1983

Anisotropy in the orbital susceptibilities of hcp metals

Carol M. Theisen
Iowa State University

Follow this and additional works at: https://lib.dr.iastate.edu/rtd
Part of the Condensed Matter Physics Commons

Recommended Citation
https://lib.dr.iastate.edu/rtd/7655

This Dissertation is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Retrospective Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
INFORMATION TO USERS

This reproduction was made from a copy of a document sent to us for microfilming. While the most advanced technology has been used to photograph and reproduce this document, the quality of the reproduction is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help clarify markings or notations which may appear on this reproduction.

1. The sign or “target” for pages apparently lacking from the document photographed is “Missing Page(s)”. If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure complete continuity.

2. When an image on the film is obliterated with a round black mark, it is an indication of either blurred copy because of movement during exposure, duplicate copy, or copyrighted materials that should not have been filmed. For blurred pages, a good image of the page can be found in the adjacent frame. If copyrighted materials were deleted, a target note will appear listing the pages in the adjacent frame.

3. When a map, drawing or chart, etc., is part of the material being photographed, a definite method of “sectioning” the material has been followed. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.

4. For illustrations that cannot be satisfactorily reproduced by xerographic means, photographic prints can be purchased at additional cost and inserted into your xerographic copy. These prints are available upon request from the Dissertations Customer Services Department.

5. Some pages in any document may have indistinct print. In all cases the best available copy has been filmed.

University Microfilms International
300 N. Zeeb Road
Ann Arbor, MI 48106
Theisen, Carol M.

ANISOTROPY IN THE ORBITAL SUSCEPTIBILITIES OF HCP METALS

Iowa State University

University Microfilms International 300 N. Zeeb Road, Ann Arbor, MI 48106
PLEASE NOTE:

In all cases this material has been filmed in the best possible way from the available copy. Problems encountered with this document have been identified here with a check mark ✓.

1. Glossy photographs or pages 
2. Colored illustrations, paper or print 
3. Photographs with dark background 
4. Illustrations are poor copy 
5. Pages with black marks, not original copy 
6. Print shows through as there is text on both sides of page 
7. Indistinct, broken or small print on several pages ✓
8. Print exceeds margin requirements 
9. Tightly bound copy with print lost in spine 
10. Computer printout pages with indistinct print 
11. Page(s) _______ lacking when material received, and not available from school or author.
12. Page(s) _______ seem to be missing in numbering only as text follows.
13. Two pages numbered ___________. Text follows.
14. Curling and wrinkled pages 
15. Other ____________________________

University Microfilms International
Anisotropy in the orbital susceptibilities of hcp metals

by

Carol M. Theisen

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Physics
Major: Solid State Physics

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For The Graduate College

Iowa State University
Ames, Iowa

1983
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>CHAPTER I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Definition of Magnetic Susceptibility</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Contributions to $\chi$</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Core electrons</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Localized outer d or f electrons</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Nuclei with nonzero spins</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Overview of Study</td>
<td>4</td>
</tr>
<tr>
<td>II</td>
<td>CHAPTER II. PARAMAGNETIC TRANSITION METALS</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Introduction</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Contributions to $\chi$</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Review of experimental situation</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>Experimental results for Zr</td>
<td>19</td>
</tr>
<tr>
<td>III</td>
<td>CHAPTER III. COMPUTATIONAL METHODS</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>Van Vleck Orbital Susceptibility</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>LAPW method</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>Angular momentum matrix elements</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>Shimizu method</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>Diamagnetic Susceptibility</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>Core contribution</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>Valence contribution</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>Pauli Spin Susceptibility</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>Exchange enhancement</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>Tetrahedron method</td>
<td>44</td>
</tr>
<tr>
<td>Chapter/I Section</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>------------------------------------------------------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>CHAPTER IV. RESULTS AND DISCUSSION</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>Bulk Susceptibility for Sc and Zr</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>Band structure and density of states</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>Comparison with experiment</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Comparison with tight-binding calculation</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>Future Directions</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>Summary</td>
<td>59</td>
<td></td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>APPENDIX</td>
<td>65</td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER I. INTRODUCTION

In the present study, we are interested in calculating the magnetic susceptibility of certain paramagnetic hcp transition metals. In particular, we wish to determine the orbital susceptibilities of scandium and zirconium. Sc and Zr are similar to one another in many important respects (e.g., they both have Fermi levels near the bottom of the d-bands). Therefore, we expect the magnetic behavior of these two materials to be comparable. However, the measured susceptibility of Zr is highly anisotropic while that of Sc is only slightly anisotropic. It is this difference, between two otherwise similar materials, which provides the motivation for the present study.

Definition of Magnetic Susceptibility

The magnetic susceptibility of a material is a function which directly measures the response of the material to an applied magnetic field. As such, it provides a natural scheme for the classification of materials according to their magnetic properties. The susceptibility \( \chi \) is defined by the relation (1)

\[
\vec{M} = \chi \vec{H}
\]

where \( \vec{M} \) is the magnetization density (magnetic moment per unit volume) and \( \vec{H} \) is the applied field. In general, the susceptibility is a function of both the field, \( \vec{H} \), and the temperature, \( T \). For magnetically isotropic materials, \( \chi \) is a scalar, whereas \( \chi \) is a tensor for anisotropic materials. For hcp materials, the materials of interest in this study,
the susceptibility tensor has two independent nonzero components. That is, one value for the susceptibility is obtained when the field is applied along the symmetry axis (c-axis) of an hcp crystal and a different value is obtained when the field is applied perpendicular to this axis.

Because it is a spatially averaged quantity, the susceptibility does not provide any information concerning the spatial distribution of the magnetization. Information regarding the spatial distribution is supplied by the magnetic form factor which is the Fourier transform of the magnetization density.

Contributions to $\chi$

The magnetic susceptibility (or form factor) of a solid is generally composed of several terms. Although these terms are not all independent (i.e., they may interfere with one another), for the purpose of instruction we will treat them independently in the following paragraphs.

The most important contributions to the susceptibility of metals arise from the band electrons. These electrons are responsible for three major terms in the magnetic susceptibility, namely the Pauli, Van Vleck and Landau-Peierls contributions. The Pauli and Van Vleck susceptibilities are paramagnetic contributions, while the Landau-Peierls term is diamagnetic. Since these are the most important contributions to the susceptibility in transition metals, they will be the focus of the discussion in the following chapter.
We should point out that the band electrons also give rise to a spin-orbit interaction term. However, according to Kubo and Obata (2) the spin-orbit component is usually negligible compared to other terms in the susceptibility of transition metals. The spin-orbit term generally constitutes less than 1% of the total susceptibility in transition metals. As such, it is of very little consequence and in the future we will omit this term from consideration.

Other contributions to the susceptibility are associated with the following sources (3).

**Core electrons**

The core electrons are by definition paired; hence, they give rise to a diamagnetic contribution to the susceptibility. The core diamagnetic term enters calculations of the magnetic susceptibility as a small correction. Although small, this contribution is important in the interpretation of the susceptibility of many solids. Consequently, we will include the core term in our calculation of the susceptibilities of Sc and Zr.

**Localized outer d or f electrons**

These unpaired electrons exhibit a temperature dependent paramagnetism which, in the majority of cases, follows the Curie-Weiss law

\[
\chi = \frac{C}{T - T_c}
\]

(2)

where \( T_c \) is the critical temperature below which a nonzero spontaneous magnetization can be found and \( C \) is the Curie constant which is given
by the expression
\[ C = \frac{NJ(J+1)g^2\mu_B^2}{3k_B} \]
where \( J \) is a good quantum number.

**Nuclei with nonzero spins**

The nuclear spin (as well as the electron spin) interacts with the magnetic field to give rise to a nuclear contribution to the magnetic moment of a solid. However, as a result of the much greater nuclear mass, the nuclear contribution is \( 10^6 \) to \( 10^8 \) times smaller than the electronic contribution. Consequently, nuclear spin effects are usually ignored.

**Overview of Study**

In the next chapter, we discuss the magnetic susceptibility of paramagnetic transition metals. After describing the most important contributions to the susceptibility in these materials, we briefly review the current experimental situation and report the observed magnetic behavior of zirconium, the material in which we are most interested.

Details of the computational methods employed in this study are presented in Chapter III. Included in the analysis is a brief review of the Augmented Plane Wave (APW) method and a discussion of the angular momentum matrix elements. In addition, Chapter III contains an account of an alternative procedure, developed by Yasui and Shimizu (4), for the determination of the orbital susceptibility. Finally, we summarize the techniques used to evaluate the spin and diamagnetic contributions.
to the susceptibility including a description of the tetrahedron method for evaluating phase space integrals.

In Chapter IV, we present the results of our susceptibility calculation for Sc and Zr, and compare these results to experimental measurements (5,6) and the outcome of a previous calculation (7) based on the tight-binding model. Also included in Chapter IV is a discussion of possible future avenues of investigation.
CHAPTER II. PARAMAGNETIC TRANSITION METALS

Introduction

As stated in Chapter I, the major contributions to the magnetic susceptibility in transition metals arise from the band electrons. In most cases, it is sufficient to write the magnetic susceptibility as

\[ \chi = \chi_p + \chi_{V\text{V}} + \chi_D \]  

where \( \chi_p \) is the Pauli spin contribution, \( \chi_{V\text{V}} \) is the Van Vleck orbital susceptibility and \( \chi_D \) is the diamagnetic term, which is usually subdivided into a core contribution and a Landau-Peierls contribution from the outer electrons. A detailed analysis of the magnetic susceptibility in terms of these contributions is generally quite difficult. Only when the spin susceptibility clearly dominates, is the calculation relatively straightforward. Unfortunately, in transition metals, the orbital contributions are significant and the calculation of the generalized susceptibility is very complicated.

