k)-values calculated by the Slater-Koster interpolation scheme (denoted by "x") together with E(k) -values computed by the Green's function method ("o").

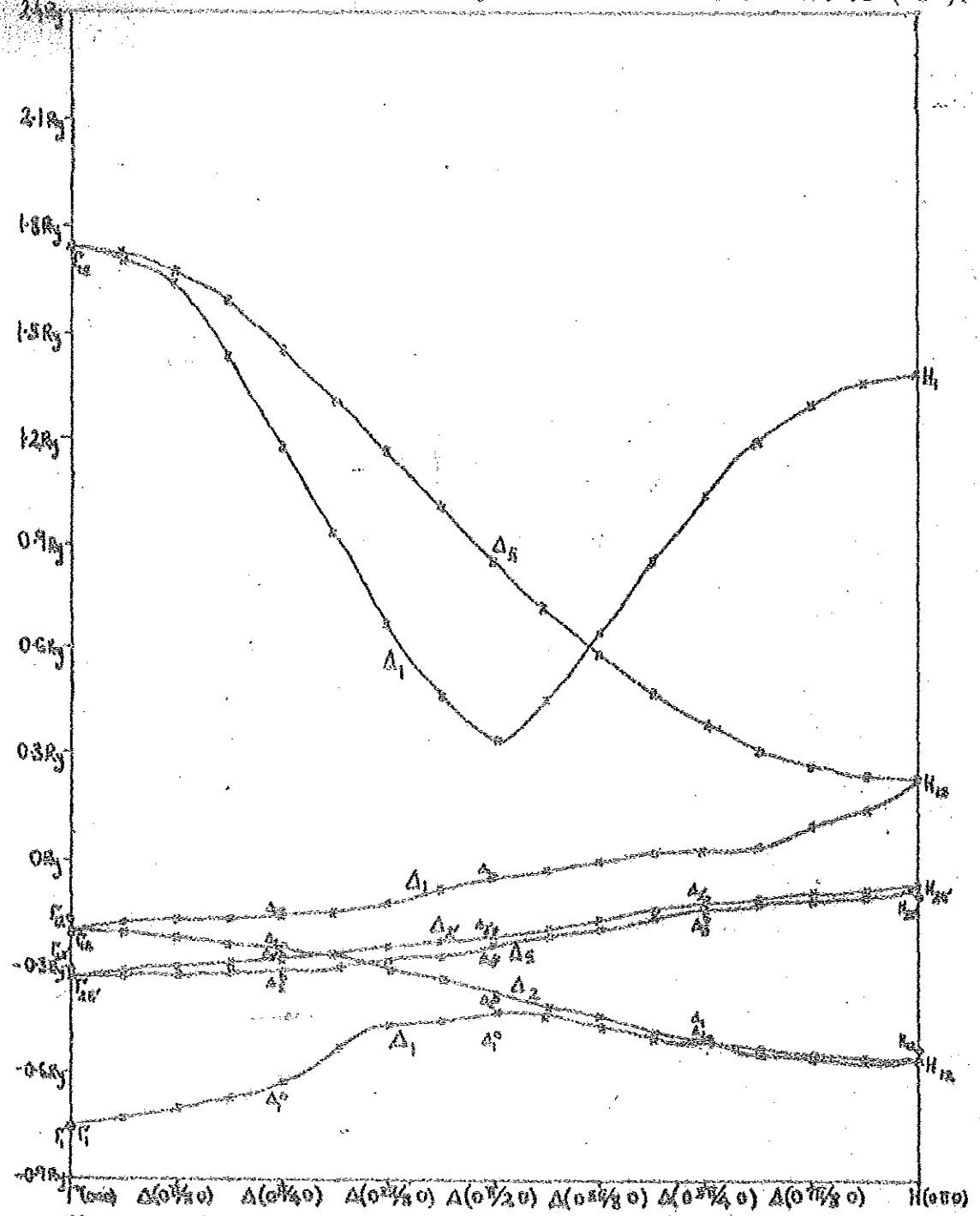


Fig.f. E(k)-values of Cr along Δ-direction in BZ..

