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THE STUDY OF $ZrCl$ BY SELF-CONSISTENT BAND CALCULATION

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The study of ZrCl by self-consistent band calculation

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A nonrelativistic self-consistent electronic band structure calculation has been performed on zirconium monochloride using the KKR method. The exchange potential was approximated by the $X\alpha$ method. The compound contains homoatomic layers in the sequence Cl-Zr-Zr-Cl and has the characteristics of a graphite-like two-dimensional metal. We find a substantial charge transfer toward the metallic layers and away from the loosely bonded halogen layer. There is also significant admixture of Zr-d character within the filled Cl-3p bands. The total density of states is in good agreement with the valence band photoemission results.

We have attempted a renormalized atom approximation to determine the relative positions of the bands and to estimate the charge transfer occurring in ZrCl . Unlike in pure metals, charge transfer and hybridization may occur between different atomic species in intermetallic compounds, and the Wigner-Seitz sphere radii are not unique. These complications render the method unsuitable for ZrCl and similar layer compounds.

I. INTRODUCTION

A. Experimental Motivation

Recently, there has been much interest in transition metal compounds exhibiting two dimensional electronic behavior (1-4). These compounds are characterized by alternating layers of metal and nonmetal atoms. The nonmetal atoms form insulating barriers between the metallic planes so that the conductivity within the layers may be more than three orders of magnitude larger than that measured perpendicular to the layers. This may be seen in a rather large number of compounds. Among these are the metallic double layered monohalides, such as ZrCl , ZrBr , ScCl , and HfCl . We shall restrict our attention to zirconium monochloride, ZrCl , which has been found to be stable.

ZrCl was found to be a very unusual metal. It is unusual not only because it is a halide rich metal, but also because of its crystal structure. Upon synthesis, the phase occurs as small shiny black platelets with a graphite-like character. Each platelet is a single crystal with a characteristic size on the order of .1 mm. Each crystallite is constructed from a parallel array of weakly bound sheets. This helps to explain its easy cleavage and its tendency toward polycrystallinity. Within each sheet is four tightly bound homoatomic layers of atoms in the sequence: Cl-Zr-Zr-Cl . This is in accord with its high thermal stability. Its melting point is above 1100°C . The magnetic susceptibility has been measured and found to be essentially independent of

temperature (5). Expressed in units of 10^{-6} emu/mole, its value at 300°K is 97, while at 50°K, it is 102. The evidence that the compound is metallic comes from x-ray photoelectron spectra (XPS) results (4). It revealed a nonvanishing density of occupied states at the Fermi level which has been identified as the Zr (4d) valence band. Several core energy levels were reported and it is interesting to note that the distinct contributions from the Cl (3p) electrons were found to lie 5 eV below that of Zr (4d).

Although the compound is virtually a powder, a single crystallite was reported (2) to measure $4 \times 4 \times .1$ mm as compared to the usually encountered sizes of $.1 \times .1 \times .02$ mm. This single crystal has provided further evidence into the compound's two dimensional character. Across this platelet, electrical conductivity measurements were reported to be about $1.5 \times 10^{-3} \text{ (ohm-cm)}^{-1}$ normal to the layers and about 55 (ohm-cm)^{-1} within the layers. Unfortunately, a crystal of this size is extremely difficult to grow. This has prevented many experiments which require crystals of a suitable size from being performed. These would include reflection experiments which would reveal information about the allowed optical transitions, as well as de Haas-van Alphen experiments which would locate extremal portions of the Fermi surface.

Nevertheless, further experiments of a different sort have been performed. These have been concerned with how the compound reacts with other materials. Since the compound is layered, intercalation experiments similar to those for the layered transition metal disulfides (6), have been attempted. These experiments yielded negative results based upon

detecting neither swelling nor changes in the lattice parameters. Reactants tested included NH_3 , N_2H_4 , I_2 , and pypidine. Yet, the compound readily reacts reversibly with hydrogen to form some rather interesting hydride phases (7,8,9). Principal phases are $\text{ZrClH}_{.5}$ and ZrClH , i.e., the hemi-hydride and monohydride respectively. Both are thermodynamically stable with respect to isothermal disproportionation into binary halides and hydrides. The nature of the reactions suggests here that a separate phase forms rather than a smoothly varying nonstoichiometric interstitial product.

Nuclear magnetic resonance, NMR, spectra have been taken on these hydrides (8,9). The results suggest that the positions of the hydrogen lie at sites within the metallic bilayer that are tetrahedrally coordinated with the Zr atoms. Here, the Knight shift is quite interesting. It reflects the symmetry of the environment at the site of the nuclear spin as well as providing a measure of the magnetic shielding of the nuclear site by the conduction electrons from the externally applied magnetic field. The magnetic shielding can be described by an axially symmetric Knight shift tensor. The isotropic part is nearly that of pure water, while the anisotropic part has a record breaking value of 102 ppm. Contrasting with ZrCl , the previously largest hydrogen magnetic shielding anisotropy was 44 ppm for KHF_2 (9,10). This anisotropy is interesting for at least two reasons. The first is that it exists, because tetrahedrally coordinated sites often have higher symmetry, e.g., cubic, forcing the anisotropy to vanish as is the case with most metals containing hydrogen. But in ZrClH the tetrahedral sites have only C_{3v} symmetry when regions

slightly beyond the four vertices of the Zr tetrahedron are considered. The conduction electrons are sufficiently constrained along the metallic bilayer so as to be unable to raise the symmetry at the tetrahedral site. Secondly, the magnitude is interesting. The magnetic shielding at the hydrogen sites is greater when the applied field is perpendicular to the layers than when the field is directed along a direction within the layers. This results from having available a larger current which circulates and shields the proton from the applied field. This further demonstrates the compound's two dimensional character.

The existence of these metallic double layered monohalides have generated many questions. We shall be concerned with those requiring an explanation of the metallic properties. These structures offer extreme conditions to test the calculations of their electronic behavior. Approximations which are valid for compact pure metals should provide reasonable descriptions within the tightly bound adjacent metallic layers, i.e., a delocalization of charge. This is contrasted by the weak attraction between the chlorine layers where a significant deficiency of charge is most likely to occur, and the metallic approximations may be less applicable. Also there are questions concerning the role of the core states in the binding of the crystal. These effects are seen through the chemical shifts in electron photoemission spectra.