Although a great deal of effort has been invested in the study of orbital paramagnetism in solids, many of the formalisms which have been developed do not lend themselves to numerical evaluation. Hebborn and Sondheimer (9), Misra and Roth (10), and Fukuyama (11), for instance, give complete expressions for the susceptibility but, in each case, the expressions obtained are remarkably intricate. They involve various higher order derivatives of the energies and wavefunctions with respect to the wavevector and accurate numerical evaluation of these derivatives is not presently possible. Hence, even with the advanced computational
techniques available, it is exceedingly difficult to calculate precisely the electronic response of a paramagnetic transition metal to an applied magnetic field. Only in the case of chromium has a detailed calculation been attempted (12). As can be seen in Fig. 1, the outcome of this calculation is consistent with the results of previous calculations based on the atomic model (13). However, unlike most transition metals, Cr has a d-band complex which is nearly half full. Hence, it would be inappropriate to extend these results to materials which do not feature approximately half-filled d-bands.

Contributions to $\chi$

In a paramagnetic material, each spin up state is degenerate with a spin down state and there is no net spin magnetic moment (Fig. 2(a)). However, when a magnetic field is applied, the electron spin interacts with the field to shift the spin up states by an amount $2\mu_B H$ relative to the spin down states (Fig. 2(b)). The electrons are thus redistributed, the number of electrons in the two directions differing by $2\mu_B H N(E_F)$ where $N(E_F)$ is the density of states at the Fermi surface. The resulting susceptibility, called the Pauli spin susceptibility (1,14-15), can be written

$$\chi = 2\mu_B^2 N(E_F) \quad .\tag{4}$$

Ordinarily the above expression is corrected for electron-electron interactions which produce an effective magnetic field proportional to the spin density. The expression for the Pauli susceptibility then becomes
Figure 1. Comparison of APW and atomic calculations of the spin and orbital magnetic form factors of Cr.
Figure 2a. In the absence of a magnetic field, the occupancy of the spin up band is equal to that of the spin down band.
Figure 2b. When a magnetic field is applied, the occupancy of the up and down bands adjust to make the energies equal at the Fermi level, resulting in Pauli paramagnetism.
\[ \chi = \frac{2\mu_B^2 N(E_F)}{1 - \ln(E_F)} = \frac{2\mu_B^2 N(E_F)}{1 - \lambda} \]  

where \( \chi \) is an integral representing the interaction energy. Smaller corrections arising from spin independent interactions are usually ignored. In transition metals, the density of states of the d-bands is ordinarily quite high and consequently, the Pauli susceptibility is usually substantial. However, since the nature of Pauli paramagnetism is well-understood, many of the details involved in the calculation of this term will be omitted from the present study.

Another typically large contribution to the magnetic moment of a transition metal is the Van Vleck orbital contribution (2,16-18). The calculation of this particular term will be emphasized here in an attempt to better understand the mechanism of orbital paramagnetism. In transition metals, the orbital magnetic moment is often quenched (the orbital angular momentum components average to zero) in the absence of a magnetic field. But, when a field is applied, excited states become mixed with the unperturbed ground state, resulting in a new ground state with a nonzero angular momentum and a corresponding orbital moment. This orbital moment gives rise to a paramagnetic contribution to the susceptibility called the Van Vleck orbital susceptibility (14). In transition metals, this term in the susceptibility can be as large as, or even larger than, the Pauli spin susceptibility.

The Van Vleck orbital contribution is not the only orbital term in the susceptibility. Other smaller, yet significant, contributions to the orbital susceptibility are the diamagnetic terms. The Landau-
Peierls (19,20) diamagnetic contribution arises from the quantized orbital motions of the outer electrons in the presence of a magnetic field, while the core diamagnetism is associated with the tendency of electrons to shield the interior of a body from an applied magnetic field.

In a transition metal, each of the contributions to the susceptibility mentioned above is important. Thus, any accurate calculation of the magnetic response of such a material must include the evaluation of each of these terms. Consequently, the theoretical analysis of the magnetic behavior of a transition metal is quite complicated.

Review of experimental situation

With the introduction of polarized beam diffractometers (21) in the early 1960s, it became possible to measure the small induced moments in paramagnetic materials. Prior to this time, the behavior of d electrons in transition metals was understood only qualitatively. It was believed that wavefunctions for energies near the top of the d-band were very similar to those calculated for the corresponding free atom, whereas the wavefunctions for states near the bottom of the band were significantly expanded relative to the free atom case.

To understand the origin of this behavior, consider what happens when two atoms are brought together to form a molecule. Two states with different energies result. The lower energy state, called the bonding state, is characterized by a buildup of the charge density between the atoms, leading to an increase in the binding energy. The other state, with a lower binding energy, a more expanded wavefunction
and a reduction in the charge density between the atoms, is called the antibonding state.

An analogous argument can be used to explain the behavior of d electrons in transition metals. Since the induced spin in a paramagnet is associated with states near the Fermi level, this behavior of the d electrons implies that for metals close to the right end of the transition series (nearly full d-bands), the spin form factors are similar to free atom form factors. However, as we move left across the periodic table, the spin form factors fall off faster than their atomic counterparts as functions of momentum transfer, indicating expanded wavefunctions. Although orbital contributions complicate the actual situation, the general trend should be that atomic models of the magnetic moment density grow progressively worse as we move right to left across the periodic table (22). As stated above, this predicted breakdown of the atomic model is due to the expanded wavefunctions at the bottom of a d-band.

The breakdown in the atomic model was not observed until the introduction of the polarized beam technique. In an early investigation, the polarized beam technique was used to determine the form factor of chromium in the paramagnetic state. As a typical itinerant electron metal, the electronic wavefunctions of Cr are expected to be more extended in space than those of the corresponding free ion. In Fig. 3, measurements of the induced moment form factor of Cr, made by Stassis et al. (23,24), are compared to the free ion 3d form factors of Freeman and Watson (13). The agreement between the experimental results and
Figure 3. Comparison of the measured induced moment form factor of Cr with atomic calculations.
calculations based on the atomic model suggest that the electronic wavefunctions are not significantly different from those of the free ion. As mentioned above, a detailed band theoretical APW (Augmented Plane Wave) calculation carried out by Oh et al. (25) confirms this result. Oh et al. (25) also calculated the orbital form factor of Cr and found it to be in agreement with the free ion form factor. By assuming a 40% 3d-spin-60% 3d-orbital distribution of the induced moment, Oh et al. (25) obtain excellent agreement with the experimental results of Stassis et al. (23,24).

The attempt to observe the expansion of the wavefunctions near the left end of the transition series, in part, motivated experimental investigations of scandium, yttrium and lutetium. The crystal structure of each of these metals is hexagonal. Furthermore, all three elements have a single electron in a d-shell; so the Fermi level in each case lies close to the bottom of a d-band. Hence, one expects the experimental form factors to be in poor agreement with the free ion results. The induced moment form factors of Sc, Y and Lu were measured by Koehler and Moon (26), Moon et al. (22), and Stassis et al. (27), respectively. In Figs. 4 and 5, the experimental form factors of Sc and Lu are compared to free atom and APW calculations (27,28), while in Fig. 6 a comparison is made between the free atom and measured form factors of Y. In all three cases, the measured form factor falls off faster with increasing scattering angle than the calculated atomic spin form factor, implying that the magnetization density in the solid is more extended in space than it is in the free ion. The observed form factors drop off sharply
Figure 4. Comparison of the induced moment form factor of Sc with atomic and APW calculations.
Figure 5. Comparison of the induced moment form factor of Lu with atomic and APW calculations
Figure 6. Comparison of the measured form factor of Y with atomic calculations.
at small scattering angles and at large angles exhibit nonnegative oscillatory behavior. The presence of this behavior in all three cases (Sc, Y and Lu) suggests that it is a characteristic of the conduction electrons in isoelectronic hcp crystals. Furthermore, the calculated APW spin-only form factors of Sc and Lu are in remarkably good agreement with the experimental results. Since orbital form factors are more expanded than their spin counterparts, these results present us with a dilemma. If we assume that the APW wavefunctions are correct, then we must conclude that the orbital contribution to the scattering is negligible. However, measurements of the bulk susceptibility (5) in Sc reveal a significant anisotropy. Since we neglect the spin-orbit interaction, only the orbital contribution can be anisotropic. The implication here is that there is a large orbital contribution to the scattering, in contradiction to the conclusion arrived at above. Furthermore, theoretical work by Das (7) suggests that the Van Vleck orbital susceptibility should be about one-third of the total in Sc. These contradictions indicate that either the spatial distribution of the orbital magnetization is different in the free ions than it is in the corresponding solids or that nonself-consistent APW calculations produce inaccurate wavefunctions. Recent calculations of the form factor of Lu (29), using self-consistent APW wavefunctions, support the former.

**Experimental results for Zr**

To gather additional information, induced moment form factor experiments on hcp zirconium were undertaken by Stassis et al. (30).
As in the case of Sc, the Fermi level of Zr is near the bottom of a d-band (Zr has one more d electron than Sc). According to specific heat (6) and susceptibility (6,31) measurements, the induced magnetization in Zr is largely orbital in character. The results are summarized in Figs. 7 and 8. The observed form factor falls off faster with increasing scattering angle than the calculated atomic 4d orbital form factor of Zr (Fig. 7). If we assume that the spatial distribution of the induced orbital magnetization in the solid is not significantly different from that of the free atom, we are led to conclude there is a substantial spin contribution to the induced moment. In Fig. 8, we compare the experimental results with calculations based on a 64% spin-36% orbital distribution of the induced moment. The form factors plotted in Fig. 7 are those used in the calculation. The theoretical form factor has been normalized to the bulk susceptibility measured (6) with the field perpendicular to the c-axis (symmetry axis) and corrected for core diamagnetism (32).

