THE BAND STRUCTURE OF MnF2

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by

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SCOPE AND CONTENTS:

The Augmented Plane Wave method has been used to calculate the one-electron energy band structure of MnF_2 . The bands were computed at the Γ point and along the Λ line for cases representing the "paramagnetic" and anti-ferromagnetic states of MnF_2 .

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CHAPTER

INTRODUCTION

The aim of the present work is the determination of the one-electron energy band picture of manganese fluoride (MnF_2) by means of the Augmented Plane Wave (APW) method. The potentials used in the calculations are considered to be representative of the "paramagnetic" and antiferromagnetic states of MnF_2 . Since MnF_2 may be considered a classic antiferromagnet, the study of its energy band structure is of importance in investigating the properties of insulating antiferromagnets.

The remainder of the introduction gives a brief historical background of the APW calculation and presents a general description of the assumptions necessary for its implementation. Chapter II is a description of the theory involved in setting up the one-electron Schrödinger equation, including the determination of the Muffin-Tin potential, the APW functions, and the APW matrix elements. A simplified secular equation is given in terms of two and three dimensional arrays which are energy independent. The modifications in the secular equation arising from the application of group theory are also considered. In Chapter III, the general APW method is applied to the specific Case of MnF₂.

The crystal structure and the lattice parameters are given and the various quantities appearing in the secular equation are evaluated for the "paramagnetic" and antiferromagnetic cases. This includes the applicable group theory for MnF_2 at the T point (centre of the Brillouin zone) and along the A line (the (0,0,C^{*}) direction in the reciprocal lattice). Chapter IV presents the results of the band structure calculation for the "paramagnetic" and antiferromagnetic states of MnF_2 .

The APW method for computing the energy band structure of a periodic solid was first proposed by Slater in 1937¹. Owing to the general unavailability of high speed, large memory computers, widespread use of this approach was not possible until the 1960's. Interest then began to shift from the study of the simple metals by the nearly-free electron model to that of the transition elements requiring a more sophisticated treatment, such as the APW. The adaptability of the APW method to different solids and crystal structures has led to a great increase in the number of calculations performed over the last few years. An excellent survey of such calculations, reported in the literature, is given by Loucks². Also reported there is a comparison of the available methods for the calculation of the band structure of a solid, with an explanation of the conditions necessary for their application.

Basically, the APW method involves solving the oneelectron Schrödinger equation. The potential used in this equation is that due to the presence of the nuclei, which are assumed to be stationary, and the other electrons in the material. This is a simplification of the problem in that the motion of the nuclei should be accounted for in an exact solution rather than assuming that they remain motionless in a perfect lattice. The electron contribution to the one-electron potential must also be approximated. Usually this is accomplished by an average-field calculation such as the Hartree^{3,4} or the Hartree-Fock-Slater⁵ methods. A potential is set up which reflects the action on an electron due to the nuclei and some averaged field of the remaining electrons. This potential is substituted into the one-electron Schrödinger equation. The energy eigenvalues are computed by solving a secular equation which is developed from the one-electron Schrödinger equation given in Chapter II. The wave functions which correspond to occupied states are used to calculate the charge density which then yields a new potential. This potential should then be compared with the original, and through a process of iteration, the potential is made self-consistent. The requirement of self-consistency leads to a relatively accurate approximation of the true potential in the crystal. It must be noted that although the self-consistency criterion is

applied in atomic structure calculations, usually only the first iteration is used in band structure determinations because of computer time requirements.

CHAPTER II

THEORETICAL DEVELOPMENT

A. BACKGROUND

The electronic potential energy in a single ideal crystal may be written as

$$V(r) = V(r+T)$$
(1)

where <u>r</u> is some vector in the crystal as shown in Fig. 1, and <u>T</u> represents the lattice vectors or the positions of the unit cells in the crystal. The vector <u>T</u> may be written as

$$\underline{\mathbf{T}} = \mathbf{T}_1 \underline{\mathbf{a}} + \mathbf{T}_2 \underline{\mathbf{b}} + \mathbf{T}_3 \underline{\mathbf{c}} \tag{2}$$

where <u>a</u>, <u>b</u> and <u>c</u> are the basic or primitive translation vectors for the lattice and T_1 , T_2 and T_3 are integers. The objective of the energy band problem is to solve the one-electron Schrödinger equation for an electron in a periodic solid under the influence of a potential of the type given by equation (1). The one-electron Schrödinger equation may be written as

$$H\psi(\underline{r},\underline{k}) = [-\nabla^2 + V(\underline{r})]\psi(\underline{r},\underline{k}) = E(\underline{k})\psi(\underline{r},\underline{k}).$$
(3)

Atomic units have been introduced in equation (3). In the atomic unit system energy is given in Rydbergs (1 Rydberg = 13.6 electron volts) and distances are expressed

in Bohr radii (l Bohr radius = 0.52 A).

The wave functions $\psi(\underline{r},\underline{k})$ in equation (3) are acknowledged to be of the Bloch form^{6,7,8}, meaning that they satisfy the condition

$$\psi(\underline{\mathbf{r}}+\underline{\mathbf{T}},\underline{\mathbf{k}}) = \exp(i\underline{\mathbf{k}}\cdot\underline{\mathbf{T}})\psi(\underline{\mathbf{r}},\underline{\mathbf{k}}) \quad . \tag{4}$$

Additionally, Bloch's Theorem states that the eigenfunctions of the wave equation for a periodic potential are of the form

$$\psi(\underline{\mathbf{r}},\underline{\mathbf{k}}) = \exp(i\underline{\mathbf{k}}\cdot\underline{\mathbf{r}})u(\underline{\mathbf{r}},\underline{\mathbf{k}})$$
(5)

where $u(\underline{r},\underline{k})$ has the periodicity of the crystal lattice⁶, ie. of the potential V(r). Therefore

$$u(\underline{r}+\underline{T},\underline{k}) = u(\underline{r},\underline{k}).$$
 (6)

From equations (4), (5) and (6), it may be seen that $|\psi(\underline{r},\underline{k})|^2$, the charge density, obeys an equation similar to equation (1), but the effect of a translation, \underline{T} , on the wave function $\psi(\underline{r},\underline{k})$ is multiplication by a phase factor, $\exp(i\underline{k}\cdot\underline{T})$. A reciprocal lattice vector, \underline{G} , may now be defined as

$$G = 2\pi (ha^* + kb^* + lc^*)$$
 (7)

where \underline{a}^* , \underline{b}^* and \underline{c}^* are the primitive vectors of the reciprocal lattice of the crystal, and h , k and l are integers. If, in equation (4), the wave vector \underline{k} is identical to a reciprocal lattice vector \underline{G} , then the phase factor $\exp(i\underline{G}\cdot\underline{T})$ is equal to unity. This means that the wave function $\psi(\underline{r}, \underline{k}')$ with wave vector $\underline{k}' = \underline{k}+\underline{G}$ satisfies equation (4) as if it had the wave vector \underline{k} . The problem is now simplified in that to construct the complete picture of the electronic behaviour in a crystal only wave vectors inside the first Brillouin zone need be considered.

As well as simplifications resulting from translational symmetry, the introduction of group theory eases some of the complexity of the APW calculation. According to Koster⁹, the wave function $\psi(\underline{r},\underline{k})$ transforms according to an irreducible representation of the group of the wave vector, \underline{k} . This group consists of all space group operations whose rotational (proper or improper) parts R satisfy the relation¹⁰

$$\underline{R\underline{k}} = \underline{\underline{k}} + \underline{\underline{K}}$$
(8)

where \underline{K}_{i} is a reciprocal lattice vector.

B. THE MUFFIN-TIN POTENTIAL -

One of the most important aspects of an APW calculation is the determination of the periodic potential $V(\underline{r})$. The APW method presupposes a periodic potential aptly named by Slater¹ the "Muffin-Tin Potential". In this picture, the crystal is divided into two distinct regions, with a different form of potential assumed for each region. "Muffin-Tin Spheres"² are chosen around each unit cell atomic site, inside of which the potential is assumed to be spherically symmetric, ie. of the form $V(|\underline{r}-\underline{r}_n|)$. The sphere radius is labelled R_n , where the subscript n represents one of the different atoms in the unit cell. An illustration of this convention is shown in Fig. 1. The region between the spheres is chosen to be of constant potential, V_{c} . The sphere radii, R_{n} , in the unit cell are chosen so that the spheres from neighbouring atomic sites do not overlap. The spheres are usually made to touch along a line joining the nearest-neighbour atoms. The resulting potential is of the form given in Fig. 2 for a direction in a two-dimensional lattice in which the spheres do not touch. The actual calculations of the spherically symmetric potentials for this work on MnF, were performed by E. R. Cowley, and thus only the general procedure involved will be discussed here.

The Muffin-Tin Potential is usually considered to consist of two main contributions: the Coulomb potential V_c ($|\underline{r}-\underline{r}_n|$), due to the nuclei and all the electrons, and an approximated averaged exchange potential V_x ($|\underline{r}-\underline{r}_n|$). These two contributions are evaluated separately and then added to give the total potential inside the spheres.