To address these questions, we have performed a nonrelativistic self-consistent electronic structure calculation for a single representative compound, ZrCl . Since the elements involved are light, any relativistic corrections are small. Self-consistency was necessary to

determine whether the model would provide a reasonable description of the structure and reveal any effects caused by the redistribution of charge. Since self-consistency is, in fact, unnecessary when discussing trends in the electronic behavior for a number of related compounds, our prototype calculation will also provide a useful aid with interpreting the nonself-consistent results for these other compounds.

B. Crystal Structure

Figures 1 and 2 help to visualize the crystal structure of ZrCl . Figure 1 is a projection onto a plane perpendicular to the layers (010). The z axis (001) is normal to the layers. The stacking order of the atomic layers is /abca/bcab/cabc/ so that every third sheet is identical. The open and filled circles correspond to atoms that are located at different distances from the projection plane. The separation between the sheets is $8.87 \text{ \AA}$, and the thickness of a sheet which corresponds to the minimal distance between two chlorine atoms lying on opposing sides of a metal bilayer is $5.83 \text{ \AA}$. Figure 2 is a projection onto a plane parallel with the layers (001). Each layer of atoms has hexagonal structure, so that each Zr atom has three nearest neighbors in an adjacent plane and six neighbors in the same plane.

The bravais lattice is trigonal and the point group of the symmorphic space group is $D_{3d}(\bar{R}3m)$. To see this, we have chosen our primitive lattice translation vectors different from that of the usual trigonal set. They are $\bar{a}_1$ and $\bar{a}_2$ which lie within the layers as shown in Figure 2 and $\bar{a}_3$ which has a component normal to the layers as shown

Figure 1. Projection of the ZrCl structure on the (010) plane. Open circles correspond to atoms with $y = 0$; filled circles correspond to atoms with $y = a/2$

Figure 2. Projection of one sheet of the ZrCl structure on the (001) plane. The solid and shaded circles differentiate between atoms in the two metal layers

in Figure 1. The magnitude of three translations, i.e., lattice constants, are $|\bar{a}_1| = |\bar{a}_2| = 3.43 \text{ \AA}$, and $|\bar{a}_3| = 9.09 \text{ \AA}$. The unit cell is $90.39 \text{ \AA}^3$ in volume and contains four atoms. The nearest neighbor distances or bond lengths are $3.09 \text{ \AA}$ for Zr-Zr, $2.63 \text{ \AA}$ for Zr-Cl, and $3.61 \text{ \AA}$ for Cl-Cl. The Zr-Zr nearest neighbor distance may be compared with that of pure Zr metal which has a value of $3.19 \text{ \AA}$, so that the zirconium atoms are closer by $.1 \text{ \AA}$ in ZrCl.

Recalling the results suggested by the NMR experiments, the tetrahedral sites populated by the hydrogen are located in two equivalent positions. These are designated by '+' in Figure 1. One is directly above a Zr(1) atom and surrounded by the three nearest Zr(2) atoms, and the other is directly below a Zr(2) atom and surrounded by the three nearest Zr(1) atoms.

There are two more interstitial positions which shall be considered. They are important for improving our calculation; their significance is discussed in section 2. The first is located midway between two chlorine atoms, one on either side of the metallic bilayer. This is designated by a ' Δ ' shown in Figure 1. It is also a site occupied by the hydrogen (NMR), but with much smaller probability than the tetrahedral sites. This site is referred to as E1. The second position is located between adjacent chlorine layers and is always unoccupied. In Figure 1, it is midway between two Zr atoms shown by the dotted line and midway between the two Cl atoms shown by the dashed line. In Figure 2, this position will appear to be congruent with the Zr(2) positions. This site is referred to as E2. Both, E1 and E2 occur only once in the unit cell.

II. FORMULATION

While studying the physical properties of crystalline solids, we are led to the rather formidable quantum mechanical many body problem of determining the wavefunctions of all the electrons in the crystal. To make any reasonable progress, it is necessary to utilize approximations that reduce the overwhelming difficulty of this problem. This involves neglecting and modifying certain interactions whose effects, although observable, are in some sense small. These neglected effects include a wealth of so called low energy elementary excitations. Electron-electron correlation is necessary in describing such cooperative phenomenon as magnetism in metals. The electron-phonon interaction is necessary for understanding superconductivity. If the approximations are not too severe, we may expect a good estimate of those neglected effects by making suitable corrections.

The most important approximation is contained in the one electron model. It reduces the many electron problem to that of a single electron moving in an effective crystal potential due to the remaining electrons and nuclei. This reduction is accomplished in the spirit of the Hartree-Fock approximation, HFA, which assumes a single Slater determinant wavefunction for the electrons (11,12). Each wavefunction sees its own distinct potential and each potential depends upon all the wavefunctions. This type of potential is an operator and is nonlocal. This makes an extremely difficult problem to solve for any system involving more than a single atom (13,14). Slater simplified this problem by

making a local approximation, by assuming that the potential only depends upon the local charge density (15), $V(\rho)$, where the density is given by

$$\rho(\bar{x}) = \sum_{\text{occupied}} |\psi(\bar{x})|^2 .$$

His approximation has been very successful for single atoms as well as for an entire array of atoms. His work has been generalized (16-19) by other workers but they still make use of the local approximation. This resulting single particle Schrodinger's equation (SE) has the form

$$(-\nabla^2 + V(\bar{x}))\psi(\bar{x}) = E \psi(\bar{x}) .$$

where the potential V and the wavefunction ψ contain the symmetry of the crystal, and the energy eigenvalue E is expressed in Rydbergs.

One may consider the crystal lattice as being formed by bringing isolated free atoms together and allowing their electron clouds to overlap and interact. The core electrons remain intact, while those orbitals of higher energy which have an appreciable density in the vicinity of neighboring atoms, see a competing periodic potential and become delocalized by forming conduction bands. This describes, in some manner, only the s, p and d metals. Metals which involve localized f electrons with energies comparable to those in the conduction bands further complicate this picture and will not be considered in this work.