The most remarkable feature of Fig. 8 is the lack, to within experimental accuracy, of any magnetic anisotropy; that is, the data obtained with the field applied perpendicular to the c-axis of the crystal agree

---

1Measurements of the specific heat of a material can be related to its density of states, which in turn can be used to estimate the Pauli spin susceptibility. Specific heat measurements of Zr indicate the Pauli susceptibility is approximately $30 \times 10^{-6}$ emu/mole. An estimate of the orbital contribution to the susceptibility can be obtained by subtracting the spin susceptibility from measurements of the total susceptibility. This procedure gives an orbital susceptibility for Zr of approximately $100 \times 10^{-6}$ emu/mole. Hence, we conclude the induced magnetization in Zr is largely orbital in character.
Figure 7. Calculated RAPW spin and atomic 4d orbital form factors of hcp Zr.
Figure 8. Comparison of the experimental results with calculations (Δ) based on a 64% spin-36% orbital distribution of the induced moment. For H || c-axis, the bulk susceptibility has the value 22.8.
with those obtained with the field applied parallel to the c-axis. This agreement conflicts with the large anisotropy \( \chi_\parallel = 1.43 \chi_\perp \) observed in bulk susceptibility measurements (6) and suggests the spatial distribution of the induced orbital moment may be anisotropic. It is these difficulties that provide the motivation for the present study. Band theoretical calculations of the magnetic response of Zr, especially the orbital susceptibility, should prove useful in resolving these difficulties.
CHAPTER III. COMPUTATIONAL METHODS

Van Vleck Orbital Susceptibility

The generalized susceptibility of a material is composed of orbital and spin parts. In transition metals, the paramagnetic contribution to the orbital part, the Van Vleck orbital susceptibility, has been found to be quite large, sometimes larger than the spin susceptibility. In such cases, the Van Vleck susceptibility is the dominant contribution to the generalized susceptibility. Since, in the present study, we are concerned with transition metals, we will emphasize the calculation of the Van Vleck term in the susceptibility.

The APW wavefunctions and eigenvalues obtained according to the prescription laid out below are used in conjunction with the Kubo-Obata formula (2) to calculate the Van Vleck orbital susceptibility. The Kubo-Obata formula is an approximation to the general expression derived by Hebborn and Sondheimer for the orbital contribution to the magnetic susceptibility in a metal. For transition metals, it is reasonable to treat the electronic band structure as if it is a combination of a d-band and a conduction band. The major contribution to the orbital susceptibility is expected to come from the d-band, which may be dealt with in the tight-binding approximation (33).

In the limit of tight-binding, only one term in Hebborn and Sondheimer's expression survives and this term is composed of atomic diamagnetic and Van Vleck paramagnetic parts. In transition metals, the atomic diamagnetic contribution is generally much smaller in magnitude than the Van Vleck susceptibility. Thus, in the tight-binding
limit, only the Van Vleck paramagnetic contribution to the susceptibility is important. This contribution can be expressed in terms of the Kubo-Obata formula (2, 34)

\[ \chi_i = 2\mu_B^2 \sum_{nn'} \int \frac{d\vec{k}}{(2\pi)^3} \frac{f(E_n(\vec{k}))(1-f(E_{n'}(\vec{k})))}{E_{n'}(\vec{k}) - E_n(\vec{k})} |\langle n\vec{k}|L_i|n'\vec{k}\rangle|^2 . \quad (6) \]

In Eq. (6), \( n \) and \( n' \) are band indices, \( f \) is the Fermi function, \( L_i \) denotes the \( i \)th component of angular momentum and \( \mu_B \) is the Bohr magneton. This equation provides us with a means for evaluating the Van Vleck orbital susceptibility.

To better understand the origin of the Kubo-Obata formula, consider a molecular system which has no magnetic moment in its ground state. Since we are primarily concerned with the orbital response of a material to an applied field, we shall ignore all effects associated with electron spin. Then in the presence of a uniform magnetic field, the Hamiltonian becomes

\[ H = \frac{1}{2m} \left( \vec{p} - \frac{e}{c} \hat{A}(\vec{r}) \right)^2 + V(\vec{r}) \]  

(7)

where \( V(\vec{r}) \) is the electrostatic potential of the system and \( \hat{A}(\vec{r}) \) is the vector potential. \( \hat{A}(\vec{r}) \) is chosen to have the form

\[ \hat{A}(\vec{r}) = -\frac{1}{2} (\hat{\mathbf{r}} \times \hat{\mathbf{r}}) \quad . \]

With this choice of vector potential, the Hamiltonian becomes

\[ H = \frac{1}{2m} \left( \vec{p} + \frac{e}{2c} \hat{H} \times \vec{r} \right)^2 + V(\vec{r}) \]
\[ H_o = \frac{p^2}{2m} + V(\vec{r}) \quad (9) \]

and

\[ \Delta H = \mu_B \vec{L} \cdot \vec{H} + \frac{e^2}{8mc} \frac{1}{H^2} (x^2 + y^2) \quad . \quad (10) \]

In Eq. (10), \( \vec{L} \) represents the total electronic orbital angular momentum:

\[ \vec{L} = \vec{r} \times \vec{p} \quad . \]

Recall that the magnetic susceptibility is by definition the derivative of the magnetic moment with respect to the field and the magnetic moment is in turn the derivative of the ground-state energy with respect to the field. Consequently, to determine the susceptibility, we must compute the change in the ground-state energy induced by the field. Since the energy shifts produced by \( \Delta H \) are generally quite small on the scale of atomic excitation energies, we can use ordinary perturbation theory to compute the shifts. According to second-order perturbation theory, the shift in the ground-state energy is given by

\[ \Delta E_o = \langle 0 | \Delta H | 0 \rangle - \sum_n \frac{|\langle 0 | \Delta H | n \rangle|^2}{E_n - E_o} \quad . \quad (11) \]

If we insert Eq. (10) into Eq. (11) and retain terms up to the second order in \( \vec{H} \), we find
\[ \Delta E_o = \mu_B \vec{H} \cdot \langle 0 | \vec{L} | 0 \rangle - \sum_n \frac{|\langle 0 | \mu_B \vec{H} \cdot \vec{L} | n \rangle|^2}{E_n - E_o} + \frac{e^2}{8mc^2} H^2 \langle 0 | x^2 + y^2 | 0 \rangle. \]  

However, for a system with no magnetic moment in its ground state, the first term in the above expression vanishes. Hence, we obtain

\[ \Delta E_o = - \sum_n \frac{|\langle 0 | \mu_B \vec{H} \cdot \vec{L} | n \rangle|^2}{E_n - E_o} + \frac{e^2}{12mc^2} H^2 \langle 0 | r^2 | 0 \rangle. \]  

Differentiating Eq. (13) twice with respect to the field yields the following expression for the susceptibility

\[ \chi = 2\mu_B^2 \sum_n \frac{|\langle 0 | \vec{L} | n \rangle|^2}{E_n - E_o} - \frac{e^2}{6mc^2} \langle 0 | r^2 | 0 \rangle. \]  

The first term in Eq. (14) is the Van Vleck paramagnetic contribution to the susceptibility while the second is the ordinary atomic diamagnetism.

A similar expression for the susceptibility of d electrons in transition metals can be obtained using linear response theory (35) and the tight-binding approximation. However, in transition metals, the atomic diamagnetic contribution is generally negligible in comparison to the Van Vleck term. Thus, we arrive at Eq. (6), the Kubo-Obata formula for the orbital susceptibility of a transition metal.

**LAPW method**

To obtain the energy bands and wavefunctions needed to determine the Van Vleck orbital susceptibility, we use the Linearized Augmented Plane Wave (LAPW) method (36), a modification of the Augmented Plane Wave (APW) method developed by Slater (37).
The APW method provides a scheme for solving the Schrödinger equation for a crystal variationally. In applying the APW method, we make use of the muffin-tin potential approximation, according to which the unit cell is divided into two regions by nonoverlapping spheres centered at the atomic sites. The potential is assumed to be spherically symmetric inside the spheres and constant outside. However, since non-spherical components of the charge density have been found to be sensitive to corrections to the muffin-tin potential (38), a warped muffin-tin (WMT) potential, rather than a flat potential, was generated in the interstitial region following a procedure mapped out by Koelling (39). This potential, while maintaining the approximation of a spherically averaged potential inside the spheres, properly takes into account the variations of the potential in the interstitial region (40).

Having selected a potential, we now solve the Schrödinger equation using the variational principle. Our trial wavefunction is chosen to have a dual representation; it consists of a linear combination of atomic-like functions inside the muffin-tin spheres and is composed of plane waves in the interstitial region. Since the APW method has been reviewed in detail elsewhere (41), we will include only those aspects of the method relevant to an understanding of our particular problem.