The Coulomb potential inside a particular sphere is made up of two terms. The first term is due to the charges from the ion inside the sphere. Ionic wave func-

Figure 1

The nth unit cell atomic site or APW sphere showing the convention of symbols used in the calculations

Figure 2

APW or Muffin-Tin potential for a direction in a two-dimensional lattice in which the spheres do not touch



nth APW SPHERE



tions obtained by Clementi¹¹ by means of an analytical Hartree-Fock procedure are used to calculate the charge density. The resulting contribution to the Coulomb potential is then computed by integration ie. Gauss' Law of electrostatics. The second term of the Coulomb potential has two parts. The contribution from the distant charges is handled by a Madelung sum which is evaluated by a computer program based on the procedure given by Born and Huang¹². The nearby charges which overlap into the sphere are spherically averaged by a Löwdin procedure¹³. The charge density which extends into the sphere is computed from the ionic wave functions. These two terms are added to arrive at the total Coulomb potential, $V_c(|\underline{r}-\underline{r}_p|)$.

The exchange potential is calculated by a method which is referred to as the Slater free electron exchange approximation. About an ion at \underline{r}_n (Fig. 1), the electron charge density is computed from the ionic wave functions. In what is called "Slater's $\rho^{1/3}$ term", the exchange potential is proportional to the cube root of the charge density. This result is quite good for a free electron gas and is thought to be a reasonable approximation in band structure calculations. The exchange contribution to the potential may then be written²

$$V_{x}(|\underline{r}-\underline{r}_{n}|) = -6(\frac{3}{8\pi}\rho(|\underline{r}-\underline{r}_{n}|))^{1/3}$$
 (9)

where $\rho(|\underline{r}-\underline{r}_n|)$ represents the crystal electron density. It has been suggested that alternative schemes be used for the calculation of the exchange term. One of these is the exact Hartree-Fock method, which is discussed by Slater¹⁴. The other is a modification of the free electron exchange suggested by Kohn and Scham¹⁵ in which an exchange potential that is 2/3 as large as Slater's is proposed. It is thought that a multiplicative parameter which may vary from 2/3 to 1 should be included in equation (9) to give accurate energy band results.

A shift in the potential is usually made to make the contribution between the spheres equal to zero. The potential inside the APW spheres is then given by

$$V(|\underline{r}-\underline{r}_n|) = V_T(|\underline{r}-\underline{r}_n|) - V_C.$$
(10)

 $V_{T}(|\underline{r}-\underline{r}_{n}|)$ is the total Muffin-Tin Potential which is the sum of the Coulomb and exchange contributions. The spherically symmetric potentials from nearest neighbour ions are plotted as in Figs. 4 and 5. The energy at which they intersect is V_{c} , which is then subtracted from the potentials to make the potential between the spheres equal to zero.

Corrections to this potential are discussed by Mattheiss, Wood and Switendick¹⁰, Schlosser and Marcus¹⁶ and DeCicco¹⁷. As these refinements were not used in the calculations, they will not be discussed here.

C. APW FUNCTIONS AND MATRIX ELEMENTS

The solution to the one electron Schrödinger equation (3) may be written as a linear combination of linearly independent basis functions, $\phi(\mathbf{r}; \mathbf{k}_i, \mathbf{E})$:

$$\psi(\underline{\mathbf{r}},\underline{\mathbf{k}}) = \sum_{i} \mathbf{c}(\underline{\mathbf{k}}_{i}) \phi(\underline{\mathbf{r}};\underline{\mathbf{k}}_{i},\mathbf{E})$$
(11)

where $\underline{k}_{i} = \underline{k} + \underline{K}_{i}$, and \underline{K}_{i} are reciprocal lattice vectors. This means that the sum is carried out over the reciprocal lattice vectors. The number of terms which are included in the sum is dependent on the degree of convergence which is required. An upper limit to the number of terms is determined by time limitations on the computer. The $c(\underline{k}_{i})$ are variational coefficients or expansion parameters, and the $\phi(\underline{r};\underline{k}_{i},E)$ are Augmented Plane Waves.

Outside the APW spheres, the Muffin-Tin Potential has been set equal to zero. This means that solution of the Schrödinger equation yields plane waves with wave vectors \underline{k}_i , and the APW function is given by

$$\phi(\underline{\mathbf{r}};\underline{\mathbf{k}};\mathbf{E}) = \exp(i\underline{\mathbf{k}};\mathbf{\cdot}\underline{\mathbf{r}}). \qquad (12)$$

This solution is acceptable as it satisfies the Bloch condition (4).

Inside the APW spheres, the solution is more difficult. The potential here is spherically symmetric, and the APW function $\phi(\underline{r}; \underline{k}_i, E)$ is expanded in spherical harmonics about the sphere centre \underline{r}_n as

$$\phi(\underline{\mathbf{r}};\underline{\mathbf{k}}_{i},\mathbf{E}) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} A_{\ell m}(\underline{\mathbf{k}}_{i}) u_{\ell}(|\underline{\mathbf{R}}|;\mathbf{E}) Y_{\ell m}(\theta,\phi)$$
(13)

where $\underline{\mathbf{R}} = \underline{\mathbf{r}} - \underline{\mathbf{r}}_{\mathbf{n}}$, according to the convention of Fig. 1. The functions $u_{\ell}(|\underline{\mathbf{R}}|; \mathbf{E})$ are solutions of the radial Schrödinger equation

$$-\frac{1}{R^2}\frac{d}{dR}\left(R^2\frac{du_{\ell}}{dR}\right) + \left(\frac{\ell(\ell+1)}{R^2} + V_n(|\underline{R}|)\right)u_{\ell} = Eu_{\ell} \quad (14)$$

where $V_n(|\underline{R}|)$ is the spherically symmetric potential $V(|\underline{r}-\underline{r}_n|)$ which is centred about the atomic site at \underline{r}_n . The solutions to the angular counterpart of equation (14) may be written as

$$Y_{\ell_{m}}(\theta,\phi) = (-1)^{m} \sqrt{\frac{2\ell+1}{4\pi} \frac{(\ell-m)!}{(\ell+m)!}} \exp(im\phi) P_{\ell_{m}} (\cos\theta) (15)$$

The coefficients $A_{l_m}(\underline{k}_i)$ in equation (13) are evaluated by requiring that the two solutions represented by equations (12) and (13) be continuous at the nth APW sphere boundary. The slope of these functions, however, is not continuous at this point.

The plane wave solution, (12) is expanded in spherical harmonics about the nth sphere centre at \underline{r}_n . It may then be written as

$$\phi(\underline{\mathbf{r}};\underline{\mathbf{k}}_{i},\mathbf{E}) = \exp(i\underline{\mathbf{k}}_{i}\cdot\underline{\mathbf{r}}) = \exp[i\underline{\mathbf{k}}_{i}\cdot(\underline{\mathbf{r}}_{n}+\underline{\mathbf{R}})]$$
$$= \exp(i\underline{\mathbf{k}}_{i}\cdot\underline{\mathbf{r}}_{n})\exp(i\underline{\mathbf{k}}_{i}\cdot\underline{\mathbf{R}})$$
(16)

According to Slater¹, and Powell and Crasemann¹⁸, the second term, $\exp(i\underline{k}_i \cdot \underline{R})$, may be expanded as

$$\exp(i\underline{k}_{i}\cdot\underline{R}) = 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} i^{\ell}j_{\ell}(k_{i}R)Y_{\ell}^{*}(\hat{k}_{i})Y_{\ell}(\hat{R})$$
(17)

where \hat{k}_{i} and \hat{R} represent the angular parts of \underline{k}_{i} and \underline{R} respectively and $j_{\ell}(k_{i}R)$ is a spherical Bessel function of order ℓ . The plane wave expansion of the APW then becomes $\phi(\underline{r};\underline{k}_{i},E)=4\pi\exp(i\underline{k}_{i}\cdot\underline{r}_{n})\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}i^{\ell}j_{\ell}(k_{i}R)Y_{\ell_{m}}^{*}(\hat{k}_{i})Y_{\ell_{m}}(\hat{R}).$ (18)

This function may then be evaluated at the surface of the n^{th} sphere of radius R_n , and set equal to the $\phi(\underline{r};\underline{k}_i,E)$ appearing in equation (13), as both functions are now centred about the atomic site at \underline{r}_n . As a result, the $A_{k_m}(\underline{k}_i)$ may be readily evaluated.

 $A_{\ell_{m}}(\underline{k}_{i}) = 4\pi \exp(i\underline{k}_{i} \cdot \underline{r}_{n}) i^{\ell} j_{\ell}(\underline{k}_{i}\underline{R}_{n}) Y_{\ell_{m}}^{*}(\hat{k}_{i}) / u_{\ell}(\underline{R}_{n}; E)$ (19) Here \underline{R}_{n} represents the radius of the nth APW sphere. The detailed form of the spherical harmonics is given by Powell and Crasemann¹⁸.

$$Y_{\ell_{m}}^{*}(\hat{k}_{i}) = (-)^{m} \sqrt{\frac{2\ell+1}{4\pi} \frac{(\ell-m)!}{(\ell+m)!}} \exp(-im\phi_{i}) P_{\ell_{m}} (\cos\theta_{i})$$
(20)

Substitution of (20), (19) and (15) into equation (13) then yields the detailed form of the APW function inside the nth sphere. The total solution is then given by

 $\phi(\underline{\mathbf{r}};\underline{\mathbf{k}}_{i},\mathbf{E}) = \exp(i\underline{\mathbf{k}}_{i}\cdot\underline{\mathbf{r}}) \qquad (\text{outside sphere n}) \qquad (21)$ $\phi(\underline{\mathbf{r}};\underline{\mathbf{k}}_{i},\mathbf{E}) = \exp(i\underline{\mathbf{k}}_{i}\cdot\underline{\mathbf{r}}_{n}) \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} (2\ell+1) i^{\ell} [\frac{\mathbf{j}_{\ell}(\mathbf{k}_{i}\mathbf{R}_{n})}{u_{\ell}(\mathbf{R}_{n};\mathbf{E})}] u_{\ell}(|\underline{\mathbf{R}}|;\mathbf{E})$

$$\times \frac{(\ell - |\mathbf{m}|)!}{(\ell + |\mathbf{m}|)!} P_{\ell |\mathbf{m}|} (\cos\theta) P_{\ell |\mathbf{m}|} (\cos\theta_{i}) \exp[im(\phi - \phi_{i})]$$

(inside sphere n). (22)

Equations (21) and (22) are the exact solutions for the APW functions outside and inside the Muffin-Tin sphere, n, respectively. However, their slopes are discontinuous at the sphere boundary, R_n , which is an unacceptable condition for a solution of the Schrödinger equation. To correct this condition, a linear combination of these APW's must be taken as indicated by equation (11) with the coefficients $c(k_i)$ to be determined variationally.^{1,2,16}

The expansion of equation (11) for $\psi(\underline{r},\underline{k})$ is then substituted into equation (3).