For the crystal problem we may simplify the periodic potential further with the muffin-tin approximation (MTA). This saves much labor in solving SE and gives most often excellent results. With the MTA the

unit cell contains a set of nonoverlapping spheres, one about each ion. Within each sphere the potential is assumed to be spherically symmetric, i.e., $V(|\bar{x}|)$, but uniform and constant between the spheres. It is discontinuous across the sphere boundary. This is a reasonable approximation for the potential when the structure is compact so that the volume outside the spheres is relatively small. But when the structure is not compact, the approximation may be poor because the charge density may become localized and directed between the atoms. ZrCl is not compact because of its close metallic bilayer but loose halogen bilayer.

To improve the model of the potential, two methods are commonly used. The first is warping (20,21) which adds a correction to the muffin-tin potential to account for the nonuniform part of the interstitial potential. Usually the energy eigenvalues are not affected very much, whereas the distribution of the bonding charges is affected (22). This method was not used in our study because it is very time-consuming to apply in conjunction with the KKR method. We used the second method which involves the insertion of more spheres (23). These added interstitial spheres lie between those spheres which surround ions. They also contain a spherically symmetric potential but have no nucleus. Besides improving the representation of the crystal potential, the interstitial spheres may be viewed as simple probes in detecting charge transfers in the interstitial environment.

Upon solving Schrodinger's equation, we find that a charge is deposited within the spheres. This charge is seen to vary with

dampened oscillations between successive iterations until convergence is achieved. In our case two interstitial spheres were inserted, one within the metallic bilayer (E1) and one within the halogen bilayer (E2). The volume of E2 was six times larger than E1, so that the total volume contained in the spheres increased from 45% to 60% with their inclusion. The radii of the muffin-tin spheres were chosen to be 1.532 Å for Zr, 1.086 Å for Cl, .770 Å for E1, and 1.395 Å for E2. The radii are restricted by the nearest neighbor distances and are unique only for elemental solids. The radius for Zr was determined first, then Cl, and finally E1 and E2. The actual radii used were chosen to lie on the logarithmic largest radial (24) grid point that was smaller than the calculated radii.

A. Self-Consistent Procedure

Under Slater's approximation to the Hartree-Fock equations, the crystal potential is separable into three terms.

$$V = V_N + V_H + V_X \quad (2.1)$$

V_N describes the interaction between the single electron and all the nuclei in the solid. It is given by

$$V_N(\vec{x}) = - \sum_{s,j} \frac{Z_j e^2}{|\vec{x} - \vec{b}_j - \vec{r}_s|} \quad (2.2)$$

where Z_j is the atomic number of the j -th basis atom located at $\vec{b}_j$ within the unit cell, and s indexes all the real lattice translation vectors.

V_H is the Hartree potential which is the electrostatic potential of the charge distribution of all the electrons and is given by

$$V_H(\bar{x}) = e^2 \int d\bar{x}' \frac{\rho(\bar{x}')}{|\bar{x} - \bar{x}'|} \quad (2.3)$$

Together, V_H and V_N , is the coulomb potential, V_C . The exchange potential V_X , which corrects for the self energy term in the Hartree potential, is given by

$$V_X(\bar{x}) = -3e^2 \alpha \left(\frac{3}{8\pi} \right)^{1/3} \rho(\bar{x})^{1/3}, \quad (2.4)$$

where α is Slater's famous exchange parameter. The α is different for each element and is adjustable to help account for correlation effects between electrons of different spin. It varies between $\frac{2}{3}$ and 1, and was .7 for Zr, .72 for Cl, and .71 for E1, E2, and the interstitial region. The values of α for the atoms are determined by comparing the total energy of a neutral atom configuration using Slater's exchange with that of a configurationally averaged Hartree-Fock calculation. The values are tabulated (14,25,26) and are quite stable with respect to differing configurations. The value of α used in the interstitial region, E1, and E2, is an average of the α used for the atoms. Because ZrCl is a paramagnetic metal, the spin up and spin down states are degenerate, so all spin indices have been suppressed.

In order to get accurate eigenvalues, it is necessary that the SE be solved self-consistently. Usually several iterations are required to achieve a convergent crystal charge density. To provide a starting

estimate of the crystal charge density, it is customary (27) to overlap the atomic charge densities from isolated free atoms with configurations most likely to occur in the solid. We used ground state neutral atom configurations with Zr as the $4d^2 5s^2$ transition metal and Cl as the $3p^5$ halogen. The overlapping procedure made use of the Löwdin alpha expansion (28) to superpose the atomic charge densities from the five nearest neighboring shells of atoms and yields a spherically averaged crystal charge density within the muffin-tin spheres. Averaging out the angular dependence in the charge density has relatively little effect on the energy eigenvalues and is convenient in the self-consistent procedure for constructing the crystal potential.

This model charge distribution does not automatically lead to the muffin-tin potential. The MTA must be made at each step of the procedure. But, before discussing the actual construction of the potential, recall again that we must iterate toward self-consistency. The overlapped charge density is used to construct a "first" crystal muffin-tin potential. Schrodinger's equation is then solved. The solutions or wavefunctions have the form

$$\psi_j(\bar{x}) = \sum_{\ell=0}^{\ell_{\max}} \sum_{m=-\ell}^{\ell} C_{j\ell m}(\bar{k}, E) R_{j\ell}(|\bar{x} - \bar{b}_j|) Y_{\ell m}(\bar{x} - \bar{b}_j) \quad (2.5)$$

where $\bar{x}$ is inside the j -th sphere centered at $\bar{b}_j$, $Y_{\ell m}$ are the unit normalized spherical harmonics, $C_{j\ell m}$ are the coefficients solving the crystal eigenvalue problem, and $R_{j\ell}$ are the regular functions satisfying

$$\left(-\frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} + \frac{l(l+1)}{r^2} + v_j(r) - E \right) R_{jl}(r) = 0 \quad (2.6)$$

From the solutions an updated charge density is constructed, spherically averaged, and then used to construct the potential for the next iteration.