Atomic charge densities calculated by the Hartree-Fock-Slater method are superposed to create a crystal charge density \( \rho(r) \) and the crystal potential is constructed according to a procedure developed by Mattheiss (42). The crystal potential is made up of two components, the Coulomb potential and the exchange potential. The atomic Coulomb
potential and the spherical terms of a Löwdin alpha expansion for neighboring atomic Coulomb potentials are summed to construct the crystal Coulomb potential. Slater's free electron exchange approximation (43)

\[ V_{ex}(r) = -6\left(\frac{3}{8\pi} \rho(r)\right)^{1/3} \]  

(15)
is then used to obtain the exchange potential. The warped potential in the interstitial region is created in the same way as the spherical potential inside the muffin-tin sphere, with the exception that the expansion is in terms of symmetrized plane waves \( S_{\vec{k}_n} (r) \); that is, in the interstitial region

\[ V(r) = \sum_{\vec{k}_n} C(\vec{k}_n) S_{\vec{k}_n} (r) \]  

(16)

where

\[ S_{\vec{k}_n} (r) = \frac{1}{g} \sum_{\alpha=1}^{g} e^{i\alpha \vec{k}_n \cdot r} \]  

(17)

In Eq. (17), \( g \) is the number of group operations \( \alpha \) and \( \vec{k}_n \) denotes a reciprocal lattice vector.

The crystal wavefunction for one atom per unit cell is given by the expansion

\[ \phi_{\vec{k},E} (r) = \sum_i A_i (\vec{k},E) \chi_{\vec{k}_i} (r) \]  

(18)

with
\[ x_{k_i}^r(r) = \Omega^{-1/2} e^{i\mathbf{k}_i \cdot \mathbf{r}} , \quad r \geq r_{MT} \]  

\[ x_{k_i}^r(r) = \sum_{\omega m} [A_{\omega m} R_{\omega m}(r) + B_{\omega m} \hat{R}_{\omega m}(r)] Y_{\omega m}(r) , \quad r \leq r_{MT} \]  

where \( \mathbf{k}_i = \mathbf{k} + \mathbf{K}_i \), \( \mathbf{k} \) is the reduced wavevector and \( \mathbf{K}_i \) is a reciprocal lattice vector. \( \Omega \) in Eq. (19) is the volume of the unit cell and in Eq. (20) the dot denotes differentiation with respect to energy. For \( j \) atoms per unit cell, Eq. (18) generalizes to

\[ \phi_{k_i E}(r) = \sum_{ij} A_i(\mathbf{k}_i, E) x_{k_i}(r - r_j) \]  

where \( r_j \) denotes the position of the jth atom in the unit cell. The function \( R_{\ell, E}(r) \) in Eq. (20) is the solution of the radial Schrödinger equation corresponding to the energy \( E \); that is, \( R_{\ell, E}(r) \) satisfies the equation

\[ \left[ -\frac{1}{2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) + [V(r) + \frac{\ell(\ell + 1)}{r^2}] \right] R_{\ell, E}(r) = E R_{\ell, E}(r) . \]  

The coefficients \( A_{\omega m} \) and \( B_{\omega m} \) in Eq. (20) are determined by requiring the basis functions of Eqs. (19) and (20) and their derivatives to be continuous at \( r = r_{MT} \), where \( r_{MT} \) is the radius of the muffin-tin sphere. Thus, we obtain

\[ A_{\omega m} = 4\pi\Omega^{-1/2} r_{MT}^{2} i^{\omega} \iota_{\omega m}(k) \left[ j_{\ell}^{\dagger}(k, r_{MT}) \hat{R}_{\omega m}(r) - j_{\ell}^{}(k, r_{MT}) \hat{R}_{\omega m}^{\dagger}(r) \right] \]  

and
B_{\ell m} = 4\pi \Omega -1/2 \sum_{\ell=MT} R_{\ell,\ell}(r) \left[ j_{\ell}(k_{i}r_{MT})R_{\ell,\ell}(r) - j'_{\ell}(k_{i}r_{MT})R_{\ell,\ell}(r) \right] (24)

where the prime denotes differentiation with respect to \( r \). The wavefunctions and eigenvalues are then evaluated using a Rayleigh-Ritz variational procedure in which the energy is minimized with respect to the coefficients \( A_{i} \) in Eq. (18). This results in a determinantal equation which is solved to obtain the energy, \( E \), as a function of the wavevector, \( \vec{k} \). The plane wave expansion coefficients \( A_{i} \) are then determined by back transformation and finally the \( A_{\ell m} \) and \( B_{\ell m} \) are found by applying the continuity conditions at the surface of the muffin-tin sphere.

**Angular momentum matrix elements**

Given the APW wavefunctions, in principle, one can determine the angular momentum matrix elements. However, due to the complicated geometry of the integrals, it is very difficult to evaluate the matrix elements using the exact wavefunctions. To simplify the calculation, one generally replaces the unit cell by a sphere of the same volume called the Wigner-Seitz sphere. The spherical waves from inside the muffin-tin sphere are extended outward from the muffin-tin radius to approximate the wavefunctions in the interstitial region. In this approximation, the matrix elements corresponding to the \( z \) component of angular momentum are given by

\[
\langle \phi_{k',E} | L_{z} | \phi_{k,E} \rangle = \int_{WS} \phi_{k',E}^{*} L_{z} \phi_{k,E}^{*} d\tau
\] (25)
Because of the orthogonality of the spherical harmonics, Eq. (26) reduces to

\[
\langle \phi_{\ell', m'} | L_z | \phi_{\ell, m} \rangle = \sum_{\ell m} \left[ A_{\ell m}^{*} A_{\ell', m'} \int_{0}^{\infty} R_{\ell, E}(r) R_{\ell', E'}(r) r^2 dr + B_{\ell m}^{*} B_{\ell', m'} \int_{0}^{\infty} \hat{R}_{\ell, E}(r) \hat{R}_{\ell', E'}(r) r^2 dr + (B_{\ell m}^{*} A_{\ell', m} + A_{\ell m}^{*} B_{\ell', m}) \int_{0}^{\infty} \hat{R}_{\ell, E}(r) R_{\ell', E'}(r) r^2 dr \right].
\]

To find the matrix elements corresponding to the x and y components of angular momentum, we first determine the matrix elements of \( L_+ \) and \( L_- \), the angular momentum raising and lowering operators. These matrix elements are given by the expressions
\[
\langle \phi_{k',E}^* L_{\pm} \phi_{k,E}^* \rangle = \int_{\text{WS}} \phi_{k,E}^* L_{\pm} \phi_{k',E'}^* \, dr
\]

\[
= \sum_{\ell m} \sqrt{(2\ell + 1)(2\ell + 1)} \delta_{m,m'+1} \left[ A_{\ell m - \ell m'}^* A_{\ell m'} \int_0^{r_{\text{WS}}} R_{\ell,E}(r) \, dr \right]
\times R_{\ell',E'}(r) r^2 dr + B_{\ell m - \ell m'}^* B_{\ell m'} \int_0^{r_{\text{WS}}} \hat{R}_{\ell,E}(r) \hat{R}_{\ell',E'}(r) r^2 dr
\]

\[
+ (B_{\ell m - \ell m'}^* A_{\ell m'} + A_{\ell m - \ell m'}^* B_{\ell m'}) \int_0^{r_{\text{WS}}} \hat{R}_{\ell,E}(r) R_{\ell',E'}(r) r^2 dr \]  

We then use Eq. (29) together with the relations

\[
L_{\pm} = L_x \pm i L_y
\]

to obtain the matrix elements corresponding to x and y components of angular momentum. Finally, we substitute the APW eigenvalues and matrix elements, obtained according to the procedure outlined above, into Eq. (6), the Kubo-Obata formula, and sum over k points to get the Van Vleck contribution to the orbital susceptibility.

**Shimizu method**

There is an alternative numerical scheme available for the evaluation of the Van Vleck orbital susceptibility. This method (4), developed by Shimizu, avoids the conceptual difficulties inherent in many approaches and appears to give reasonable results for the 3d series of bcc transition metals.

To evaluate the susceptibility, Shimizu uses an expression given by Hebborn and March (35) for the generalized orbital susceptibility, \( \chi(q) \),
and extrapolates $\chi(q)$ to $q = 0$. According to Hebborn and March, the generalized orbital magnetic susceptibility can be written as

$$\chi(q) = \frac{8K}{q^2} [N(q) - n]$$

where $q$ is the wavevector and

$$K = \frac{\mu_B^2 \hbar^2}{m_e}$$

$$N(q) = \sum_{ij} N_{ij}(q) = \frac{4}{\Omega} \sum_{ij} \int \frac{f(E_i(\vec{k})) \left(1 - f(E_j(\vec{k} + \vec{q}))\right)}{E_j(\vec{k} + \vec{q}) - E_i(\vec{k})}$$

$$\times |<\vec{k} + \vec{q},j| e^{i\vec{q} \cdot \vec{r}} \frac{\partial}{\partial x} |\vec{k},i>|^2 d\vec{k}$$

and

$$n = \sum_i n_i = \frac{1}{\Omega} \sum_i \int f(E_i(\vec{k})) d\vec{k}$$

Shimizu argues that extrapolation to $q = 0$ using Eq. (32) leads to numerical problems. The error is due to incomplete cancellation between $\lim_{q \to 0} N(q)$ and $n$ which in turn results from $N(q)$ and $n$ being calculated by the two different expressions, Eqs. (32) and (33). In order to circumvent this problem, $N(q)$ is expanded in a power series in $q^2$; i.e.,

$$N(q) = a + bq^2 + cq^4 + \ldots$$
Substitution of Eq. (34) into Eq. (31) and extrapolation to \( q = 0 \) gives the orbital contribution to the susceptibility

\[
\chi_{\text{orb}} = \lim_{q \to 0} \chi(q) = 8Kb
\]  

where we have used the fact that \( \lim_{q \to 0} N(q) = n \) (i.e., \( n = a \)).