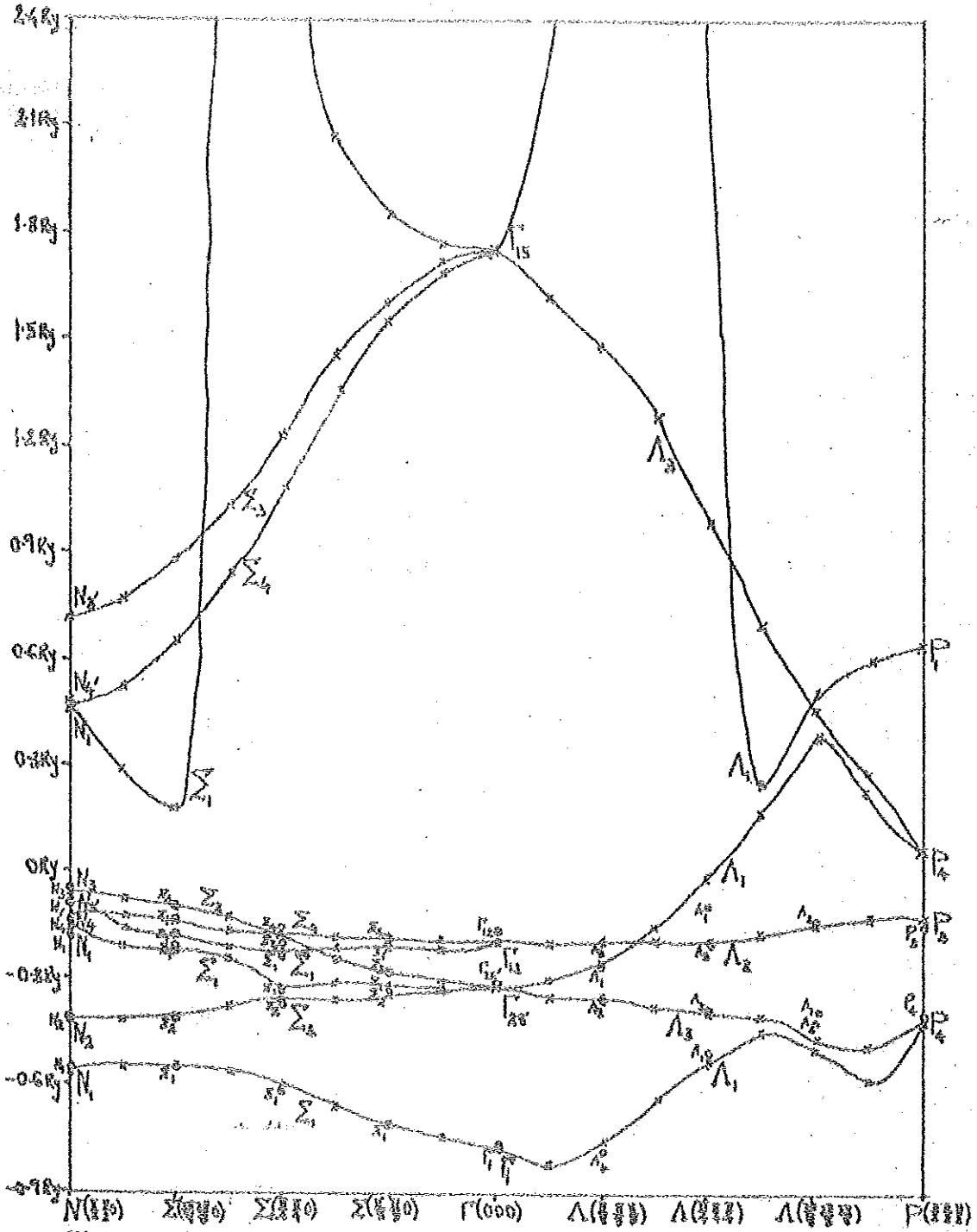
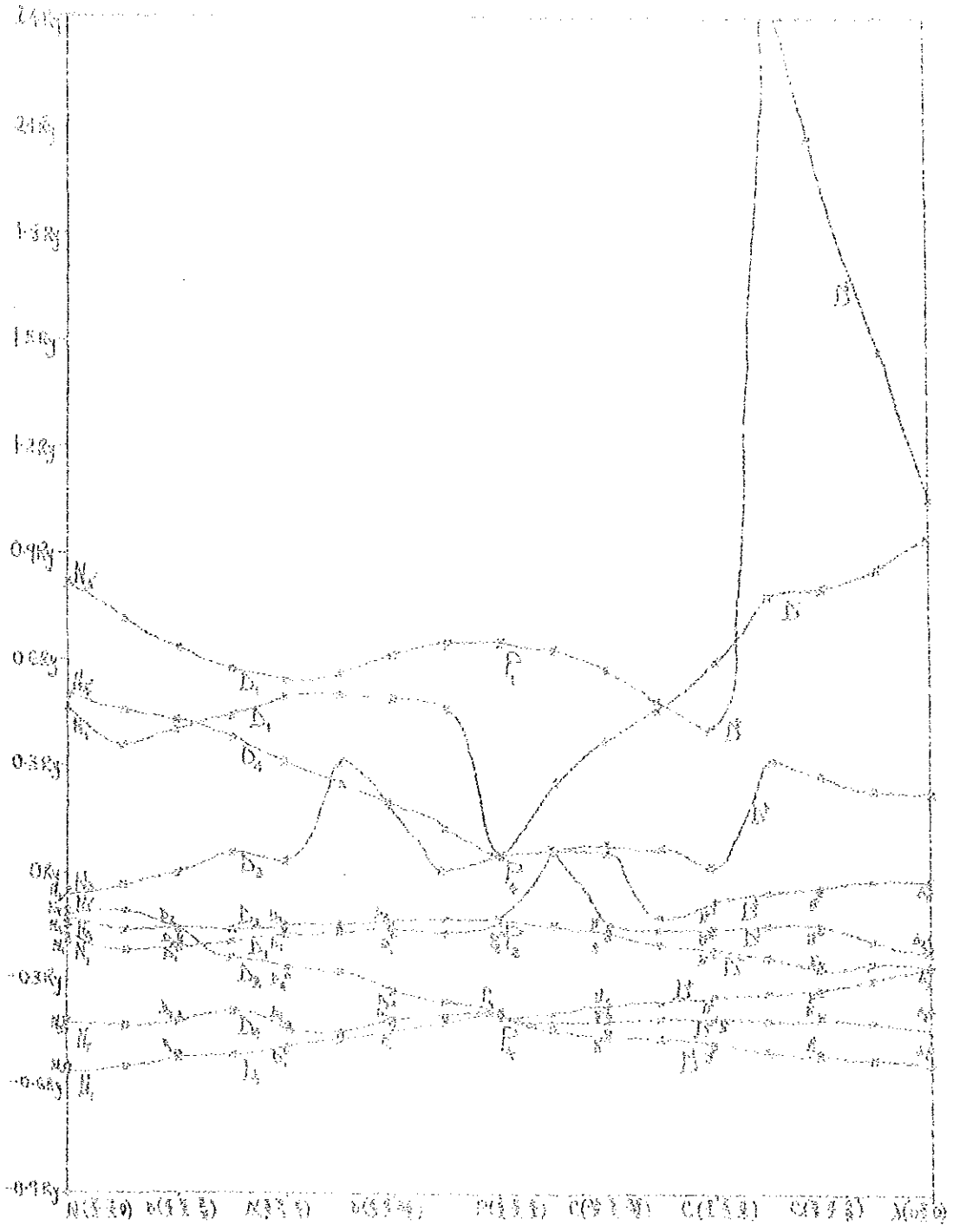


Fig.6. E(k)-values of Cr along the Σ and Λ-directions in BZ.