Along with any iterative procedure comes the question and nature of the convergence. Hopefully the system is suitably stable to allow the initial estimates to relax toward the true solution within a few iterations. But often the system or calculation over corrects its inputs and then solutions are known to oscillate with each iteration. In our case this physically means that some small amount of charge is moving in and out of the muffin-tin spheres. In an effort to critically dampen these oscillations, a so-called mixing parameter γ , is used. It mixes some fraction of the charge density found by the calculation with that used for the input of the same iteration. This mixture is used to start the next iteration and may be expressed as

$$\rho_{j+1}^{\text{in}} = \gamma \rho_j^{\text{out}} + (1 - \gamma) \rho_j^{\text{in}}$$

where j indexes the iteration sequence. Unlike many atomic calculations where γ is increased toward 50% to accelerate convergence as the fixed point or solution is approached, it has been found that a constant value of γ on the order of 25% gives very good results (29), where few iterations were required to achieve self-consistency. Our γ value was 30%.

Now consider the problem of constructing a crystal muffin-tin potential from a crystal charge density, that is assumed to be

spherically symmetric, in a self-consistent manner. Since the coulomb term of the crystal potential must satisfy Poisson's equation within the spheres, it is given by

$$V_C(r_j) = -e^2 \left[\frac{Z}{r_j} - \frac{1}{r_j} \int_0^{r_j} dr 4\pi r^2 \rho(r) - \int_0^{R_j} dr 4\pi r \rho(r) + C_j \right] \quad (2.7)$$

where R_j is the radius of the j -th sphere, and C_j is the integration constant which is due to the spherical average potential from all the other muffin-tin spheres. Only the C_j remain to be evaluated. This problem was first addressed by De Cicco (30,31), who recognized that it could be made equivalent to Madelung's problem with x-ray diffraction studies.

De Cicco's approach was to consider an auxiliary potential, V_E , the so-called Ewald potential (32), arising from a lattice of point charges q_j , one at each atomic site, and a uniform background charge density, $-\bar{q}$, to guarantee neutrality. By solving Poisson's equation, the Ewald potential is found to be

$$V_E(\vec{x}) = \sum_j q_j \left[\frac{4\pi}{\Omega} \sum_n' \frac{e^{i\vec{K}_n \cdot (\vec{x} - \vec{b}_j) - K_n^2/4\epsilon^2}}{K_n^2} + \sum_s \frac{\text{erfc}(\epsilon |\vec{x} - \vec{b}_j - \vec{r}_s|)}{|\vec{x} - \vec{b}_j - \vec{r}_s|} - \frac{\pi}{\Omega \epsilon^2} \right] \quad (2.8)$$

where n and s index the reciprocal and real lattices respectively, erfc is the coerror function (33), and ϵ is an arbitrary positive parameter which is necessary for convergence of the finite sums. The Ewald potential is independent of ϵ . The primed summation excludes the singular term.

If V_E is put into muffin-tin form, then V_E and V_C must agree in the inner surface of each sphere. We now wish to put Equation (2.8) into muffin-tin form. The spherically symmetric average of the Ewald potential is

$$-V_E(r_j) = e^2 \left[\frac{2\pi}{3} \bar{q} r_j^2 + \frac{q_j}{r_j} + A_j \right] \quad (2.9)$$

where A_j is a constant that is determined by equating Equation (2.8) and (2.9) in the limit as $\bar{x}_j \rightarrow \bar{b}_j$ in the j -th sphere.

$$A_i = \sum_j q_j \left[\frac{4\pi}{\Omega} \sum_n' \frac{e^{i\bar{K}_n \cdot (\bar{a}_i - \bar{a}_j) - K_n^2/4\epsilon^2}}{K_n^2} + \sum_s' \frac{\text{erfc}(\epsilon |\bar{r}_s + \bar{a}_i - \bar{a}_j|)}{|\bar{r}_s + \bar{a}_i - \bar{a}_j|} - \frac{\pi}{\Omega \epsilon^2} - \delta_{ij} \frac{2\epsilon}{\sqrt{\pi}} \right] \quad (2.10)$$

Now the C_j for the true crystal coulomb muffin-tin potential is obtained by equating Equations (2.7) and (2.9) on the muffin-tin surface. The interstitial Ewald muffin-tin potential is determined by observing that the average of V_E over the entire unit cell is zero. This can be seen by letting $\epsilon \rightarrow \infty$ in Equation (2.8). Then, the interstitial Ewald muffin-tin potential, which is equal to the interstitial crystal muffin-tin potential, is determined by integrating only over the spheres. We have now obtained a muffin-tin crystal potential from an arbitrary muffin-tin charge density.

B. The KKR Method

The KKR method (34-37) is just one of several methods of solving Schrodinger's equation in a periodic system. It is quite popular because of its rapid convergence and accuracy. Since there are several excellent reviews (11,38-41), only a brief presentation will be given. The method used in this work follows from that originally proposed by Korringa (34) and Kohn and Rostoker (35). Full use is made of the Ewald summation (36) procedure for evaluating the expansion coefficients of the Greens function, as well as Ham and Segall's (37) method of handling compounds. The final formulas have been presented by Myron (41).

The KKR method makes use of the so-called Green's function G , satisfying

$$(\nabla^2 + E)G(\bar{k}, E, \bar{x}_1 - \bar{x}_2) = \delta(\bar{x}_1 - \bar{x}_2) \quad (2.11)$$

to express SE as an integral equation,

$$\psi(\bar{k}, E, \bar{x}_1) = \int_{\Omega_2} d\bar{x}_2 G(\bar{k}, E, \bar{x}_1 - \bar{x}_2) V(\bar{x}_2) \psi(\bar{k}, E, \bar{x}_2) \quad (2.12)$$

where $\bar{k}$ is the wavevector of the solution. The wavefunction satisfies Bloch's theorem as a boundary condition. This also makes G satisfy Bloch's theorem which can be seen from its representation

$$G(\bar{k}, E, \bar{x}_1 - \bar{x}_2) = -\frac{1}{\Omega} \sum_n \frac{e^{i(\bar{K}_n + \bar{k}) \cdot (\bar{x}_1 - \bar{x}_2)}}{(\bar{K}_n + \bar{k})^2 - E} \quad (2.13)$$