Numerical values of the expansion coefficients \( b, c, ... \) can be determined by calculating \( N(q) \) at several small values of \( q \) (using Eq. (32)) and fitting the expansion formula, Eq. (34), to these calculated values. Shimizu's procedure is straightforward and easy to implement. Unfortunately, for finite meshes, \( \chi(q) \) diverges at \( q = 0 \). However, the claim is made that the errors are systematic and, therefore, accurate values of the orbital susceptibility can still be obtained using this method. Nevertheless, the method loses a certain appeal in light of these divergences.

**Diamagnetic Susceptibility**

The orbital susceptibility contains not only a paramagnetic contribution but diamagnetic terms as well. Although they are not as large as the Van Vleck susceptibility, the diamagnetic contributions are nevertheless important in transition metals. In the following paragraphs, we adopt a formalism for the evaluation of the diamagnetic contributions to the susceptibility.

The diamagnetic susceptibility is composed of two parts - a core term and a valence term. The core and valence contributions are calculated separately and then summed to give the total diamagnetic contribution to the susceptibility.
Core contribution

For the core electrons, it is convenient to write (44)

\[ f_d(\theta) = -\frac{3}{<r^2>} \frac{1}{q} \frac{df(q)}{dq} \]  

(36)

where \( f_d(\theta) \) is the normalized diamagnetic form factor of the atom, \( f(q) \) is the normalized charge form factor of the atom, \( q \) is the scattering vector of magnitude \((4\pi/\lambda)\sin \theta\) and \(<r^2>\) is the second moment of the atomic charge distribution. The \( q = 0 \) limit of the above expression can be used in obtaining the diamagnetic contribution to the static susceptibility. \( \frac{1}{q} \frac{df}{dq} \) can be evaluated numerically. Then in the limit as \( q \) approaches zero, Eq. (36) can be used to find \(<r^2>\). Finally, the core contribution to the diamagnetic susceptibility can be related to \(<r^2>\) by the expression (32)

\[ \chi_{D}(\text{core}) = -\frac{N_A}{6} \frac{a_o^3}{a} <r^2> \]  

(37)

where \( N_A \) = Avogadro's number

\( a = \) fine structure constant

\( a_o = \) Bohr radius.

In Eq. (37), \( \chi_D \) is in units of emu/mole and \(<r^2>\) is in atomic units.

Valence contribution

For the valence electrons, we again use the Wigner-Seitz approximation and write the expression for the diamagnetic susceptibility (14) as

\[ \chi_D(\text{valence}) = -\frac{2e^2N}{6mc^2H^2} \int_{WS} \rho(\mathbf{r})(\mathbf{r} \times \mathbf{H})^2 d\mathbf{r} \]  

(38)
where $\rho(\hat{r})$ = valence charge density

$\mathbf{H}$ = magnetic field intensity

$N$ = number of valence electrons.

The factor of two in the numerator is a consequence of spin degeneracy. Furthermore, the valence charge density is subject to the normalization condition

$$N = \int_{WS}^{} \rho(\hat{r}) \, d\hat{r}^+ \quad (39)$$

In an hcp material, the direction of the magnetic field relative to the crystallographic axes determines the form of Eq. (38). For $\mathbf{H}$ parallel to the c-axis (symmetry axis) of an hcp crystal, we find

$$\chi_D^c(\text{valence}) = -\frac{e^2 N}{3mc^2} \int_{\text{WS}}^{} \rho(\hat{r}) r^2 \sin^2 \theta \, d\hat{r}^+ \quad (40)$$

$$= -\frac{e^2 N}{3mc^2} \int_{\text{WS}}^{} \sum_{LM} c_{LM}(r) \tilde{Z}_{LM}(\hat{r}) \sin^2 \theta \, d\hat{r}^+ \quad (41)$$

where the charge density has been expanded in terms of lattice harmonics $Z_{LM}(\hat{r})$. On the other hand, if $\mathbf{H}$ is perpendicular to the c-axis of the crystal, Eq. (38) becomes

$$\chi_D^a(\text{valence}) = -\frac{e^2 N}{3mc^2} \int_{\text{WS}}^{} \rho(\hat{r}) r^2 [\cos^2 \theta + \sin^2 \theta \sin^2(\phi' - \phi)] \, d\hat{r}^+ \quad (42)$$

$$= -\frac{e^2 N}{3mc^2} \int_{\text{WS}}^{} \sum_{LM} c_{LM}(r) \tilde{Z}_{LM}(\hat{r}) [\cos^2 \theta + \sin^2 \theta \sin^2 \phi] \, d\hat{r}^+ \quad (43)$$

where $\phi'$, the angle between the x-axis and the magnetic field, is taken
to be zero; that is, the x-axis is chosen to coincide with the direction of the magnetic field. Again the charge density is expanded in lattice harmonics $Z_{LM}(\vec{r})$ with the coefficients in both Eqs. (41) and (43) being obtained from the APW expansion. The lattice harmonics for the hcp structure are

$$
Z_{00} = Y_{00} \\
Z_{20} = Y_{20} \\
Z_{33} = \frac{1}{\sqrt{2}} (Y_{33} - Y_{3-3}) \\
Z_{40} = Y_{40} \\
Z_{53} = \frac{1}{\sqrt{2}} (Y_{53} - Y_{5-3}) \\
Z_{60} = Y_{60} \\
Z_{66} = \frac{1}{\sqrt{2}} (Y_{66} + Y_{6-6})
$$

where the $Y_{LM}$ are the spherical harmonics. Using the proper expansion coefficients and carrying out the integration in Eqs. (41) and (43), yields the valence contribution to the diamagnetic susceptibility. Finally, by combining the results of Eqs. (37) and (41) or (43), we obtain the total diamagnetic contribution to the susceptibility.

Pauli Spin Susceptibility

Even in the absence of certain orbital contributions to the susceptibility, the intrinsic spin magnetic moment of the electron gives rise
to a spin contribution. In fact, the Pauli spin susceptibility is often the largest contribution to the susceptibility. Although the Pauli susceptibility is not always the dominant contribution in transition metals, it is ordinarily quite large and, therefore, constitutes an important contribution to the total susceptibility in these materials.

To obtain an expression for the Pauli susceptibility in a metal, we consider a system of noninteracting band electrons. The energy of an electron in band \( n \) with wavevector \( \vec{k} \) is denoted \( E_{\vec{n}k^+} \). If we now apply a magnetic field, the spin up and spin down electrons will no longer have the same energy. The energy of a spin up electron becomes

\[
E_{\vec{n}k^+} = E_{\vec{n}k} + \mu_B H
\]

(44)

while that of a spin down electron is now

\[
E_{\vec{n}k^-} = E_{\vec{n}k} - \mu_B H
\]

(45)

Furthermore, the probability for occupancy of the state \( \vec{n}k^+ \) is given by

\[
N_+ = f(E_{\vec{n}k^+}) = \left\{ \exp[\frac{(E_{\vec{n}k^+} - E_F)}{kT}] + 1 \right\}^{-1}
\]

(46)

and similarly for the state \( \vec{n}k^- \), we find

\[
N_- = f(E_{\vec{n}k^-}) = \left\{ \exp[\frac{(E_{\vec{n}k^-} - E_F)}{kT}] + 1 \right\}^{-1}
\]

(47)

The Fermi energy, \( E_F \), in Eqs. (46) and (47) is determined by the total number of electrons \( N \)

\[
N = N_+ + N_- = \sum_{\vec{n}k} [f(E_{\vec{n}k^+}) + f(E_{\vec{n}k^-})]
\]

(48)
Now each spin up (down) electron contributes an amount $-\mu_B \ (+\mu_B)$ to the magnetic moment. Hence, the total magnetic moment is

$$M = -\mu_B N_+ + \mu_B N_- = -\mu_B \sum_{\mathbf{n}\mathbf{k}} \left[ f(E_{\mathbf{n}\mathbf{k}+}) - f(E_{\mathbf{n}\mathbf{k}+}) \right]$$

But

$$\frac{\partial f(E_{\mathbf{n}\mathbf{k}+})}{\partial E_{\mathbf{n}\mathbf{k}+}} = -\delta(E_{\mathbf{n}\mathbf{k}+} - E_F)$$

and so Eq. (49) becomes

$$M = 2\mu_B^2 H \sum_{\mathbf{n}\mathbf{k}} \delta(E_{\mathbf{n}\mathbf{k}+} - E_F)$$

$$= 2\mu_B^2 H N(E_F)$$

where $N(E_F)$ represents the density of states at the Fermi level. Thus, we obtain the following expression for the Pauli spin susceptibility

$$\chi = \frac{\partial M}{\partial H} = 2\mu_B^2 N(E_F) .$$

Unfortunately, Eq. (4) does not yield accurate results in transition metals. To obtain accurate results, we must include electron-electron interactions in our analysis. Since it is impossible (in any practical way) to include these interactions exactly, approximations for the effects of exchange and correlation are introduced.
Exchange enhancement

The exchange interaction is an attractive interaction between parallel spin electrons which results in the enhancement of the Pauli spin susceptibility. Underlying this interaction is nothing but the Pauli exclusion principle. Including exchange, the expressions for the energy of the electrons in the presence of a magnetic field become

\[ E_{n\mathbf{k}^+} = E_{n\mathbf{k}} + \mu_B H - \Delta_+(n\mathbf{k}) \quad (52) \]

and

\[ E_{n\mathbf{k}^-} = E_{n\mathbf{k}} - \mu_B H - \Delta_-(n\mathbf{k}) \quad (53) \]

where \( \Delta_\pm(n\mathbf{k}) \) is the change in exchange energy due to repopulation. In the following discussion, we assume \( \Delta \) is independent of wavevector \( \mathbf{k} \) and band index \( n \). Although not valid in general, this approximation is useful for illustrative purposes.