 $[-\nabla^{2}+\nabla(|\underline{r}-\underline{r}_{n}|)] \sum_{j} c(\underline{k}_{j}) \phi(\underline{r};\underline{k}_{j},E) = E(\underline{k}) \sum_{j} c(\underline{k}_{j}) \phi(\underline{r};\underline{k}_{j},E) \quad (23)$ Multiplication through on the left by $\phi^{*}(\underline{r};\underline{k}_{i},E)$ and integration over a unit cell of the crystal yields the secular equation

$$\sum_{j=1}^{N} (H-E)_{ij} C(k_j) = 0 \quad i = 1, 2, ... N$$
 (24)

where N is the total number of reciprocal lattice vectors taken for the calculation. Substitution for ϕ along with its orthogonality property yields the result given by Slater¹ for the matrix element (H-E)₁₁.

$$\frac{(H-E)_{ij}}{\Omega} = (\underline{k}_{i} \cdot \underline{k}_{j} - E) \delta(\underline{k}_{i} \cdot \underline{k}_{j}) + \Omega^{-1} \sum_{n} \exp[i(\underline{k}_{j} - \underline{k}_{i}) \cdot \underline{r}_{n}]F_{n,ij}$$
(25)

where Ω is the volume of the unit cell for the crystal and $F_{n,ij}$ is given by the expression

$$\mathbf{F}_{n,ij} = 4\pi \mathbf{R}_n^2 \left[- \left(\underline{\mathbf{k}}_i \cdot \underline{\mathbf{k}}_j - \mathbf{E} \right) \mathbf{j}_1 \left(\left| \underline{\mathbf{k}}_j - \underline{\mathbf{k}}_i \right| \mathbf{R}_n \right) / \left| \underline{\mathbf{k}}_j - \underline{\mathbf{k}}_i \right| \right]$$

+
$$\sum_{\ell=0}^{\infty} (2\ell+1) P_{\ell}(\hat{k}_{i} \cdot \hat{k}_{j}) j_{\ell}(k_{i}R_{n}) j_{\ell}(k_{j}R_{n}) u_{\ell}'(R_{n};E) / u_{\ell}(R_{n};E)]. (26)$$

In equation (26), \hat{k}_i is the unit vector $\frac{k_i}{|k_i|}$ and the P_ℓ represent Legendre polynomials. The quantities $u_\ell'(R_n; E)/u_\ell(R_n; E)$ are called logarithmic derivatives and are dependent on energy as well as angular momentum and the <u>nth</u> sphere radius. They are calculated from the radial Schrödinger equation, (14), by numerical methods as given by Loucks², pg. 56. The spherical Bessel functions, j_ℓ , and the Legendre polynomials appearing in equation (26) may also be numerically evaluated by using appropriate recursion relationships^{2,6}.

It should be noted from equation (26) that $F_{n,ij} = F_{n,ji}$ and thus the matrix (H-E)_{ij} is hermitian. When the origin of coordinates for the crystal is chosen to be at a centre of inversion, the vectors \underline{r}_n occur in pairs ie. $\underline{r}_1 = -\underline{r}_2$ etc., and the imaginary parts of the structure factor, $\exp[i(\underline{k}_j - \underline{k}_i) \cdot \underline{r}_n]$ appearing in equation (25), cancel out, leaving terms of the form $2\cos[(\underline{k}_j - \underline{k}_i) \cdot \underline{r}_n]$. Further simplifications employing group theory will be discussed below. In general, non-trivial solutions of equation (24) exist when the determinant of the matrix (H-E) goes to zero. Thus det(H-E) is evaluated as a function of energy, and the eigenvalues E_i , for which the determinant vanishes, are recorded. The determinant is evaluated for several energies for each point in the first Brillouin zone at which the energy levels are required. The resulting points are plotted for a given direction in the reciprocal lattice, yielding the energy bands.

The sum over l in equation (26) is usually cut off at about l=10 to yield an accuracy of a few thousandths of a Rydberg. In the case of MnF₂, the cutoff point was taken to be l=12. To further simplify the calculation, the terms in the matrix (H-E) which are not dependent on energy are written in two and three dimensional arrays. Equation (25) may then be written as

$$\Omega^{-1}(H-E)_{ij} = -E A_{ij} + B_{ij} + \sum_{\substack{n \ l = 0}}^{l} C_{ijl}^{(n)} \frac{u_{l}^{\prime}(R_{n};E)}{u_{l}^{\prime}(R_{n};E)}$$
(27)

where

$$A_{ij} = \delta(\underline{k}_{i}, \underline{k}_{j}) - \sum_{n} 4\pi R_{n}^{2} \Omega^{-1}$$

$$\times \left[\sum_{\nu=1}^{\nu_{n}} \exp\left[i(\underline{k}_{j}-\underline{k}_{i})\cdot\underline{r}_{\nu}\right]\right]_{1} \left(|\underline{k}_{j}-\underline{k}_{i}|R_{n}\right) / |\underline{k}_{j}-\underline{k}_{i}| (28)$$

$$B_{ij} = (\underline{k}_i \cdot \underline{k}_j) A_{ij}$$
(29)

$$C_{ijl}^{(n)} = 4\pi R_{n}^{2} \Omega^{-1} (2l+1) j_{l} (k_{i}R_{n}) j_{l} (k_{j}R_{n}) P_{l} (\hat{k}_{i} \cdot \hat{k}_{j})$$

$$\times \sum_{\substack{\nu=1 \\ \nu=1}}^{\nu} \exp[i(k_{j} - k_{i}) \cdot r_{\nu}]] \qquad (30)$$

where the sum over all atoms in the unit cell is split into two; the first, over n, represents the inequivalent atoms of the unit cell, and the second, over v counts all v_n atoms of the nth type. This is the method suggested by Mattheiss, Wood, and Switendick¹⁰.

D. SIMPLIFICATIONS USING GROUP THEORY

The previous equations for the APW matrix elements were arrived at by using only the translational symmetry of the crystal. This method must be used when one is considering general points in the first Brillouin zone. However, only a limited number of reciprocal lattice vectors, \underline{K}_i , can be included in such a calculation owing to time and space limitations on the computer. Simplifications arise when states are considered whose wave vectors are in symmetry planes or lines or at symmetry points of the Brillouin zone. The group of the wave vector, $\underline{C}_{\underline{k}}$, then includes rotations and reflections.

According to the representation theory of groups, the matrix elements of (H-E) which connect states that transform according to different irreducible representations of the

group C_k are zero¹⁹. The (H-E) matrix may then be blockdiagonalized, according to the irreducible representations of C_k , into sub-matrices which are non-interacting. In the case of two or more dimensional representations, matrix elements which connect partners of the same representation are zero ie, these represent the degeneracy of the state. Under this scheme, the resulting energy solutions (bands) may be associated with the various irreducible representations of the group.

Outlines of group-theoretical techniques for symmorphic space groups can be found in standard texts¹⁹. For the case of non-symmorphic space groups, which contain elements combining reflection or rotation with a non-primitive translation, the same basic techniques are applicable. However, care must be taken to keep track of which group operators include a non-primitive translation. The specific case of MnF₂ is discussed later.