Equation (2.12) is now solved variationally. A variational functional Λ is defined by

$$\Lambda = \int_{\Omega_1} d\bar{x}_1 \psi(\bar{x}_1) V(\bar{x}_1) \left[\psi(\bar{x}_1) - \int_{\Omega_2} G(\bar{x}_1 - \bar{x}_2) V(\bar{x}_2) \psi(\bar{x}_2) d\bar{x}_2 \right] \quad (2.14)$$

so that $\delta\Lambda = 0$, Equation (2.12) is recovered. Within the spheres, the trial wavefunctions are expanded according to Equation (2.5). The variational then has the form

$$\Lambda = \sum_{ij} C_i \Lambda_{ij} C_j \quad (2.15)$$

so that a nontrivial solution to Schrodinger's equation is given by

$$\det|\Lambda_{ij}| = 0$$

While all the matrix elements Λ_{ij} depend upon E and $\bar{k}$, the dependence upon the potential enters only in the diagonal matrix elements through the logarithmic derivatives, L_ℓ where

$$L_\ell = \left. \frac{d}{dr} \ln R_\ell(E, r) \right|_{r_{mt}}$$

In practice, a wavevector is chosen and the energy is varied incrementally. For each E , Λ_{ij} is diagonalized so that whenever an eigenvalue exists, a root of Λ_{ij} vanishes. This determines the dispersion relations, $E(\bar{k})$ or bands, while the wavefunctions are determined by finding the appropriate eigenvector of the Λ_{ij} matrix (42).

III. RESULTS

A. Band, DOS, Charge Distributions

ZrCl crystallizes with a D_{3d} point group. Shown in Figure 3 is the Brillouin zone for the rhombohedral lattice. The irreducible piece (1Z) or 1/12 of the Brillouin zone is outlined by the dashed lines. The eigenvalues and eigenfunctions were calculated on a grid of 57 k-points or wavevectors reasonably spaced within the 1Z. Figure 4 shows how the 1Z was partitioned into four layers, while Figure 5 shows how the k-points are distributed on each layer as designated by the dots. Layers one and four appear partially covered to prevent double counting due to symmetry. The lined grid equally partitions each edge of the layers.

In the evaluation of the expansion coefficients of the Green's function, the real and reciprocal lattice sums were truncated to 87 and 101 terms respectively. The Ewald parameter used for convergence was 0.4. The matrix elements were calculated within an accuracy of 10^{-5} Ry⁻¹. The criterion of convergence was that the total charge deposited in a sphere differ by less than .01 electrons between successive iterations. This was satisfied within fifteen iterations. Eleven eigenvalues were determined at each k-point to within ± 1 mRy.

Figure 6 shows the bands along certain symmetry directions in the zone for the last iteration. The Fermi level is located at the zero of the energy. The degeneracy at the Fermi level shows the compound to be a metal. Along Λ , the bands are generally flatter than along Δ . This reveals that there is greater electron delocalization and stronger

 $R\bar{3}m$

Figure 3. Brillouin zone of $ZrCl$. The irreducible piece of the Brillouin zone is outlined by the dashed lines

Figure 4. Layers showing the partitioning of the irreducible piece of the Brillouin zone

Figure 5. Distribution of k -points on the layers of the irreducible piece of the Brillouin zone

Figure 6. Self-consistent band structure of ZrCl

metallic binding occurring within the layers than perpendicular to the layers. So, we would expect the conductivity between the sheets to be much smaller than that along the sheets.

Again, because of the negligible dispersion along Λ near the Fermi level, the Fermi surface may be seen to form a long thin cylinder perpendicular to the sheets with Λ as its axis. This is only a qualitative estimate because nonmuffin-tin effects, as well as relativistic effects may, in fact, bring down the 10-th band at X. Then an extra band crossing near the zone boundary, could make the Fermi surface exhibit an interesting geometry.

Also shown in Figure 6 are the Cl-3s core states which lie at -16 eV below the Fermi level. These bottom two bands were determined for the sake of comparison with the XPS results shown in Figure 9. The core states were recalculated at each step of the iteration and any core charge lying outside the spheres, was placed in the interstitial region as opposed to renormalizing the core.

Figures 7 and 8 show the total density of states (DOS), as well as its angular momentum decomposition. Again, the Fermi level is zero. The calculated energy bands were fitted by least squares method to a Fourier series which was truncated after the first 23 symmetrized plane waves. The Fourier coefficients were used to evaluate the bands at arbitrary points in the Brillouin zone for use in calculating the DOS by the tetrahedron method (43-45). The root mean square error of the fitted bands was within a few milli-Rydbergs.

Figure 7. Density of states of ZrCl using the linear tetrahedron method.

Figure 8. Total density of states and angular momentum resolved density of states

Figure 7 shows the DOS as calculated by the tetrahedron method. At the top of Figure 8, there are two DOS curves. These have been smoothed by the spline fitting procedure devised by Kopp (46). The larger curve integrates to the total charge in the bands, i.e., 22 electrons. The smaller curve integrates to the charge in the spheres so that the difference is the interstitial charge. Below these two curves are the angular resolved DOS which integrate to the charge within the spheres due to the bands in that energy region. Table 1 lists the net charges contained by the angular resolved DOS in the appropriate energy range. Note that the third column of Table 1 involves energies across the Fermi level and includes the charge of the unoccupied bands above the Fermi level.

The states within the energies between -6 eV and -3 eV are shown to be predominately Cl-3p character (3.35 electrons) within the chlorine sphere along with significant Zr-4d character (.6 electrons) within the zirconium spheres. Wavefunctions giving rise to a charge density in these two spheres, are of the form necessary to explain the high thermal stability of ZrCl. There is a net lowering of energy due to the interaction between the Zr and Cl atoms.