For plane wave states, the average exchange energy per electron is given by the expression

\[ E_{\text{ex}}(\pm) = \frac{3e^2}{2\pi} k_F(\pm) = 3e^2 \left( \frac{3}{8\pi} \frac{N_{\pm}}{\Omega} \right)^{1/3} . \quad (54) \]

In the above equation, \( N_+ \) (\( N_- \)) represents the occupancy of the spin up (down) states, i.e.,

\[ N_{\pm} = N \int_0^{E_F} N(E)f(E \pm \mu_B H - \Delta_\pm)dE \]
\[
\begin{align*}
N(E) &= \int_0^{E_F + \mu B + \Delta_\pm} N(E) dE \\
&= \frac{1}{2} N_e + N N(E_F)(\tau \mu B + \Delta_\pm) 
\end{align*}
\] (55)

where \( N_e \) = number of electrons
\( N \) = number of atoms
\( N(E_F) \) = density of states per atom (at \( E = E_F \)).

Substitution of Eq. (55) into Eq. (54) gives

\[
E_{ex}^{(\pm)} = 3e^2 \left[ \frac{3 N_e}{8\pi} + \frac{3N}{4\pi\Omega} N(E_F)(\tau \mu B + \Delta_\pm) \right]^{1/3} .
\] (56)

After some manipulation, the above equation reduces to

\[
E_{ex}^{(\pm)} = E_{ex} \left[ 1 + \frac{2}{3} \frac{N(E_F)}{Z} (\tau \mu B + \Delta_\pm) \right]
\] (57)

with

\[
E_{ex} = 3e^2 \left( \frac{3 N_e}{8\pi} \right)^{1/3}
\]

and \( Z \) = number of valence electrons per atom.

Now by definition

\[
\Delta_\pm = E_{ex}^{(\pm)} - E_{ex}
\] (58)

which, with the aid of Eq. (57), becomes

\[
\Delta_\pm = E_{ex} \left[ \frac{2}{3} \frac{N(E_F)}{Z} (\tau \mu B + \Delta_\pm) \right]
\]
where $\lambda$ is defined by the expression

$$
\lambda = \frac{2}{3} \frac{E_{\text{ex}}}{Z} N(E_F)
$$

The quantity $(1 - \lambda)^{-1}$ in Eq. (59) is referred to as the enhancement factor. Upon substitution of Eq. (59) into Eqs. (52) and (53), we obtain the following expressions for the exchange enhanced energy.

$$
E_{nk^+} = E_{nk} + \frac{\mu_{B}^H}{1 - \lambda}
$$

and

$$
E_{nk^-} = E_{nk} - \frac{\mu_{B}^H}{1 - \lambda}
$$

Comparison of Eqs. (60) and (61) with Eqs. (44) and (45) shows that the exchange energy modifies the field by the factor $(1 - \lambda)^{-1}$. Consequently, after an analysis similar to that carried out in the previous section, we find

$$
\chi = \frac{2\mu_{B}^2 N(E_F)}{1 - \lambda}
$$

the usual expression for the exchange enhanced Pauli susceptibility (45,46). It is this equation that is used in calculating the Pauli spin susceptibility. The density of states at the Fermi level, $N(E_F)$, is determined by the tetrahedron method discussed below while the enhancement factor, $(1 - \lambda)^{-1}$, is tabulated by Janak (45) for the 3d and 4d
series of transition metals. In obtaining his results, Janak uses the spin-polarized exchange-correlation functional of von Barth and Hedin (47) and self-consistent nonmagnetic ground-state energy bands and wavefunctions to evaluate the Vosko-Perdew approximate formal solution (48) of the linear response problem.

**Tetrahedron method**

From Eq. (5), we see that any attempt to evaluate the Pauli spin susceptibility involves the calculation of the density of states at the Fermi level

\[ N(E_F) = \frac{2}{(2\pi)^3} \int_{E(k)=E_F} \frac{dS}{|\nabla_k E|} \]  

(62)

This in turn requires that we have at our disposal some method for calculating phase space integrals. Although many different schemes have been proposed (49), central to each of these methods is the same basic procedure. One begins by dividing the Brillouin zone (or its irreducible part) into microzones (e.g., cubes, tetrahedra). Then some sort of approximation to the behavior of the energy eigenvalues throughout the microzone is assumed and finally an integration procedure is adopted to carry out the k-space integration.

The method we employ is based on extensions made by Rath and Freeman (50) to work done by Jepsen and Andersen (51) and Lehmann et al. (52) and Lehmann and Taut (53). In this method, called the analytic tetrahedron linear energy method, or more briefly the tetrahedron method, the irreducible part of the Brillouin zone is divided into
nonoverlapping tetrahedra of arbitrary shape but equal volume. The integral for the density of states, Eq. (62), is approximated by a sum over tetrahedra

\[ N(E) \approx \frac{2\Omega}{(2\pi)^3} \sum_{n_i} \frac{\Delta S_n (E, \vec{k}_i)}{|\nabla E_n (\vec{k}_i)|} \]

where the \( \vec{k}_i \) (\( i = 1,2,3,4 \)) represent the coordinates of the four corners of a tetrahedron. The energy \( E(\vec{k}) \) is linearly expanded inside the tetrahedra, with the coefficients of linear expansion being completely determined by the coordinates of and energies at the corners of the tetrahedra. As a consequence of the linear expansion, the surfaces of constant energy are planes. Because energy gradients do not occur explicitly in this formalism, the tetrahedron method is easy to implement. Furthermore, it gives accurate results for the density of states provided the Brillouin zone is divided into a sufficiently large number of tetrahedra.

Having obtained the density of states, we can now use Eq. (5) together with the appropriate tabulated value of the enhancement factor to evaluate the Pauli spin susceptibility for a given material. Then by adding together spin, diamagnetic and Van Vleck orbital terms, we obtain the total static susceptibility. Finally, we can compare our calculated results to the measured values for a particular material.

In the next chapter, we present the details of the above calculations for the hcp transition metals Sc and Zr.
CHAPTER IV. RESULTS AND DISCUSSION

Bulk Susceptibility for Sc and Zr

In Chapter III, analytic expressions were given for the Van Vleck, diamagnetic and Pauli contributions to the magnetic susceptibility. We will use those expressions in this chapter to evaluate the bulk susceptibility for scandium and zirconium. We begin by reviewing important features of the band structures and densities of states of these materials. The numerical methods used to evaluate the various terms in the susceptibility are then described and finally the calculated results are presented and compared to experimental measurements (5,6). We also briefly discuss an earlier tight-binding calculation (7) of the Van Vleck contribution to the susceptibility and compare the result of the two methods for both Sc and Zr.

Band structure and density of states

Sc and Zr are both transition metals which crystallize in the hexagonal close-packed (hcp) structure. The Brillouin zone for the hcp lattice and its irreducible sector (shaded region) are shown in Fig. 9. Because their structure is hcp, the magnetic susceptibility of these materials is anisotropic; that is, the susceptibility depends on the direction of the magnetic field \( \vec{H} \). As stated in the introduction, it was the unusually large anisotropy observed in measurements of the susceptibility of Zr which provided the motivation for the present study.

To determine the electronic band structures of Zr and Sc, the LAPW method was used. The warped muffin-tin crystal potential was created
Figure 9. First Brillouin zone of hcp lattice. The shaded region is the irreducible sector.
using the overlapping atomic charge density method of Mattheiss (42). The atomic charge densities were obtained from Hartree-Fock-Slater calculations utilizing the full value of the Slater exchange parameter \( \alpha = 1 \) and \( 3d^24s^1 \) and \( 4d^35s^1 \) atomic configurations for Sc and Zr, respectively. The low temperature lattice constants were used throughout the calculations. For Sc, the lattice constants, \( a = 6.2391 \) a.u. and \( c = 9.9316 \) a.u., were determined by Mueller (54), while Goldak et al. (55) measured the values \( a = 6.1026 \) a.u. and \( c = 9.7158 \) a.u. for Zr.

The energy eigenvalues and wavefunctions were evaluated on a 375 point mesh in one-eighth of the Brillouin zone. To generate the mesh points, three nonequivalent (possessing different wavefunctions) irreducible sectors of the Brillouin zone were each divided into 125 equal volume triangular prisms. The eigenvalues and eigenfunctions were computed at the center of mass of each prism and the results were combined to yield the wavefunctions and eigenvalues at 375 k-points in one-eighth of the Brillouin zone. In Fig. 30, we show the projection of the 125 point mesh onto the hexagonal plane. As indicated in the figure, a hexagonal rather than a rectangular coordinate system was employed; that is, each k-point was identified by its coordinates with respect to \( s, t \) and \( z \) axes. Apart from the small differences arising from the different atomic configurations and lattice constants used, the band structures we computed were found to be in agreement with earlier results (56-58).

The energy bands for 125 k points were least squares Fourier fitted with sixty symmetrized plane waves. For the lowest thirteen bands of
Figure 10. Projection of mesh points onto hexagonal plane
both Zr and Sc, the root-mean-square errors in the fitted energy were a few milli-Rydbergs. The resulting fitting coefficients were used in determining the energies at the four corners of 1536 tetrahedra in the irreducible one-twenty-fourth of the Brillouin zone. Subsequently, the tetrahedron method (described in Chapter III) was employed to obtain the density of states and the Fermi energy. The resulting density of states curves of Sc and Zr are shown in Figs. 11 and 12, respectively. The Fermi energy of Sc was found to be 0.4589 Ry corresponding to a density of states of 31.2 states per atom per Rydberg, while for Zr the Fermi energy was found to be 0.5310 Rydbergs corresponding to a density of states of 14.1 states per atom per Rydberg.