If one designates a space group operation by R, which is represented by a matrix, $\Gamma_{ij}^{\alpha}(R)$, α being the representation under consideration, then the basic equations given by Mattheiss, Wood, and Switendick¹⁰ are valid. The equation for the (H-E) matrix then becomes, for the α^{th} representation:

$$(H-E)_{ij}^{\alpha} = (\underline{q}_{n_{\alpha}}) \sum_{R} [\Gamma_{11}^{\alpha}(R)]^{*} < \phi(\underline{r}; \underline{k}_{i}, E) | H-E | \phi(\underline{r}; \underline{Rk}_{j}, E) > (31)$$

Upon substitution for $\phi(\underline{r};\underline{k}_i,E)$ and integration, the symmet-

rized equivalent to equation (25) becomes

$$\Omega^{-1}(H-E)_{ij}^{\alpha} = \left(\frac{g}{n_{\alpha}}\right) \sum_{R} \left[\Gamma_{11}^{\alpha}(R)\right]^{*} \left\{\left(\underline{k}_{i} \cdot \underline{Rk}_{j} - E\right) \delta\left(\underline{Rk}_{j}, \underline{k}_{i}\right) + \Omega^{-1} \sum_{n} \exp\left[i\left(\underline{Rk}_{j} - \underline{k}_{i}\right) \cdot \underline{r}_{n}\right] F_{n,ij}(R)\right\}, \quad (32)$$

where the expression for $F_{n,ij}(R)$ is given by

$$F_{n,ij}(R) = 4\pi R_n^2 \{-(\underline{k}_i \cdot \underline{R}\underline{k}_j - E)j_1(|\underline{R}\underline{k}_j - \underline{k}_i|R_n)/|\underline{R}\underline{k}_j - \underline{k}_i| + \sum_{\ell=0}^{\infty} (2\ell+1)P_\ell(\hat{\underline{k}}_i \cdot \underline{R}\hat{\underline{k}}_j)j_\ell(k_iR_n)j_\ell(k_jR_n) \frac{u_\ell'(R_n;E)}{u_\ell(R_n;E)} \}$$
(33)

In equation (32), n_{α} is the dimension of the α^{th} irreducible representation, g is the order of the group, $G_{\underline{k}}$, and \underline{R} indicates that the space group operation R, when acting on a wave vector yields another vector.

Equation (32) may also be written in terms of two and three dimensional arrays similar to equation (27) for the unsymmetrized matrix element.

$$\Omega^{-1}(H-E)_{ij}^{\alpha} = -EA_{ij}^{\alpha} + B_{ij}^{\alpha} + \sum_{n \ k=0}^{\ell} C_{ijk}^{\alpha(n)} \left[\frac{u_{\ell}'(R_{n};E)}{u_{\ell}(R_{n};E)} \right], \quad (34)$$

where

$$A_{ij}^{\alpha} = \left(\frac{g}{n_{\alpha}}\right) \sum_{R} \left[\Gamma_{11}^{\alpha}(R)\right]^{*} \left\{\delta\left(\frac{Rk}{2}j, \frac{k}{2}i\right) - \sum_{n} 4\pi R_{n}^{2}\Omega^{-1} \\ \times \left(\sum_{\nu=1}^{\nu} \exp\left[i\left(\frac{Rk}{2}j-\frac{k}{2}i\right)\cdot \underline{r}_{\nu}\right]\right) j_{1}\left(\frac{Rk}{2}j-\frac{k}{2}i|R_{n}\right) / \frac{Rk}{2}j-\frac{k}{2}i|\right\} (35)$$

$$B_{ij}^{\alpha} = \left(\frac{g}{n_{\alpha}}\right) \sum_{R} \left[\Gamma_{11}^{\alpha}(R)\right]^{*} \left(\underline{k}_{i} \cdot \underline{Rk}_{j}\right) \left\{\delta\left(\underline{Rk}_{j}, \underline{k}_{i}\right) - \sum_{n} 4\pi R_{n}^{2} \Omega^{-1} \right\}$$

$$\times \left(\sum_{\nu=1}^{\nu} \exp\left[i\left(\underline{Rk}_{j} - \underline{k}_{i}\right) \cdot \underline{r}_{\nu}\right]\right) j_{1} \left(|\underline{Rk}_{j} - \underline{k}_{i}|R_{n}\right) / |\underline{Rk}_{j} - \underline{k}_{i}|\} (36)$$

$$C_{ijl}^{\alpha(n)} = \left(\frac{g}{n_{\alpha}}\right) 4\pi R_{n}^{2} \Omega^{-1} (2l+1) j_{l} (k_{j}R_{n}) j_{l} (k_{i}R_{n})$$

$$\times \left\{ \sum_{R} \left[\Gamma_{11}^{\alpha}(R) \right]^{*} \left(\sum_{\nu=1}^{\nu} \exp\left[i\left(\frac{Rk}{\nu-j} - \frac{k}{i}\right) \cdot \underline{r}_{\nu} \right] \right) P_{l} (\hat{k}_{i} \cdot \frac{Rk}{\nu} j) \right\} (37)$$

Although the use of Symmetrized Augmented Plane Wave functions (SAPW's) complicates the form of the (H-E) matrix elements, the resulting block diagonalization decreases the number of such elements which must be calculated. The above equations have been programmed for MnF_2 using the outline given by Loucks² in Appendix 5.

CHAPTER III

IMPLEMENTATION FOR MnF2

 ${\rm MnF}_2$ has a tetragonal crystal structure, with two ${\rm Mn}^{+2}$ ions and four F⁻ ions per unit cell. The cell dimensions are given by the lattice parameters c and a, which have been found to be 6.25490 A.U. and 9.2095 A.U. respectively²⁰. The positions of the various ions in the unit cell are specified by

Mn⁺²: $\pm (0, 0, 0), (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$

F'': ±(u,u,o), (u + $\frac{1}{2}$, $\frac{1}{2}$ - u, $\frac{1}{2}$)

where $u \approx 0.31^{20}$. The projection of the structure on the a-b plane is shown in Fig. 3.

A. DETERMINATION OF LOGARITHMIC DERIVATIVES

The first step in the calculation is to determine the muffin-tin sphere radii for the manganese and fluorine ions. Two distinct cases have been treated, that of "paramagnetic" MnF_2 and antiferromagnetic MnF_2 . In the latter case, the two manganese ions in the unit cell are considered different, one having all five d electrons with spin up, and the other with all five spins down. This means that an up-spin electron experiences a different potential in the regions of these

Figure 3

The projection of the MnF_2 crystal structure on the a-b plane.



 $Mn^{*2}, z = 0$ $) Mn^{+2}, z = \frac{c}{2}$

 \odot F⁻, z = 0 O F⁻, z = $\frac{c}{2}$ two ions. As we shall later see, this effectively reduces the symmetry for the SAPW calculations.

The ionic potentials, including Coulomb and exchange contributions, were supplied by E. R. Cowley, on a logarithmic grid described by Loucks². The grid has been linearized and the results plotted as functions of distance from the particular ions involved, in steps of 0.05 A.U. The shortest inter-ionic distance is between Mn^{+2} at(0,0,0) and F⁻ at $(-u+\frac{1}{2}, -\frac{1}{2}+u, \frac{1}{2})$ ie approximately (1.75, -1.75, 3.13) A.U. All potentials as well have been corrected for the Madelung Constant as supplied by C. V. Stager. For the Mn^{+2} potential, this correction is +1.528 Rydbergs and for the F⁻ potential it is -0.875 Rydbergs. Figs. 4 and 5 show the corrected potentials for the "paramagnetic" and antiferromagnetic cases respectively.

The intersection of Mn^{+2} and F^{-} potentials from Fig. 4 is seen to be at 2.125 A.U. from Mn^{+2} and 1.863 A.U. from F^{-} . The corresponding points on Loucks' logarithmic grid may be calculated as 192 for Mn^{+2} and 189 for F^{-} . These are the muffin-tin sphere radii for the manganese and fluorine ions. The constant correction to the muffin-tin potential to make it equal to zero between the spheres is seen from Fig. 4 to be 1.1 Rydbergs for the case of "paramagnetic" MnF_2 .

Similarly, for antiferromagnetic MnF₂, the corrected potentials have been plotted in Fig. 5. As discussed previously,

Figure 4

The ionic potentials for the Mn^{+2} and F^{-} ions used in "paramagnetic" case. Corrections have been included for the Madelung Constant



N5
there are two types of manganese ions in the unit cell. These have been labelled Mn⁺²A and Mn⁺²B, corresponding to spin up and spin down respectively. It is seen that the Mn⁺²A intersection with F occurs at 2,180 A.U. from Mn⁺²A and the Mn⁺²B intersection occurs at 2.035 A.U. from Mn⁺²B, or at grid points 192 and 191 of Loucks' grid respectively. The fluorine sphere radius is chosen to be the distance from the F site to the intersection of the F potential curve with that of $Mn^{+2}A$ to eliminate the possibility of overlapping spheres. This distance is found to be 1.8081 A.U. or Loucks' grid point 188. It is evident in this case that there are two possible constant energies which could be added to the potentials in an attempt to make the potential between the muffin-tin spheres equal to zero. These correspond to the intersections of $Mn^{+2}A$ and $Mn^{+2}B$ with F. The constant chosen was that appropriate to the $Mn^{+2}B$ case and may be seen from Fig. 5 to be 1.01 Rydbergs. The smaller constant was used to ensure that at no time would the muffin-tin potential become positive.

The parameters determined above may now be used to generate the logarithmic derivatives, $\frac{u_{\ell}'(R_n; E)}{u_{\ell}(R_n; E)}$, for each ion. These are required in the calculation of the SAPW matrix elements given in equation (34).

The computer program used to calculate the logarithmic derivatives was that given by Loucks² in Appendix 3, with

The ionic potentials for the $Mn^{+2}A$, $Mn^{+2}B$ and F^{-} ions used in antiferromagnetic case. Corrections have been included for the Madelung Constant.



the energy dependence of the radial function and its derivative being fitted to polynomials of degree seven. The polynomial coefficients of energy have been evaluated for values of & from 0 to 12. The equation for the logarithmic derivative as a function of energy is then given by

$$L_{\ell}(E) = \frac{u_{\ell}'(R_{n};E)}{u_{\ell}(R_{n};E)} = \frac{\sum_{i=0}^{r} (QC)_{i}E^{i}}{\sum_{\sum_{i=0}^{r} (QD)_{i}E^{i}}}$$
(38)

where QC and QD are the polynomial coefficients used to fit the energy dependence of the radial function $u_{\ell}(R_n; E)$ and its derivative $u'_{\ell}(R_n; E)$ respectively.