The remaining states above -2.5 eV shown are predominately of Zr-4d character. The contribution from E1 may be associated with a rather uniform charge density within the layer. This is in accord with the delocalization of the Zr valence electrons to the metallic binding. The contributions from E2 shows that there is a very small quantity of charge found to lie between the adjacent chlorine layers. Associating

Table 1. Muffin-tin charges within manifolds for ZrCl

	-6 eV < E < -3 eV	-3 eV < E < -1.6 eV	-1.6 eV < E < 1.25 eV
Zr-s	.172	.046	.102
p	.115	.064	.203
d	.604	.468	2.551
Cl-s	.018	.001	.005
p	3.347	.095	.244
d	.008	.005	.032
E1-s	.026	.169	.031
p	.005	.001	.057
E2-s	.105	.004	.008
p	.149	.007	.022

charge with binding, this is an approximate explanation of the easy cleavage of ZrCl.

The magnitude of the DOS is very sensitive to the placement of the Fermi energy. Its value is $.5 \text{ (eV-cell)}^{-1}$ at the Fermi level. The Pauli spin susceptibility then has a value near $8 \times 10^{-6} \text{ emu/mole ZrCl}$. This is much smaller than the measured total magnetic susceptibility on ZrCl powder, i.e., $97 \times 10^{-6} \text{ emu/mole}$. The difference arises from orbital contributions. This may be clarified further by investigating the anisotropy in the susceptibility when suitably sized crystals are grown. Nevertheless a very good estimate of the orbital contribution may be formed when the polarization of the states of the system is considered. This is given by the Van Vleck susceptibility.

$$\chi = 2\mu_B^2 \sum_{\substack{nn' \\ n < n'}} \frac{|\langle n | L_z | n' \rangle|^2}{(E_{n'} - E_n)} (f_n - f_{n'})$$

where μ_B is the Bohr magneton, n indexes the band states, and f is the Fermi function which determines whether the band state is an occupied ground state or an unoccupied excited state. The crystal field with the hexagonal symmetry of the layers, removes the degeneracy of the wavefunction which has predominately Zr-4d character, and gives a non-vanishing matrix element to the Van Vleck susceptibility. From Figure 8, the energy difference between the states split near the Fermi level is about 1.6 eV. This provides an estimate of $70 \times 10^{-6} \text{ emu/mole ZrCl}$ for the orbital magnetic susceptibility. This is exactly the order of magnitude necessary to understand the size of the measured susceptibility.

Figure 9 compares the x-ray photoelectron spectra (solid line) of the valence region with the calculated DOS (dashed line) of the final iteration. There is good agreement with the predominately Zr-4d states. The set of states associated mainly with the Cl-3p electrons is high by 2 eV. Correspondence is made by neglecting the optical matrix elements in the DOS. To improve the comparison with the spectra, the gap between the chlorine and zirconium states may be increased most simply by increasing the value of Slater's exchange parameter, α , for the Cl atoms while decreasing it for the Zr atoms, because the exchange is an attractive potential. The calculated Cl-3s states, shown in Figure 6, is also high by 2 eV compared with the XPS results.

Tables 2 and 3 compare the placement of the core energies with respect to the Fermi level for several iterations. Also listed are the core energies resulting from atomic calculations using both, the Slater $X\alpha$ method and the configurationally averaged Hartree-Fock method (14), (HF). The energies are listed in Rydbergs. The $X\alpha$ core energies were found to lie above the HF core energies. So, using the HF as a standard, we may expect the core energies from the band calculation, which uses the $X\alpha$ method, to lie rather high.

Table 4 compares some results for a few iterations. The first result is the total charge in the spheres at the start of each iteration. For iteration 1, this is just due to the overlapping of atomic charge densities. Consideration of the first and last iteration reveals that Zr lost $.09 e^-$, Cl gained $.16 e^-$, E1 gained $.02 e^-$, and E2 lost $.48 e^-$. This further confirms our ideas of the two dimensional metallic bonding.

Figure 9. Comparison between x-ray photoelectron spectra (solid line) and total density of states from self-consistent band calculation (broken line)

Table 2. Comparison of zirconium core energies for the Hartree-Fock, Slater $X\alpha$, and muffin-tin potentials. The core energies for the muffin-tin potentials is given with respect to the Fermi level

	Atom HF (Mann)	Atom $\alpha=.70$ (Slater)	Iteration			
			1	2	3	15
1S	-1301.420	-1279.68	-1279.21	-1279.207	-1279.22	-1279.22
2S	-182.768	-174.78	-174.315	-174.312	-174.325	-174.328
2P	-166.970	-160.36	-159.89	-159.889	-159.902	-159.905
3S	-32.123	-28.579	-29.112	-28.110	-28.121	-28.126
3P	-26.053	-23.147	-22.679	-22.677	-22.289	-22.694
3D	-15.045	-13.198	-12.730	-12.728	-12.740	-12.744
4S	-4.849	-3.882	-3.4553	-3.4515	-3.457	-3.458
4P	-2.985	-2.414	-2.001	-1.9973	-2.002	-2.002

Table 3. Comparison of chlorine core energies for the Hartree-Fock, Slater $X\alpha$, and muffin-tin potentials. The core energies for the muffin-tin potentials is given with respect to the Fermi level

	Atom HF (Mann)	Atom $\alpha=.72$ (Slater)	Iteration			
			1	2	3	15
1S	-209.768	-201.488	-201.059	-200.005	-200.941	-200.948
2S	-21.215	-18.600	-18.176	-18.133	-18.090	-18.194
2P	-16.144	-14.308	-13.883	-13.838	-13.794	-13.798
3S	-2.1458	-1.574	-1.180	-1.177	-1.161	-1.171

Table 4. Results of the ZrCl band calculation for a few representative iterations

Iteration	1	2	3	14	15
Total charge in the spheres at the start of each iteration:					
Zr	38.821	38.813	38.788	38.729	38.731
Cl	15.055	15.120	15.171	15.224	15.220
(Zr-Zr) E1	.217	.227	.235	.251	.251
(Cl-Cl) E2	.758	.618	.512	.278	.278
Interstitial	5.272	5.290	5.335	5.566	5.568
Total charge in the spheres from the band calculation:					
Zr	2.874	2.810	2.834	2.817	2.808
Cl	5.270	3.673	3.625	3.607	3.618
E1	.250	.253	.253	.251	.251
E2	.291	.264	.272	.279	.279
Core Charge:					
Zr	35.920	35.920	35.919	35.919	35.919
Cl	10.000	11.619	11.611	11.606	11.606

The interstitial region gained $.3 e^-$, a clear indication of metallic bonding. The second result lists the charge deposited in the spheres from the band calculation. One may note that the Cl-3s core electrons were included in the bands only for the first iteration. The third result in Table 4 is the core charge arising from the core states in the muffin-tin potential.