Comparison with experiment

With the above information and the analytical expressions of Chapter III at our disposal, we are able to evaluate the various contributions to the susceptibility. To determine the Van Vleck orbital susceptibility, APW wavefunctions and eigenvalues were used in conjunction with the Kubo-Obata formula, Eq. (6)

\[
\chi_i = 2\mu_B^2 \sum_{nn'} \int \frac{d^3 \vec{k}}{(2\pi)^3} \frac{f(E_n(\vec{k}))(1 - f(E_{n'}(\vec{k})))}{E_{n'}(\vec{k}) - E_n(\vec{k})} |\langle n\vec{k}|L_1|n'\vec{k}\rangle|^2.
\]

Equation (6) was evaluated at each of the 375 mesh points described in the previous section and the results were summed to obtain a value for the Van Vleck orbital susceptibility. Then numerical estimates of the diamagnetic contributions were obtained using Eqs. (37), (41) and (43), and finally the exchange enhanced Pauli spin susceptibility was
Figure 11. Density of states of Sc
Figure 12. Density of states of Zr
calculated using Eq. (5)

\[ \chi = \frac{2\mu_B^2 N(E_F)}{1 - \lambda} \]  

(5)

Values of \( N(E_F) \) for Sc and Zr are recorded in the previous section and the enhancement factor, \((1 - \lambda)^{-1}\), is taken as 1.67 for Zr (45) and 4.03 for Sc (59). The Pauli, Van Vleck and diamagnetic contributions to the susceptibility are then added together to obtain an estimate of the bulk susceptibility. It is this sum which is compared to measurements of the susceptibility.

Our calculated results for Sc and Zr are summarized in Table 1. To expedite comparison, measured values of the susceptibilities of Sc and Zr are also presented. From the table, we see that the calculated anisotropies in Sc and Zr are in the same direction while the experimental anisotropies are opposite in direction. In light of the similarities between Sc and Zr, the reversal in the direction of the measured anisotropy is puzzling. Note also that the Pauli susceptibility is dominant in Sc while the Van Vleck contribution is the largest term in the susceptibility of Zr. In both cases, the Van Vleck term is the primary source of anisotropy, although it is substantially more anisotropic in Sc than in Zr. Concerning the diamagnetic contributions, observe that the Landau-Peierls term is essentially isotropic in both Sc and Zr and that taken as a unit the diamagnetic contributions are relatively more important in Zr than in Sc. In the final analysis, we see that for Sc the calculated and measured values of the susceptibility agree quite well with one another. Unfortunately, the same cannot be
Table 1. Calculated and experimental values for the bulk susceptibility in Sc and Zr. $\chi_{||}$ ($\chi_{\perp}$) denotes the susceptibility obtained with the magnetic field $\mathbf{H}$ applied parallel (perpendicular) to the symmetry axis of the crystal. The calculated susceptibility has been decomposed into Pauli, Van Vleck and diamagnetic parts. The experimental results for Sc and Zr are from Spedding and Croat (5) and Collings and Ho (6), respectively.

<table>
<thead>
<tr>
<th>Magnetic Susceptibility</th>
<th>Sc ($10^{-6}$ emu/mole)</th>
<th>Zr ($10^{-6}$ emu/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calculated</td>
<td>$\chi_{</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\chi_{\perp} = 384$</td>
<td>$\chi_{\perp} = 164$</td>
</tr>
<tr>
<td>Experimental</td>
<td>$\chi_{</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\chi_{\perp} = 384$</td>
<td>$\chi_{\perp} = 90$</td>
</tr>
<tr>
<td>Decomposition</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pauli (enhanced)</td>
<td>$\chi = 299$</td>
<td>$\chi = 55.8$</td>
</tr>
<tr>
<td>Van Vleck</td>
<td>$\chi_{</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\chi_{\perp} = 101.5$</td>
<td>$\chi_{\perp} = 135.2$</td>
</tr>
<tr>
<td>Diamagnetic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Core</td>
<td>$\chi = -9.4$</td>
<td>$\chi = -14.8$</td>
</tr>
<tr>
<td>Valence</td>
<td>$\chi_{</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\chi_{\perp} = -7.2$</td>
<td>$\chi_{\perp} = -12.5$</td>
</tr>
</tbody>
</table>
said for Zr. In Zr, the measured susceptibility is highly anisotropic while the calculated susceptibility exhibits only a small anisotropy. Furthermore, the calculated and measured anisotropies are oppositely directed.

**Comparison with tight-binding calculation**

Due to the large discrepancy between the calculated and measured values of the susceptibility in Zr, it was deemed necessary to test the validity of our method. To do so, the Van Vleck orbital susceptibility was determined via an independent method (7) first employed by S. G. Das in the investigation of the electronic and magnetic properties of Sc. To carry out her calculation, Das used the APW method in conjunction with a linear combination of atomic orbitals (LCAO) interpolation scheme. Overlapping charge densities derived from the atomic configuration $3d^{2}4s^{1}$ were superposed to create a warped muffin-tin potential and the full value of the Slater exchange parameter was used to approximate the exchange interaction. According to the interpolation scheme employed by Das, a tight-binding LCAO form for the one electron $s$-, $p$- and $d$-wavefunctions was assumed and the Hamiltonian was parameterized in terms of one- and two-center energy integrals. The energy integrals were determined by obtaining the best fit to the APW eigenvalues at high symmetry points in the Brillouin zone.

As in our method, the Kubo-Obata formula, Eq. (6), was used to evaluate the Van Vleck orbital susceptibility. The matrix elements and corresponding energy denominators were computed at 1331 randomly
generated k-points in one-eighth of the Brillouin zone. To compute the phase space integral, a quadratic interpolation scheme (60), together with Monte Carlo sampling techniques, was employed.

Using the alternative scheme, we evaluated the Van Vleck orbital susceptibility of Zr. The results obtained were in agreement with our earlier calculations and consequently at odds with experiment. In light of our previous results, this calculation indicates the Van Vleck susceptibility is not the source of the large anisotropy observed in the susceptibility of Zr. Unfortunately, we were unable to reproduce Das' results for Sc - the results of our calculation, using the tight-binding code employed by Das, differ by approximately 10% from those reported by Das. However, prior to using the tight-binding code, we discovered and corrected some minor errors involving the orbital matrix elements. Perhaps these corrections account for the discrepancy between the two sets of results.

**Future Directions**

The results of the previous section point to some term, other than the Van Vleck contribution, as the source of the anisotropy in the measured susceptibility of Zr. Hence, it becomes necessary to treat with greater rigor other anisotropic contributions to the susceptibility. For instance, a more careful analysis may reveal a substantial anisotropy in the Landau-Peierls diamagnetic susceptibility. Recall that the Landau-Peierls diamagnetism results from the quantization of the electron motion in the presence of a magnetic
field (19). However, only the motion of electrons in the plane perpendicular to the field direction is quantized. Therefore, in non-cubic crystals, the Landau-Peierls diamagnetic susceptibility need not be symmetric; that is, it may be different in different directions. Whether or not the resulting anisotropy is large enough to account for the observed magnetic behavior of Zr can only be determined by means of a detailed calculation. A procedure for evaluating the generalized orbital susceptibility, including the Landau-Peierls term, is discussed in the Appendix.

There is yet another, previously unmentioned but possibly anisotropic, contribution to the susceptibility of transition metals. This term, which arises from the itinerant nature of the conduction electrons, can be linked to surface integrals over the unit cell boundary. Contrary to our assumption, the conduction electrons are not confined to a single Wigner-Seitz cell, but are free to move throughout the crystal thereby giving rise to intercellular currents and a contribution to $\chi(q)$ near $q = 0$. In effect, the bulk susceptibility is altered while the form factor remains unchanged. Any directional dependence of the intercellular currents will manifest itself as an anisotropy in the susceptibility. To date, the topic of intercellular currents has received very little attention and explicit calculations of the corresponding contribution to the susceptibility do not exist. Shimizu's calculations for bcc transition metals (4) notwithstanding, the intercellular currents (and related surface terms) are usually dismissed as
inconsequential. However, intercellular currents may play an important role in determining the susceptibility of Zr. Consequently, they merit further consideration in future theoretical investigations of the magnetic behavior of Zr.

An alternative explanation for the discrepancy between the calculated and measured susceptibilities of Zr may lie in the necessarily approximate nature of the computational methods employed in this study. For instance, the Van Vleck orbital susceptibility of Zr may in reality be highly anisotropic but, due to the numerous simplifications and approximations involved in our analysis, the large anisotropy remains undetected. Various modifications, however, can be made in order to enhance the accuracy of the results. While certain improvements are very difficult to incorporate, others can be made with only a minimal amount of effort. One aspect of the calculation that can easily be improved concerns the choice of potential. The energy bands and wavefunctions can be refined by using a self-consistent Hedin-Lundquist exchange potential as opposed to the nonself-consistent Slater exchange potential used in this study. The resulting energy bands are expected to be somewhat broader than those corresponding to the nonself-consistent potential and consequently the calculated susceptibility should be slightly reduced. However, we do not anticipate a change in the nature of the results; that is, we do not expect the change in potential to affect the order of magnitude or the direction of the calculated anisotropy.
Further improvement in the results can be achieved by expanding the energy bands to quadratic rather than linear order. The complex nature of the energy bands in transition metals renders linear interpolation inaccurate over all but the narrowest regions of k-space. Since the overall shape as well as the detailed structure of the generalized susceptibility is strongly affected by the energy bands, the bands must be treated as accurately as possible. By using quadratic interpolation, we effectively increase the number of sampling points and thereby the accuracy of the results. Therefore, to minimize errors, future calculations should include quadratic interpolation of the energy bands.