The resulting values for the logarithmic derivative functions for the manganese and fluorine ions have also been tabulated as a function of energy. The purpose of this was to determine any singularities or zero crossings of these functions which could possibly produce spurious solutions for the (H-E) determinant.

For the "paramagnetic" case, the logarithmic derivatives corresponding to l values of 0, 1 and 2 have been plotted in the energy range -1.6 to 1.6 Rydbergs. Those for the manganese ion are shown in Fig. 6 and for the fluorine ion in Fig. 7. From Fig. 6, there is a singularity in this energy range for l=2. Using a linear interpolation technique, this singularity may be found to occur at 0.26 Rydbergs. In the "paramagnetic" case for Mn⁺², this is the only singularity

Logarithmic derivatives for l=0,1,2 for the Mn^{+2} ion in the "paramagnetic" case



Logarithmic derivatives for l=0,1,2 for the F⁻ ion in the "paramagnetic" case



which occurred in this range. There are two zero crossings: for l=0, at an energy of 0.28 Rydbergs, and for l=1, at an energy of 1.22 Rydbergs approximately. For the remaining functions corresponding to l=3 to l=12, there are no zero crossings or singularities.

Considering Fig. 7 for the fluorine ion, the singularities appearing are the one for l=0 at -1.275 Rydbergs and the one for l=1 at 0.103 Rydbergs. The only zero crossing occurs for l=1 at approximately-0.72 Rydbergs. The behaviour of the fluorine logarithmic derivative function for the higher l values is quite similar to that of the manganese ion.

Similar results for the antiferromagnetic case have been plotted in Figs. 8, 9 and 10, for the $Mn^{+2}A$, $Mn^{+2}B$, and F⁻ ions respectively, over the energy range -0.4 to 1.2 Rydbergs. Singularities occur for: $Mn^{+2}A$, l=2 at -0.16 Rydbergs, $Mn^{+2}B$, l=2, at 0.589 Rydbergs, and F⁻, l=1, at 0.365 Rydbergs. The zero crossings may be found to be: $Mn^{+2}A$, l=0 at -0.048 Rydbergs, l=1, at 0.849 Rydbergs, $Mn^{+2}B$, l=0 at 0.575 Rydbergs, l=2 at -0.131 Rydbergs. There are no such crossings for the fluorine ion in the energy range being considered.

To illustrate the general behaviour of the logarithmic derivative functions for higher ℓ values, the reader is referred to Fig. 11. Shown here are the results for the anti-ferromagnetic case of the $Mn^{+2}A$ ion over the energy range -0.4 to 1.2 Rydbergs. The energy dependence of the functions for

Logarithmic derivatives for l=0,1,2 for the $Mn^{+2}A$ ion in the antiferromagnetic case



Logarithmic derivatives for l=0,1,2 for the Mn⁺²B ion in the antiferromagnetic case



Logarithmic derivatives for l=0,1,2 for the F⁻ ion in the antiferromagnetic case



General behaviour of logarithmic derivatives for higher ℓ values for Mn⁺²A, ℓ = 3 to 12, antiferromagnetic case



l=3 through l=12 is very similar for both the "paramagnetic" and antiferromagnetic cases, and all ions concerned. At no energy is the function $u'_{l}(R_{n};E)/u_{l}(R_{n};E)$ negative, and the curves approach straight lines with very small negative slope as the l value increases. Singularities occur for none of these functions.

The various parameters and functions which serve as the input data for the main SAPW program have now been determined, with the notable exception of the results of the group theoretical calculations for "paramagnetic" and antiferromagnetic manganese fluoride.

B. GROUP THEORY FOR MANGANESE FLUORIDE

The space group $D_{4h}^{14}(P4_2/mmm)$, with the point group D_{4h} and a tetragonal Bravais lattice were used in the calculations for "paramagnetic" MnF_2 . In the point group D_{4h} , used at the Γ point, there are sixteen group operations which are represented by the symbols X_0 , $X_{\pm 1}$, X_2 , Y_0 , $Y_{\pm 1}$, Y_2 , X_0' , $X_{\pm 1}'$, X_2' , Y_0' , $Y_{\pm 1}'$ and Y_2' . The notation is that given by Slater²¹. In addition, certain of these operators involve a non-primitive $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ translation to preserve the symmetry of the structure. The resulting operators are those given by Slater²¹ with modifications as proposed by E. R. Cowley and C. V. Stager²², and are named in this work, the Slater-Cowley operators. As can be seen from equations (35), (36)

and (37), these operators act on the wave vectors $\underline{k}_{i} = \underline{k} + \underline{K}_{i}$. For the specific case of the Γ point, $\underline{k}=0$ and thus $\underline{k}_{i} = \underline{K}_{i}$. The operator matrices which were employed are given in Table 1. An operation which involves a non-primitive, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ translation is indicated by a (±) sign after the matrix.

The behaviour of the various wave vectors under action by the group elements in Table 1 must be investigated to find the irreducible representations according to which the wave vectors transform. For this calculation, the character table for the group must be used. There are ten irreducible representations for the group D_{4h} and they may be labelled $\Gamma_1^{\pm}, \Gamma_2^{\pm}, \Gamma_3^{\pm}, \Gamma_4^{\pm}, \text{ and } \Gamma_5^{\pm}$. The character table then is as given by Slater²¹ and is reproduced in Table 2. It is evident that Γ_1^{\pm} , Γ_2^{\pm} , Γ_3^{\pm} and Γ_4^{\pm} are one-dimensional representations and that Γ_5^{\pm} are two-dimensional representations. In the case of the two-dimensional representations, only the characters have been included in Table 2. To generate the characters for the primed group operators, the characters are the same as in Table 2 for the representations with the superscripts +, and the negatives of these characters for the representations with the superscripts -.

Wave vectors may be divided into sets such that all members of a given set transform among each other under the group operations. It is sufficient to consider only one member of each set. Such wave vectors are called prototype

r	Ά	В	T,	E	1	
		~~	****	****		

SLATER-COWLEY OPERATORS FOR F POINT GROUP THEORY FOR "PARAMAGNETIC" MnF₂

							c					
	[]1	0	0						[l	0	0	
x ₀ =	O	1	0				x ₀	=	0	1	0	
	0	0	1						0	0	-1]	,
•	Γο	1	0						Γo	1	0	
X, =	-1	0	0	(±)			х' Х1	=	-].	0	0	(±)
1	0	0	1				Т		0	0	-1	
	Γo	-1	0						Γo	-1	0	
X_1=	1	0	0	(±)			x_1	=	1	0	0	(±)
7	0	0	1				-	-	0	0	-1	
	[-1	0	0			¢			[-1	0	ס	
x_ =	0	-1	0				\mathbf{x}_{2}^{\prime}	=	0	-1	0	
2	0	0	1				•		0	0	-1	
	Γı	0	ō						Γı	0	٥	
$Y_0 =$	0	1	0	(±)			Y ['] 0	=	0	-1	0	(±)
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•	Γo	1	ō						Го	1	ō]	
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Y ,=	-1	0	0				У ['] .	,=	1	0	0	
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		0	ר ה						L_ []	Ω	ך ה	
37		U		1.15			1			U 1		(1)
^Y 2 ⁼		Ť	U	(±)			¥2			1	_1	(1)
	1 0	0	ㅗ							U		

TABLE	2
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	x ₀	x ₁	x_1	×2	Y ₀	Yl	Y-1	^Y 2
Γ [±]	l	1	1	1	l	1	1	1
Γ_2^{\pm}	1	1	1	1	-1	-1	-1	-1
Γ [±] ₃	1	-1	-1].	1	-1	-1	1
$\Gamma \frac{\pm}{4}$	1	-1	-1	. 1	-1	1	l	-1
$\chi(r_5^{\pm})^*$	2	0	0	-2	0	0	0	0
· . ·								· · · · · · · · · · · · · · · · · · ·

CHARACTER TABLE FOR THE GROUP D_{4h}

*For the two-dimensional representations, Γ_5^{\pm} , only the characters have been included.

wave vectors. By the standard techniques of group theory, reducible representations generated by using the prototype wave vectors as basis functions may be calculated¹⁹. It is important to distinguish between even and odd prototypes for these calculations. The effect of a group operator which contains a non-primitive translation is different for even and odd prototypes. The decomposition of the prototypes is accomplished by using the group character table and the equation

$$a_{j} = \frac{1}{g} \sum_{\text{classes}} n_{c} \chi(c) \chi_{j}(c)$$
(39)

where g is the number of elements in the group, n_c is the number of elements in the class, c, $\chi(c)$ represents the characters of the group and $\chi_j(c)$ represents the characters of the representation under consideration. a_j then is the number of times the jth irreducible representation occurs in the decomposition of the prototype wave vector under consideration. The results for the prototype wave vector decomposition at the Γ point for the "paramagnetic case" are given in Table 3. It must be noted that in Table 3 for the case of the two-dimensional representations, Γ_5^{\pm} , only specific prototype wave vectors may be used in the calculation. The details have been worked out in collaboration with C.V. Stager²³ using projection operators and are shown in Table 4.