Figures 10 and 11 show the changes in the DOS upon achieving self-consistency. The DOS from the first and last iterations are superimposed with the Fermi level at zero in Figure 10. In Figure 11, their difference is plotted. A positive value corresponds to the final iteration having a greater contribution to the DOS than the first iteration. The changes in the bandwidths and the relative positions are quite small. The Cl-3p has broadened in conjunction with the increased band charge in the Cl-sphere arising from the metallic bonding. The zirconium contributions above -3 eV have broadened toward the chlorine. The population immediately below the Fermi level has decreased because the band near the Fermi level at X, rose 2 mRy above the band at Γ . In the first iteration these two bands at Γ and X had the same energy. Also the Cl-3s core states underwent some slight dispersion. The bandwidths were .567 eV for the first iteration and .657 eV for the final iteration, a broadening of .1 eV. These bands were found to be centered at 16.04 eV and 15.91 eV below the Fermi level for the first and last iteration, respectively.

Figure 10. Comparison of the total density of states between the first and last iteration. The final iteration has a broader spectrum

Figure 11. Difference in the total density of states; between the initial and final iterations. Difference = $DOS(\text{final}) - DOS(\text{initial})$

B. Cl-Cl Lattice

As mentioned in the previous section, and shown in Figure 8, there is a significant amount of charge in both the Zr and Cl spheres in the same energy range -6 to -3 eV. The question now arises whether the charge is from the overlapping tails of the neighboring Cl-3p electrons, or is a set of Zr-4d states which provide the strong bonding between the halogen and the metal. To address the question of the role of the chlorine tails, two more band calculations were performed. Both were nonself-consistent.

To study each element individually, two separate lattices were considered; one containing only zirconium and one containing only chlorine atoms. Each unit cell still held six spheres having the same positions and sizes used in the ZrCl calculation, except that here only two spheres contained a nucleus and the other four spheres were interstitials. The method for constructing the crystal charge densities and potentials was similar to that used for ZrCl. All other parameters were left unchanged. The idea was to determine the amount of charge the band calculation would place in the empty Zr spheres in the Cl-Cl lattice and compare it with the amount of charge determined by the ZrCl calculation.

The results from both calculations are presented in Table 5 which shows the total charge in the spheres resulting from the band calculation, as well as the total charge in the spheres due to overlapping neighboring charge densities. The band calculation of the Cl-Cl lattice placed only a small amount of charge, .095 electrons, in the empty Zr spheres. This is less than 30% of the charge assumed from overlapping neighboring

Table 5. Results of the Cl-Cl and Zr-Zr band calculations

	Lattice	Zr-Zr	Cl-Cl
Total charge in each sphere from superposition of atomic charge densities:			
Zr		38.486	.335
Cl		.197	14.858
E1		.213	.004
E2		.140	.618
Total charge in each sphere from nonself-consistent band calculation:			
Zr		3.271	.095
Cl		.020	3.738
E1		.290	.000
E2		.002	.364

charges. This is the scale or order of magnitude of charge that may be associated with chlorine 3-p tails. In the ZrCl calculation, the charge within the sphere which has Zr-4d character in the appropriate energy range of -6 to -3 eV, was found to be .604 electrons. This charge is more than six times larger than the charge associated with Cl tails in the Cl-Cl lattice and tends to support the idea that in ZrCl, there is in fact, a Zr-4d bonding contribution with the halogen.

Figure 10 shows the composite total density of states. Corrections to the muffin-tin floor were included. A 'Fermi' level has been assigned to hold 18 electrons and is located at the zero of the energy.

Figure 12. Total DOS for the Cl-Cl and Zr-Zr band calculation. The "Fermi" level is at the energy zero

IV. RENORMALIZED ATOM

Electronic band structure calculations on the transition metals and noble metals have been very successful in explaining very complicated experiments such as Fermi surface measurements. When describing such data, bands and often crystal wavefunctions are required throughout the Brillouin zone. There are other experimental quantities of interest, such as the cohesive energy and bulk modulus which depend only on the total charge distribution. Then, it is rather tedious to solve for the wavefunctions over a mesh of $\bar{k}$ points in momentum space and integrate to obtain the charge distribution. A more direct method, called the renormalized atom (RA) method (47-49), has been devised to calculate a number of averaged properties of solids without recourse to a self-consistent band calculation. It has successfully described the cohesive energies in pure metals.

We shall be concerned with the determination of the cohesive energy of intermetallic compounds, especially the effects of charge transfer. For example, when electron photoemission is used to probe the core energy levels of, say, a binary alloy, it is found that the energy levels are shifted with respect to the Fermi level when compared with the energy levels of the pure metal. Such shifts may be interpreted as arising from a small net accumulation of charge in the neighborhood of one element at the expense of the other element. We would like to see whether the renormalized atom method can be adopted to the compounds so that the core level shifts can be determined without going through the band structure

calculation. In the following we give a review of the method as applied to pure metals.

The determination of the binding energy of a metal ultimately involves the calculation of the energy difference between the total energy per atom in free space and the total energy per atom in the metal. In the crystal the electron wavefunctions satisfy boundary conditions which are very different from those of the free atom. Although only the wavefunctions of the outer shell electrons change significantly between these two environments, the redistribution of the charges affect the entire self-consistent potential and the energies of the inner shells relative to the vacuum. The redistribution of the charges may then be viewed as a change in the configuration at every site from the free atom to that which is more representative of the metallic environment. The change in configuration is felt only within the atomic site. The electrons at the site may then relax to the new configuration while the electrons on the neighboring sites remain unaffected. Accounting for the energy of the inner shell electrons is the basis of the renormalized atom approximation (RAA). It is a Wigner-Seitz method (50,51) with an improved single cell calculation.