Even more dramatic changes can be induced by including the q-dependent matrix elements in the calculation of the generalized susceptibility. The q-dependent matrix elements play a very important role in determining the form of $\chi(q)$. In fact, the matrix elements, rather than the energy bands, may be responsible for an observed anisotropy in the susceptibility. Hence, any accurate calculation of the susceptibility must include these matrix elements in some suitable form.

Although it is beyond the scope of this study to include the modifications outlined above, the agreement between the calculated and measured susceptibilities of Zr should be substantially improved by incorporating changes of this nature in future calculations.

Summary

The foregoing study was undertaken to acquire a better understanding of the magnetic behavior of paramagnetic transition metals. Of
particular interest were the hcp transition metals Sc and Zr. To achieve our goal, numerical calculations were carried out to determine the bulk susceptibilities of Sc and Zr.

The bulk susceptibility of a material is, in general, composed of several parts. Typically, the largest contributions to the susceptibility of a paramagnetic transition metal are the Van Vleck orbital and Pauli spin terms. Other smaller yet significant contributions are the Landau-Peierls and core diamagnetic terms. In order to better understand the nature of orbital paramagnetism, the calculation of the Van Vleck orbital susceptibility was emphasized in the present study. To evaluate the Van Vleck orbital susceptibility, we used the Kubo-Obata formula, Eq. (6)

\[ \chi_i = \frac{2}{7} \mu_B^2 \sum_{nn'} \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{f(E_n(\mathbf{k})) (1 - f(E_{n'}(\mathbf{k})))}{E_{n'}(\mathbf{k}) - E_n(\mathbf{k})} |\langle n\mathbf{k}|L_i|n'\mathbf{k}\rangle|^2. \tag{6} \]

The energy bands and wavefunctions needed to determine the matrix elements and energy denominators in Eq. (6) were calculated via the LAPW method. Equation (6) was evaluated at 375 different k-points in one-eighth of the Brillouin zone and the resulting contributions were summed to obtain a value for the Van Vleck orbital susceptibility. Then the exchange enhanced Pauli spin susceptibility was estimated using the density of states (determined by the tetrahedron method) in conjunction with a tabulated value of the enhancement factor. Finally, estimates of the diamagnetic contributions were made and the sum of the Pauli, Van Vleck and diamagnetic contributions was computed to obtain
the bulk susceptibility. Our calculations yielded the values $\chi_\parallel = 362 \times 10^{-6}$ emu/mole and $\chi_\perp = 384 \times 10^{-6}$ emu/mole for the susceptibility of Sc and $\chi_\parallel = 159 \times 10^{-6}$ emu/mole and $\chi_\perp = 164 \times 10^{-6}$ emu/mole for Zr. These calculated results were then compared to experimental measurements of the susceptibility. The calculated susceptibility of Sc was found to be in good agreement with the measurements of Spedding and Croat (5). However, for Zr, there is a marked discrepancy between our calculated results and the values measured by Collings and Ho (6). The balance of this study was devoted to the investigation of this discrepancy. Unfortunately, additional calculations failed to resolve the problem. Therefore, further investigation is required to achieve a complete understanding of paramagnetic transition metals (in particular Zr).


APPENDIX

We present here a study of the generalized susceptibility, \( \chi(\vec{q}) \), of Zr metal determined from an APW calculation of the energy band structure. The matrix elements are assumed to be constant throughout the following discussion. Evaluation of \( \chi(\vec{q}) \) is carried out using the tetrahedron method of Rath and Freeman (50).

In the following paragraphs, we discuss the application of the tetrahedron method to the evaluation of the \( \chi(\vec{q}) \) integral. We then illustrate the method with model calculations based on two different band structures: (1) a free electron band and (2) a tight-binding s-band of an hcp crystal. The first model calculation tests the agreement between our numerical results and known analytical results for the susceptibility of a free electron gas, i.e., the Lindhard function. The second calculation is useful in determining the magnetic susceptibility of an hcp crystal as a function of the Fermi energy. After dispensing with the model calculations, we apply the method to the calculation of \( \chi(\vec{q}) \) for Zr metal.

The tetrahedron method and its application to the density of states problem was discussed in Chapter III. We now consider the extensions that must be made in order to evaluate the generalized susceptibility using the tetrahedron method. As in Chapter III, we begin by dividing the Brillouin zone into nonoverlapping tetrahedra and then linearly approximating the energy bands inside each tetrahedron. The fractional volume of a given tetrahedron that contributes to the susceptibility is determined by the intersection of constant energy planes corresponding
to $E_n(k)$ and $E_n(k + q)$. Inside this fractional volume, the product
$f(E_n(k))(1 - f(E_n(k + q)))$ must have the value unity. It can be shown (50)
that the occupied volume corresponding to $f(E_n(k))$ is either a single
tetrahedron or the sum of three tetrahedra. The same statement applies
to the unoccupied volume corresponding to $(1 - f(E_n(k + q)))$. Thus, the
fractional volume of a given tetrahedron contributing to $\chi(q)$ is either
a single tetrahedron or the sum of up to nine tetrahedra. After
accounting for the Fermi factors, we are left with the task of performing
a volume integration over a tetrahedron with a linearized energy denomina­
tor. Upon completion of the integration, we obtain the following expres­
sion for the susceptibility

$$\chi(q) = \frac{\Omega}{(2\pi)^3} \sum_{\text{occ. tets}} \frac{V_i^2}{D_i} \ln \left| \frac{V_1}{V_i} \right| + \frac{V_2^2}{D_2} \ln \left| \frac{V_2}{V_4} \right| + \frac{V_3^2}{D_3} \ln \left| \frac{V_3}{V_4} \right|$$

(A.1)

where $V_i = E_n(k_i + q) - E_n(k_i)$, $i = 1,2,3,4$

$$D_i = \prod_{j \neq i} (V_i - V_j)$$

and

$\Omega = \text{volume of tetrahedron.}$

In the event that some of the $V_i$'s are zero or equal, one must obtain
the appropriate limit of Eq. (A.1).

To test the accuracy of its numerical predictions, we applied the
method described above to a model system for which the results are known;
i.e., a free electron gas. We then compared the numerical results with
the corresponding analytical results, the so-called Lindhard function.
An hcp reciprocal lattice was chosen for the calculation and the mesh was constructed by making sixteen divisions in the Brillouin zone along \( \Gamma - A \) and thirty-two divisions along \( \Gamma - M \). The irreducible Brillouin zone was thus divided into 49,152 tetrahedra. The Fermi wavevector, \( k_F \), was taken to be 0.3162 inverse atomic units, which is approximately 98% of the \( \Gamma - A \) distance and 53% of the \( \Gamma - M \) distance in Zr. The numerical results we obtained are virtually indistinguishable from the analytical results, thereby establishing the applicability of the method.

The second model structure chosen for investigation was a tight-binding s-band of an hcp crystal. To determine the energy dispersion relation in this case, we proceed as for a cubic crystal (61,62), with the notable exception that there are now two atoms per unit cell and consequently, tight-binding orbitals centered on two sites. After a somewhat more complicated analysis, we obtain the following expression for the energy dispersion

\[
E = 2\gamma \left[ \cos(k_x a) + 2 \cos(k_x a/2) \cos(\sqrt{3} k_y a/2) \right] \times \left\{ 1 + 4 \cos(\sqrt{3} k_y a/2) \cos(k_x a/2) + 4 \cos^2(k_x a/2) \right\}^{1/2}
\]

where we have assumed the ideal c/a ratio; that is, c/a = \( \sqrt{8/3} \). \( \gamma \) is a band overlap parameter which was assigned the value 0.0167 Ry. Using the above band structure and the tetrahedron method, we calculated \( \chi(q) \) as a function of Fermi level. As in the free electron case, the irreducible Brillouin zone was divided into 49,152 tetrahedra and \( E(\mathbf{k}) \) and \( E(\mathbf{k}+\mathbf{q}) \) were calculated at the corners of each tetrahedron. The results of this calculation suggest that both the magnitude and
direction of an anisotropy in the susceptibility depend on the Fermi energy.

Although a single tight-binding s-band does not adequately approximate the band structure of a transition metal, the above results are nevertheless encouraging. They indicate that perhaps the most important features of $\chi(q)$ can be related to the band structure and consequently, detailed calculations of the matrix elements may not be necessary. We proceed to evaluate $\chi(q)$ for Zr metal assuming the matrix elements are indeed relatively unimportant and, therefore, can be fixed. The band structure of Zr was determined via the APW calculation described in Chapter IV. Only bands three, four and five were included in the calculation since the susceptibility is largely determined by states at the Fermi level and in Zr only bands three to five cross the Fermi level. The energy bands were fitted with sixty symmetrized plane waves and the resulting fitting coefficients were used in determining the energies at the four corners of 49,152 tetrahedra in the irreducible Brillouin zone. Once again the tetrahedron method was used to evaluate the $\chi(q)$ integral; to obtain a value for $\chi(q)$, it was necessary to perform a sum over all wavevectors in the star of $q$. Unfortunately, our results were not accurate enough in the small $q$ region to allow us to determine a value for the anisotropy. Since any further refinement of the mesh would have been prohibitively expensive, the calculation was redirected along other lines. Unfortunately, this alternative approach also failed to bear fruit and the decision was made to postpone further investigation. Suggestions for future calculations are included in Chapter IV.