	¢		-									
(0,0,0)	г <mark>+</mark> 1											
(a,o,o)→	Γ <mark>+</mark> +	Γ_4^+	+ r ⁺ 5									
(a,o,o) even	Γ <mark>+</mark> +	Γ_3^+ .	+ Γ <mark>+</mark> 5									
(a,a,o) odd	Γ_1^+ +	Γ_4^+	+ Γ <mark>+</mark> 5		·	,						
$(a,a,o) \xrightarrow[even]{} even$	Γ <mark>1</mark> +	Γ <mark>4</mark> ·	+ r ⁺ 5									
(0,0,c) _{odd} →	Γ_4^+ +	Γ4				¢						
(o,o,c)→	Γ <mark>1</mark> +	Γī										
(a,b,o) odd →	Г <mark>1</mark> +	Γ_2^+	+ r <mark>+</mark> 3	÷	r_4^+	+	2°5+					
$(a,b,o) \xrightarrow{\text{even}}$	г <mark>+</mark> +	Γ_2^+	+ r ⁺ 3	÷	Γ_4^+	÷	2r ⁺ 5					
(a,a,c) odd →	Γ <mark>+</mark> +	Γ_4^+	+ r <mark>+</mark> 5	÷	гī	ł	$\Gamma_4 + \Gamma$	5				
(a,a,c) even →	Γ <mark>+</mark> +	Γ_4^+	+ 1 ⁺ 5	+	Γī	+	$\Gamma_4^- + \Gamma$	- 5				
$(a, o, c)_{odd} \rightarrow$	Γ <mark>+</mark> +	Γ_4^+ ·	+ ^r 5	÷	Γ2	+	$\Gamma_4 + \Gamma$	5				
$(a, o, c) \xrightarrow{\text{even}}$	Г <mark>+</mark> +	г <mark>+</mark> -	+ Γ <mark>+</mark> 5	+	Γ <mark>-</mark>	+	$\Gamma_3 + \Gamma$	- 5				
(a,b,c) _{odd} →	Γ <mark>+</mark> +	Γ_2^+	+ r ⁺ 3	÷	Γ <mark>+</mark>	+	2r ⁺ ₅ +	Γ <mark>-</mark>	+	г <mark>-</mark> 2	+	г_3
(a,b,c) even	Г <mark>+</mark> +	Γ_2^+	+ r <mark>+</mark> 3	÷	Γ_4^+	÷	2 ⁺ ₅ +		+	г <mark>-</mark> 2	4-	г <mark>-</mark> 3
						÷	$\Gamma_4 + 2$	г <mark>-</mark> 5				

PROTOTYPE WAVE VECTOR DECOMPOSITION AT THE [POINT FOR THE "PARAMAGNETIC" STATE OF MnF₂

 $+\Gamma_4 + 2\Gamma_5$

PROTOTYPES USED FOR TWO-DIMENSIONAL REPRESENTATIONS AT THE I POINT FOR "PARAMAGNETIC" MnF₂

		· · · · · · · · · · · · · · · · · · ·
(a,o,o)	even	(±a,0,0), (0,±a,0)
(a,o,o)	odd ───	(0,±a,0)
(a,a,o) (a,a,o)	even odd	(±a,±a,0)
(a,b,o)	* even odd	(±a,±b,0), (±b,±a,0)
(a,a,c) _e	even	(±a,±a,±c)
(a,o,c)	even	(a,o,±c), (-a,o,±c)
(a,o,c)	odd	(o,a,±c), (o,-a,±c)
(a,b,c)	even	all prototypes may be used

*When two-2 dimensional representations are included in the decomposition pairs of the type (a,b,o) and (b,a,o) must be used.

**When two-2 dimensional representations are included in the decomposition the pairs (±a,±b,±c) and (±b,±a,±c) must be used with any permutation of the signs allowed.

TABLE 4

The symmetry is reduced for band structure calculations along the Λ line (0,0,c*). The group becomes C_{4v} and contains only eight operations. These are operations which do not include a horizontal reflection. The operator matrices for C_{4v} are then X_0 , $X_1(\pm)$, $X_{-1}(\pm)$, X_2 , $Y_0(\pm)$, Y_1 , Y_{-1} and $Y_{2}(t)$ where the notation and the matrices used are the same as in the case of the I point group theory. The operations are now performed on the vector $\underline{k}_{i} = \underline{k} + \underline{K}_{i}$ of equation (11). Here, k represents the point on the Λ line, (0,0,p) at which the allowed energy values are being calculated and $\frac{K_{i}}{L_{i}}$ represents a reciprocal lattice vector. The irreducible representations of the group C_{4v} may be written as Λ_1 , Λ_2 , Λ_3 , Λ_4 and Λ_5 , where Λ_5 is a two-dimensional representation. Since the horizontal mirror plane has been removed, the wave vector (a,b, -c) is not included in the same set as (a,b,c). Using the character table for C_{4v}^{21} , the wave vector decomposition is as given in Table 5.

Since for the antiferromagnetic case of MnF_2 , no known tetragonal space group could be found, it was necessary to use the orthorhombic group $D_{2h}^{19}(Cmmm)$ with eight operator matrices and eight one-dimensional irreducible representations for the I point. The $Mn^{+2}A$ ion was considered different from the $Mn^{+2}B$ ion and thus the eight (±) operations from D_{4h} connecting the two manganese ions in the unit cell were excluded. The remaining eight group operations are

TABLE 5

PROTOTYPE WAVE VECTOR DECOMPOSITION ALONG THE Λ LINE FOR THE "PARAMAGNETIC" STATE OF ${\rm MnF}_2$

 $(o, o, p) \longrightarrow \Lambda_{1}$ $(a, o, p)_{even} \longrightarrow \Lambda_{1} + \Lambda_{3} + \Lambda_{5}^{*}$ $(a, o, p)_{odd} \longrightarrow \Lambda_{2} + \Lambda_{4} + \Lambda_{5}^{**}$ $(a, a, p)_{even} \longrightarrow \Lambda_{1} + \Lambda_{4} + \Lambda_{5}$ $(a, b, p)_{even} \longrightarrow \Lambda_{1} + \Lambda_{2} + \Lambda_{3} + \Lambda_{4} + 2\Lambda_{5}^{***}$ $(a, b, p)_{even} \longrightarrow \Lambda_{1} + \Lambda_{2} + \Lambda_{3} + \Lambda_{4} + 2\Lambda_{5}^{***}$ *Wave vector for Λ_{5} must be of the form (a, o, p) or (-a, o, p).
**

** Wave vector for Λ_5 must be of the form (o,a,p) or (o,-a,p).

*** For two-2 dimensional representations the wave vectors must be of the form (a,b,p) and (b,a,p)

 $X_0, X_2, Y_1, Y_{-1}, X_0, X_2, Y_1$ and Y_{-1} where the notation is the same as for the "paramagnetic" case. The character table for this group was calculated by standard techniques using the basis functions x+y, x-y, -x+y and -x-y, with the prescription that the rows of the table be orthogonal to one another. The irreducible representations may be labelled $\Gamma_1^{\pm}, \Gamma_2^{\pm}, \Gamma_3^{\pm}$ and Γ_4^{\pm} , all of which are one-dimensional. The character table for D_{2h} is given in Table 6.

Since all operations involving a non-primitive translation from $Mn^{+2}A$ to $Mn^{+2}B$ have now been removed, it will not now be necessary to differentiate between even and odd prototype wave vectors. By procedures identical to that for the "paramagnetic" case, the decomposition of the prototypes at the Γ point may be carried out yielding the results shown in Table 7.

It must be noted, from Table 7, that the number of prototype wave vectors has increased due to the reduced symmetry. This means, for instance, that the wave vectors (a,-a,o) and (-a,a,o) are not generated by the action of any group element on the prototype (a,a,o). In this case, only the vector (-a,-a,o) is generated, and (a,-a,o) must be included in a different set. Similar results hold for the cases (a,a,c), (a,b,o) and (a,b,c).

As in the "paramagnetic" example, the horizontal reflection plane is lost for wave vectors on the Λ line. The

TABLE 6	
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CHARACTER TABLE FOR THE GROUP D2h

	a ser a com	× .		•	a george			
	x ₀	x ₂	Yl	Y-1	x'o	x'2	Y'ı	Y_1
г <mark>+</mark> г <mark>1</mark>	1	l	1	1	1	l	1	1
Γ <mark>2</mark>	1	-1	l	-1	1	_l	1	-1
г <mark>+</mark> 3	1	-1	-1	1 .	1	-1	-1	. 1
Γ_4^+	1	1	-1	-1	1	1	-1	-1
r_1^-	1	1	1	1	-1	-1	-1	-1
Γ <mark>-</mark> 2	1	-1	1	-1	-1	l	-1	1
г <mark>-</mark> 3	1	-1	-1	1.	-1	1	1	-1
Γ4	. 1	1	-1	-1	-1	-1	1	1