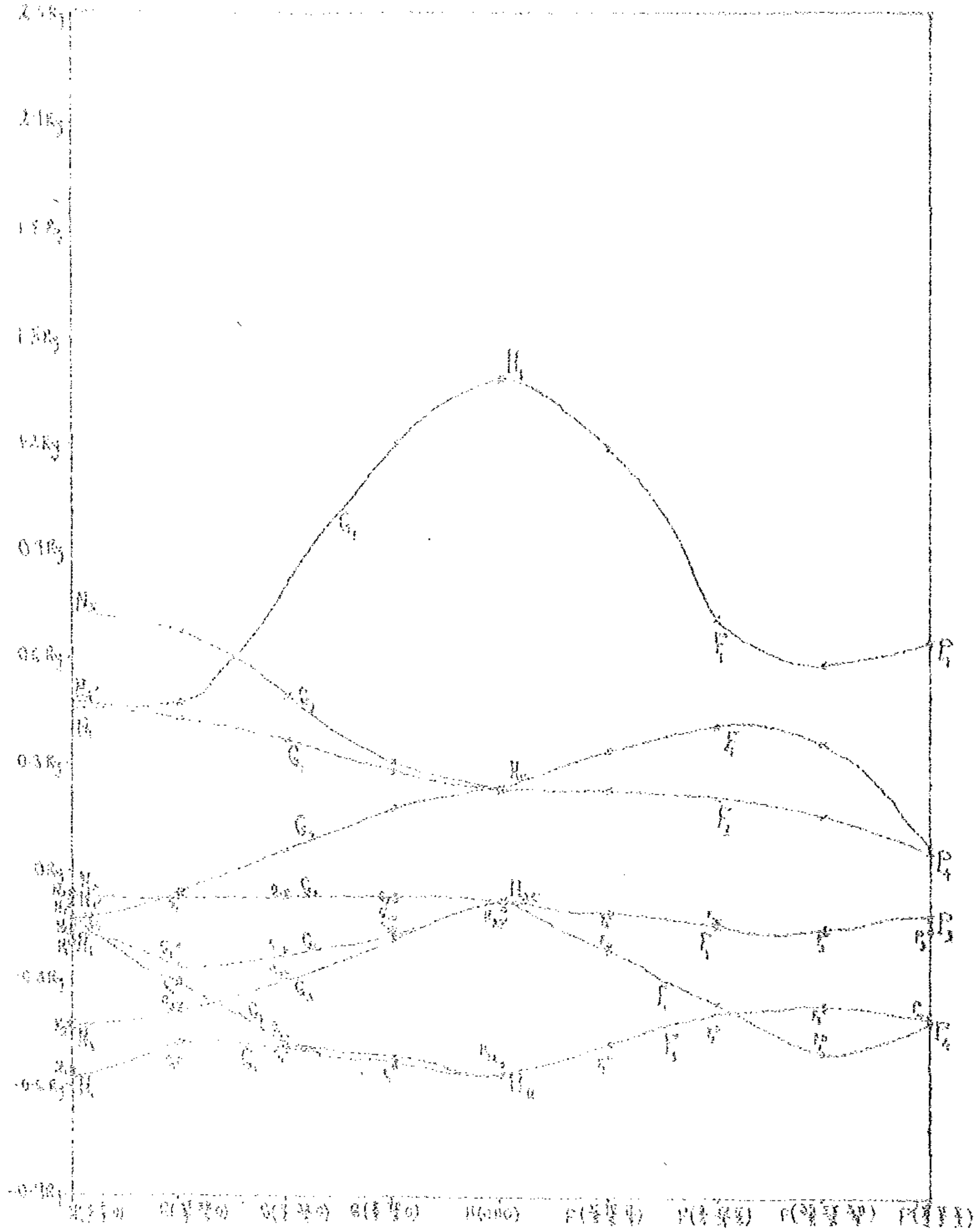


Fig. [illegible] E(k)-curves of [illegible] along G and F-directions in [illegible]

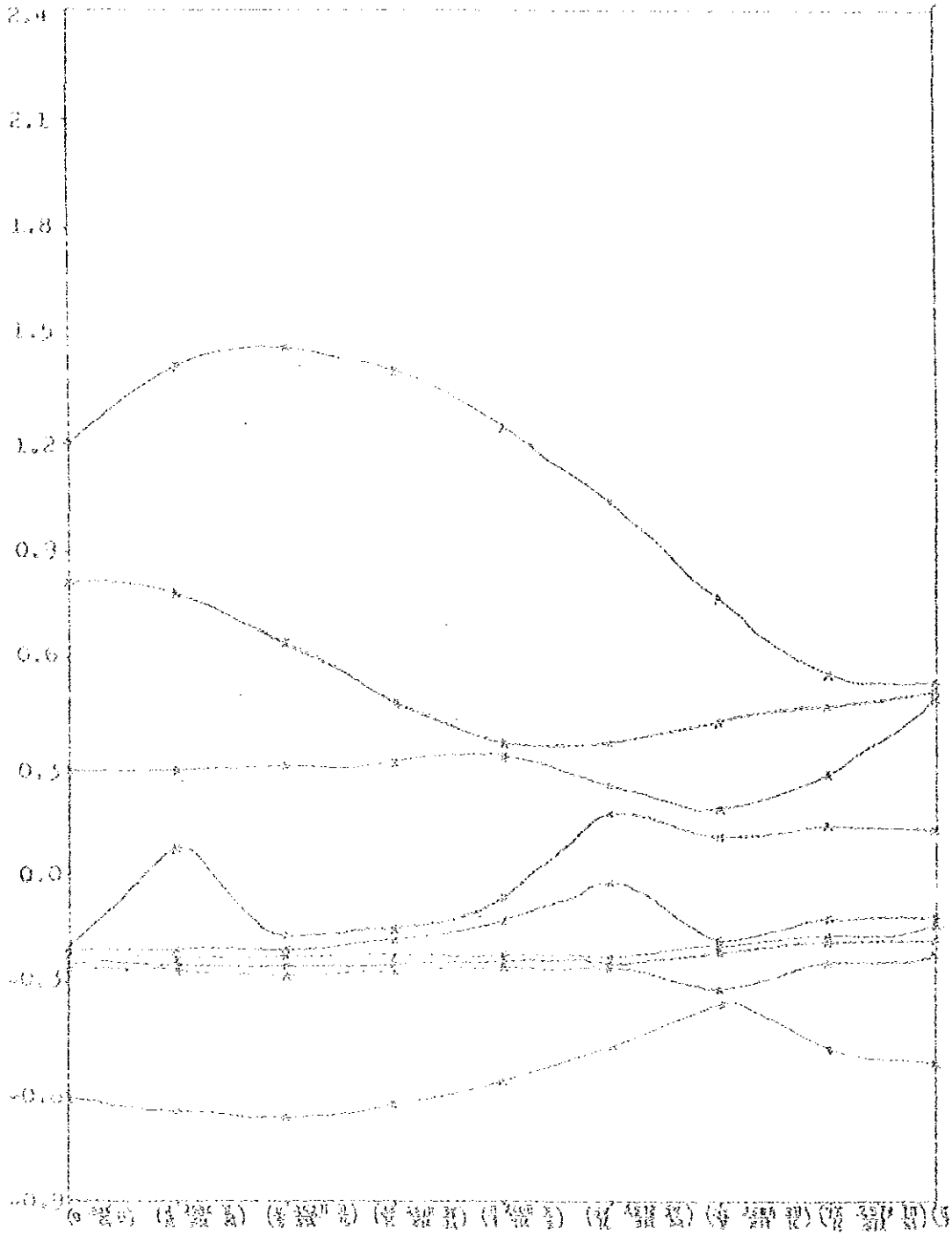


Fig. 4 . $b(\vec{k})$-values of Cr in units of rydberg computed by the Slater-Koster interpolation scheme along a general direction in $\vec{k}$.