	•						. *					•	
(0,0,0)	г <mark>+</mark> 1		· .				- lennef.t He						-
(a,o,o) →	r ₁ ++	г <mark>+</mark> -	+ r ₃ +	÷	г4								
(a,a,o)→	r <mark>+</mark> +	Г <mark>+</mark>											
(a,-a,0)→	г <mark>+</mark> +	г <mark>+</mark>											
(0,0,C)	г <mark>1</mark> +	r1											
(a,o,c)→	r <mark>1</mark> +	r <mark>+</mark> .	+ F ⁺ 3	+	г <mark>+</mark> 4	+	r_1	+	г <mark>-</mark> 2	+	г ⁻ 3	,+	Γ_4^-
$(a,a,c) \longrightarrow$	r <mark>+</mark> +	Γ <mark>+</mark> -	+ r ₁	+	г <mark>-</mark> 2								
(a,-a,c)→	Γ <mark>+</mark> +	г <mark>+</mark> -	+ r_1	, +	г <mark>-</mark>								
(a,b,o)→	Γ <mark>1</mark> +	г <mark>+</mark> -	+ r <mark>+</mark>	+	г <mark>+</mark> 4								
(a,-b,o)→	Γ <mark>+</mark> +	Γ_2^+	+ [⁺ 3	+	Γ_4^+								
$(a,b,c) \longrightarrow$	Γ <mark>1</mark> +	г <mark>+</mark> -	+ r <mark>+</mark>	+	г <mark>+</mark>	+	Γ <mark>1</mark>	+	Γ <mark>-</mark> 2	+	г <mark>-</mark> 3	+	Γ_4^-
$(a,-b,c) \longrightarrow$	Γ_1^+ +	г <mark>+</mark> -	+ r ⁺ 3	+	г <mark>4</mark>	+	Γ <mark>1</mark>	+	г <mark>-</mark> 2	+	г <mark>-</mark> З	+	Γ4

PROTOTYPE WAVE VECTOR DECOMPOSITION AT THE \mbox{F} POINT FOR THE ANTIFERROMAGNETIC STATE OF \mbox{MnF}_2

group C_{2v} , appropriate to this case, consists of only four operator matrices, namely X_0 , X_2 , Y_1 , and Y_{-1} . Analogously, for every general (a,b,c) type reciprocal lattice vector included, there must also be an (a,b,-c) vector. Again, no group operators involve a $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ translation, and thus the distinction between even and odd prototype wave vectors need not be made. The character table for the group C_{2v} is given in Table 8. The four irreducible representations of the group have been labelled Λ_1 , Λ_2 , Λ_3 and Λ_4 , and are all onedimensional.

The wave vector decomposition for the appropriate prototypes for the A line is shown in Table 9. The notation used is the same as that employed for the "paramagnetic" state.

The number of energy bands expected in the SAPW calculation and their symmetry is predicted by using a tight binding or linear combination of atomic orbitals approach. For example, consider the fluorine p electrons. There are three p orbitals (x, y and z) for each fluorine ion ie. 12 in a unit cell of MnF₂. These 12 orbitals are used as basis functions for a representation of the group appropriate to the wave vector being considered. This representation, which is in general reducible, is decomposed into irreducible representations by standard techniques. In the case of the fluorine p orbitals, this gives rise to the irreducible representations $\Gamma_1^+ + \Gamma_1^- + \Gamma_2^+ + \Gamma_3^+ + \Gamma_4^+ + \Gamma_4^- + 2\Gamma_5^+ + \Gamma_5^-$

TABLE 8

CHARACTER TABLE FOR THE GROUP C_{2v}

		x ₀	×2	Yl	Y1
Λ _l		1.	1	1	1
۸ ₂		1	-1	1	-1
۸ ₃		1	-1	-1	1
۸ ₄	·]	1	-1	-1

(0,0,p)		Λ
(0,0,-p)	}	Λ
(a,o,p)		$\Lambda_1 + \Lambda_2 + \Lambda_3 + \Lambda_4$
(a,a,p)		$\Lambda_1 + \Lambda_2$
(a,-a,p)	•••••	$\Lambda_1 + \Lambda_3$
(a,o,p)	·	$\Lambda_1 + \Lambda_2 + \Lambda_3 + \Lambda_4$
(a,o,-p)		$\Lambda_1 + \Lambda_2 + \Lambda_3 + \Lambda_4$
(a,a,-p)		$\Lambda_1 + \Lambda_2$
(a,-a,-p)		$\Lambda_1 + \Lambda_3$
(a,b,p)		$\Lambda_1 + \Lambda_2 + \Lambda_3 + \Lambda_4$
(a,-b,p)		$\Lambda_1 + \Lambda_2 + \Lambda_3 + \Lambda_4$
(a,b,-p)	-	$\Lambda_1 + \Lambda_2 + \Lambda_3 + \Lambda_4$

PROTOTYPE WAVE VECTOR DECOMPOSITION ALONG THE Λ LINE FOR THE ANTIFERROMAGNETIC STATE OF ${\tt MnF}_2$

TABLE 9

at the Γ point for the "paramagnetic" case. From the plot of the fluorine logarithmic derivatives in Fig. 7, there is a singularity for l=1 at 0.103 Rydbergs. One would expect energy bands of the above symmetry classifications near 0.103 Rydbergs. The calculations for the other appropriate atomic orbitals for the manganese and fluorine ions in the "paramagnetic" state are given in Table 10. Similar calculations have been carried out for the antiferromagnetic state of MnF₂. These results are given in Table 11. Another check on the results is obtained by the use of the compatability relations, ie. energy bands along the Λ line labelled Λ_i may only be joined to those labelled $\Gamma_i^{\frac{1}{2}}$ at the Γ point.

BASIS FU	NCTIONS	AT THE F	POINT FOR	"PARAMAGNE	TIC" MnF2
<u>Bullionente additione erregistione erre</u>	n den freger an en den ster gener an de se an	S The sub-the second state of the second sta	an and a start of the start of th	الم من 1000 من	anal de antigen and de antigen and de antigen
M_n^{+2} (ns)		$\Gamma_1^+ + \Gamma_2^+$	1 4		
F ^(ns)		$\Gamma_1^+ + \Gamma_2^+$	$\frac{1}{4} + \frac{1}{5}$		
Mn ⁺² (np)		$\Gamma_1 + \Gamma_2$	$\frac{1}{4} + 2\Gamma_{5}^{+}$		
F (np)		$\Gamma_1^+ + \Gamma_2^+$	$\frac{1}{1} + \frac{1}{2} + r$	$\frac{1}{3}$ + Γ_4^+ + Γ_4^-	+ $2\Gamma_5^+$ + Γ_5^-
Mn ⁺² (d)		$2\Gamma_{1}^{+} + 1$	$\Gamma_{2}^{+} + \Gamma_{3}^{+} +$	$2\Gamma_{4}^{+} + 2\Gamma_{5}^{-}$	

PREDICTED ENERGY BANDS FROM THE USE OF TIGHT BINDING

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TABLE 10

TABLE 11

PREDICTED ENERGY BANDS FROM THE USE OF TIGHT BINDING BASIS FUNCTIONS AT THE Γ POINT FOR ANTIFERROMAGNETIC $$^{\rm MnF}_2$$

$Mn^{+2}A(ns) \longrightarrow$	Γ ⁺ l
$Mn^{+2}B(ns) \longrightarrow$	Γ <mark>1</mark>
$F(ns) \longrightarrow$	$\Gamma_1^+ + \Gamma_4^+ + \Gamma_5^+$
$Mn^{+2}A(np) \longrightarrow$	$\Gamma_2^+ + \Gamma_3^+ + \Gamma_1^-$
$Mn^{+2}B(np) \longrightarrow$	$\Gamma_{2}^{+} + \Gamma_{3}^{+} + \Gamma_{1}^{-}$
$F(np) \longrightarrow$	$2\Gamma_{1}^{+} + 2\Gamma_{2}^{+} + 2\Gamma_{3}^{+} + 2\Gamma_{4}^{+} + 2\Gamma_{1}^{-} + \Gamma_{2}^{-} + \Gamma_{3}^{-}$
$Mn^{+2}A(d) \longrightarrow$	$2\Gamma_{1}^{+} + \Gamma_{4}^{+} + \Gamma_{2}^{-} + \Gamma_{3}^{-}$
$Mn^{+2}B(d) \longrightarrow$	$2\Gamma_{1}^{+} + \Gamma_{4}^{+} + \Gamma_{2}^{-} + \Gamma_{3}^{-}$

CHAPTER IV

RESULTS AND DISCUSSION

The main program (SAPW) for the band structure calculation was based on that outlined by Loucks², Appendix 5, using the expression for the (H-E) matrix elements that was given in equation (34). The program was adapted to handle the cases of two and three different ions in a unit cell for the "paramagnetic" and antiferromagnetic cases respectively. The determinant of (H-E) has been evaluated as a function of energy in increments of 0.01 Rydbergs for each irreducible representation of the groups appropriate to the Γ point and the Λ line for both the "paramagnetic" and the antiferromagnetic states. The energy at which det(H-E) goes to zero was found by means of a quadratic interpolation method. Eigenvalues were recorded for the P point and for five points along the A line to the zone boundary. In units of c* these five points are 0.1, 0.2, 0.3, 0.4 and 0.5. The results were plotted in the appropriate energy ranges for the two states of MnF, that were considered.

The calculated bands for the "paramagnetic" state are shown in Figs. 12 to 17. For this case, the bands have been calculated using basis sets of 39 and 121 reciprocal lattice vectors, \underline{K}_i . Fig. 12 presents the general picture
of the bands for the case of 39 reciprocal lattice vectors. The one-electron bands have been grouped together according to the atomic orbital with which they correspond. In the energy range of -1.7 Rydbergs to 0.3 Rydbergs, only the highest and lowest energy bands belonging to each orbital group have been plotted. From 0.3 Rydbergs to 1.1 Rydbergs, all the individual bands are shown. In Fig. 13, the scale from -1.61 Rydbergs to -1.55 Rydbergs and from 0.08 Rydbergs to 0.22 Rydbergs has been expanded to show the detailed structure of the one-electron bands arising from the F^{-} (2s) and the Mn^{+2} (3d) orbitals. The irreducible representation labels at the Γ point and along the Λ line are indicated. The energy range from -0.26 Rydbergs to -0.05 Rydbergs has similarly been expanded in Fig. 14 to indicate the details of the oneelectron bands that arise from the F (2p) orbitals. From Figs. 13 and 14 it may be seen that the irreducible representations appearing there are in exact agreement with those predicted by the tight binding approach and tabulated in Table 10. Figs. 15 to 17 present the results obtained for the "paramagnetic" case using 121 reciprocal lattice vectors. The bands have all been shifted downward in energy. This is expected, as the APW method is a variational method, and increasing the basis set always lowers the energy. General rules for the number of basis vectors needed to insure

General band picture for the "paramagnetic" case of MnF₂ for 39 reciprocal lattice vectors. In the energy range -1.7 to 0.3 Rydbergs only the highest and lowest energy single electron bands for each orbital group have been drawn. The crosshatching represents the bands falling in between the highest and lowest energy bands.



Structure of the one-electron bands arising from the $F^{-}(2s)$ and $Mn^{+2}(3d)$ orbitals, for "paramagnetic" case, 39 reciprocal lattice vectors. Note that the scale has been broken. The $F^{-}(2s)$ bands are in the range -1.61 to -1.55 Rydbergs. The $Mn^{+2}(3d)$ bands are in the range 0.08 to 0.22 Rydbergs.



Structure of the one-electron bands arising from the $F^{-}(2p)$ orbitals, for the "para-magnetic" case with 39 reciprocal lattice vectors.



General band picture for the "paramagnetic" case of MnF₂, for 121 reciprocal lattice vectors. In the energy range -0.4 to 0.2 Rydbergs, only the highest and lowest energy single electron bands for each orbital group have been drawn. The crosshatching represents the bands falling in between the highest and lowest bands.



The structure of the one-electron bands arising from the Mn^{+2} (3d) orbital for the "paramagnetic" case of MnF_2 for 121 reciprocal lattice vectors.



The structure of the one-electron bands arising from the $F^{-}(2p)$ orbital for the "paramagnetic" case of MnF₂, for 121 reciprocal lattice vectors.



convergence are given by Mattheiss <u>et al</u>¹⁰. Again, the number and symmetry of the bands are in agreement with those predicted in Table 10.

After determining the one-electron energy bands, the next step is to establish the position of the Fermi level. For MnF_2 there are 8 fluorine 2s electrons, 24 fluorine 2p electrons, and 10 manganese 3d electrons in the unit cell. Two electrons are assigned to each one-dimensional representation and four to each two-dimensional representation. The Fermi level is then somewhere in the bands labelled Γ_4^+ and F_5^+ at the Γ point, for 121 reciprocal lattice vectors. This would correspond to an energy of approximately 0.05 Rydbergs. It is apparent at this point that there are overlapping and hence partially filled energy bands. Thus "paramagnetic" MnF_2 is predicted to be a "metal". This is in agreement with similar calculations on "paramagnetic" NiO.

The calculated bands for the antiferromagnetic state are shown in Figs. 18 to 21 for 39 reciprocal lattice vectors. Fig. 18 shows the general band picture. There are now two sets of Mn^{+2} (3d) bands, each containing five one-electron bands. They are separated by 0.635 Rydbergs at the Γ point and by 0.699 Rydbergs at the Z point, ie the intersection of the Λ line with the zone boundary. The F^- (2p) energy bands fall in between the two groups of Mn^{+2} (3d) bands. Figs. 19, 20 and 21 show the detailed behaviour of the bands.

The general band picture for the antiferromagnetic case of MnF_2 , for 39 reciprocal lattice vectors. In the energy range -0.4 to 0.6 Rydbergs, only the highest and lowest energy single electron bands for each orbital group have been drawn. The cross-hatching represents the bands falling in between the highest and lowest bands. The band labelled Γ_1^+ at 0.5 Rydbergs does not belong to the upper Mn^{+2} (3d) orbital group.



The structure of the one-electron bands arising from the upper Mn^{+2} (3d) orbital for the antiferro-magnetic case of MnF_2 , for 39 reciprocal lattice vectors.



The structure of the one-electron bands arising from the lower Mn^{+2} (3d) orbital for the antiferromagnetic case of MnF_2 , for 39 reciprocal lattice vectors.



The structure of the one-electron bands arising from the $F^{-}(2p)$ orbital for the antiferromagnetic case of MnF₂, for 39 reciprocal lattice vectors.



The results for the antiferromagnetic state are in agreement with those predicted from the tight binding approach for Mn^{+2} (d) and F⁻ (np) as shown in Table 11.

The position of the Fermi level for antiferromagnetic MnF, may be determined by a method analogous to that used for the "paramagnetic" state. At the I point for 39 reciprocal lattice vectors, the Fermi level occurs between the F (2p) and upper Mn⁺² (3d) bands. From Fig. 18, this is in the range 0.0 to 0.38 Rydbergs. Here, there are no overlapping bands, and thus antiferromagnetic MnF₂ is predicted to be an insulator. It would appear, from Fig. 18 that the first transition in MnF_2 is from an F^- (2p) band to an Mn^{+2} (3d) band. However, experimental evidence indicates that this transition should be from Mn^{+2} (3d) to Mn^{+2} (3d)²⁴. Since the relative position of the Mn^{+2} (3d) and F^{-} (2p) bands is dependent on the exchange contribution to the potential given in Chapter II, equation (9), these results suggest that an exchange of the form given by Kohn and Scham¹⁵ should be employed to bring the $Mn^{+2}(3d)$ bands closer together. Such an exchange has been used by Cho²⁵ for the Eu chalcogenides with a reduced exchange parameter of 3/4.

Further APW calculations for MnF_2 in the antiferromagnetic state should be performed using a reduced exchange parameter varying between 2/3 and 1. It is then expected that the results will indicate that the first transition is between Mn^{+2} (3d) and Mn^{+2} (3d) and of the magnitude predicted by experiment.

BIBLIOGRAPHY

- 1. Slater, J. C., Phys. Rev., <u>51</u>, 846 (1937).
- Loucks, T. L., <u>Augmented Plane Wave Method</u> (W. A. Benjamin, Inc., New York, 1967).
- 3. Eisberg, R. M., Fundamentals of Modern Physics (J. Wiley and Sons, Inc., New York, 1961), p. 396.
- 4. Davydov, A. S., <u>Quantum Mechanics</u> (Neo Press, Ann Arbor, Michigan, 1966), p. 349.
- 5. Herman, F., and Skillman, S., Atomic Structure Calculations (Prentice-Hall, Englewood Cliffs, New Jersey, 1963).
- Kittel, C., Introduction to Solid State Physics (J. Wiley and Sons, Inc., New York, Third Edition, 1967).
- 7. Ziman, J. M., Principles of the Theory of Solids (Cambridge University Press, London, 1964).
- Seitz, F., The Modern Theory of Solids (McGraw-Hill New York, 1940).
- 9. Koster, G. F., Solid State Phys., 5, 173 (1957).
- 10. Mattheiss, L. F., Wood, J.H., and Switendick, A.C., <u>Methods in Computational Physics</u>, Vol. 8 (Energy Bands of Solids), A Procedure for Calculating Electronic Energy Bands Using Symmetrized Augmented Plane Waves (Academic Press, New York, 1968).
- 11. Clementi, E., Tables of Atomic Functions, supplement to a paper by E. Clementi entitled "Ab Initio Computations in Atoms and Molecules", IBM Journal of Research and Development 9, 2 (1965).
- 12. Born, M., and Huang, K., Dynamical Theory of Crystal Lattices (Oxford University Press, Ely House, London, 1954).
- 13. Löwdin, P. O., Adv. Phys., 5, 1 (1956).
- 14. Slater, J.C., Phys. Rev. 165, 655, 658 (1968).

- 15. Kohn, W., and Scham, L. J., Phys. Rev. 137, A1697 (1965).
- 16. Schlosser, H., and Marcus, P.M., Phys. Rev. <u>131</u>, 2529 (1965).
- 17. De Cicco, P.D., Phys. Rev. 153, 931 (1967a).
- 18. Powell, J. L. and Crasemann, B., Quantum Mechanics (Addison Wesley, Reading, Mass., 1961).
- 19. Tinkham, M., Group Theory and Quantum Mechanics (McGraw-Hill, New York, 1964).
- 20. Stout, J. W., and Reed, S. A., J. Am. Chem. Soc. <u>76</u>, 5279 (1954).
- 21. Slater, J. C., Quantum Theory of Molecules and Solids, Volume 2, Symmetry and Energy Bands in Crystals (McGraw-Hill, New York, 1965).
- 22. Cowley, E. R. and Stager, C. V., Private Communication.
- 23. Stager, C. V., Private Communication.
- 24. McClure, D. S., Electronic Spectra of Molecules and Ions in Crystals, Vol. 9, Solid State Physics (Academic Press Inc., New York, 1959).
- 25. Cho, S. J., Phys. Rev., 1, 4589 (1970).