In this scheme the change in the charge configuration from a free atom to an atom within the crystal is interpreted as occurring in three distinct steps. Each step involves a change in energy and the total energy change may be expressed as

$$\begin{aligned} \Delta E = & \Delta E \text{ (atomic preparation)} + \Delta E \text{ (renormalization)} \\ & + \Delta E \text{ (band formation)} \end{aligned}$$

The first step is the atomic preparation energy. It is the energy required to change the configuration of a free isolated atom to a free atom with a configuration appropriate to the solid. For the transition metals, this is a change from a $d^n s^2$ to a $d^{n+1} s^1$ configuration. The characteristic size of this energy is on the order of .1 Ry/atom. It vanishes for the noble metals and attains its maximum for the elements with nearly half filled shells.

The second step is the energy difference between the total energy of the neutral atom in the appropriate configuration and the total energy of the renormalized atom. The renormalized atom is formed from the neutral atom with the appropriate configuration by truncating the atomic wavefunctions at the Wigner-Seitz radius and renormalizing them to maintain charge neutrality. The core orbitals are minimally affected. The renormalized wavefunctions are then used to construct the renormalized potential in the usual manner following the Hartree-Fock or Hartree-Fock-Slater procedures. This allows the total energy of the renormalized atom to be found similarly as that of the free atom and is given by

$$E_{RA}(n, m) = \sum_i \epsilon_i - (\text{double counted electron terms})$$

where ϵ_i are the single electron energies, and n and m are the number of electrons in the core and band, respectively. This allows the effect of the crystal on the inner shell electron energies to be taken into account to the same extent as they are considered in the free atom.

The renormalization energy is typically on the order of .1 Ry/atom. Although approximately one electron is compressed inside the WS sphere

and the one electron binding energies of the s and d orbitals are consequently decreased, there is substantial cancellation of the double counted electron-electron Coulomb repulsion terms so that the net energy cost of the renormalized atom is small.

The final step is the total energy difference resulting from placing the renormalized atoms together to form the crystal and allowing the outer electron orbitals to broaden into bands. The energy in the metal is different from that of the renormalized atom because of the redistribution of the charges in the band states. The energy in the metal is given by

$$E_M(n, m) = E_{RA}(n, m) + \int_{\epsilon_b}^{\epsilon_F} d\epsilon \epsilon D(\epsilon) - \sum_{\text{bands}} \epsilon_i$$

where ϵ_b is the bottom of the band, $D(\epsilon)$ is the density of states, and the last term involves only the orbitals placed in the bands. The positioning of the bands relative to the renormalized atom states is determined by a set of so-called potential dependent parameters. It was found that in pure metals the bottom of the band, ϵ_b , occurs at the energy for which the radial wavefunction of the renormalized atom has zero slope at the WS radius, and the top of the band, ϵ_T , occurs at the energy for which the radial wavefunction of the renormalized atom has a node at the WS radius. These band extrema determine the bandwidths, as well as the positions of the s, p and d electrons. These parameters are dependent only on the renormalized potential.

The relative populations and distributions of the s, p and d electrons are obtained by scaling the density of states, $D(\epsilon)$, from a band calculation to fit the renormalization energies between the band extrema. The populations are determined self-consistently with the assumed configuration of the renormalized atom. The shape of the density of states or structure of the bands is dependent on the geometry of the crystal lattice and not on the renormalized potential.

The binding energy is then given by the difference between the total energy for the metallic atom, E_M , and that of the free atom, E_A , i.e.,

$$E_B(n, m) = E_M(n, m) - E_A(n, m)$$

All the approximations in the calculation are of such a nature that the same errors are made for both configurations, the free atom and the renormalized atom, and tend to cancel in the final step. This may be seen by considering the Hartree-Fock or Hartree-Fock-Slater methods in calculating the total energy of an atomic configuration. Both leave out the correlation energy. This is compensated by assuming that the correlation energy in the renormalized atom is the same as that of the free atom and that the change in the correlation energy due to the redistribution of the outer orbital electrons is negligible.

Gelatt et al. (49) have reported the successes of the renormalized atom method in determining the cohesive energies of the pure 3d and 4d transition metals. In nearly every case reported, the disagreement with experiment was less than .03 Ry/atom. This is comparable to the results found from band calculations (52). The maximum discrepancy was

.08 Ry for Y. The parabolic trend of the cohesive energies arising from the formation of a partially filled d band was faithfully reproduced across the transition metal series.

The renormalized atom readily reveals the various contributions to the cohesive energy. The broadening of the renormalized orbitals into bands form the largest contribution to the cohesive energy. The s-band broadening energy is a minimum for the midperiod elements because of the relatively smaller WS radii. Consequently, this raises the position of the conduction band and decreases its bonding, so that the net energy contribution is small and is on the order of $-.05$ Ry/atom. The energy difference associated with the broadening of the d band is much larger and is on the order of $-.4$ Ry/atom for the transition metals. It forms the largest contribution to the cohesive energy and provides the parabolic trend across the transition metal series. It achieves its maximum for half filled bands and vanishes for empty and full d bands. The remaining contribution to the cohesive energy is due to the hybridization of the conduction and d band at the same site. With a size on the order of $-.16$ Ry/atom, it was found to be very important. It helps provide structure to the unhybridized density of states and tends to push the s and d states away from the center of the d band. This approach has been successfully applied to pure metals.

Intermetallic compounds involving the transition metals possess a number of properties of the pure metals. There are still two species of band electrons, the free electron-like conduction electrons and the more localized d band electrons. Again, the d band may be thought of as

being centered and broadened about their atomic-like resonant level. The resonant level lies higher with respect to the vacuum than it does in the free atom because of the substantial charge compression of the conduction electrons that results when the crystal lattice is formed. The d band overlaps and hybridizes with the conduction band, and this forms a significant contribution to the cohesive energy of the metallic bonding. The cohesive energy viewed as arising from distinct changes in the configuration on a single site is well-defined for pure metals because all sites are equivalent and each Wigner-Seitz cell is neutrally charged. But, this is not the case with intermetallic compounds; the sites are not equivalent and the Wigner-Seitz cell is not neutrally charged. In this section we shall consider our attempt to adapt the formalism of the renormalized atom method to the metallic compound, ZrCl , and discuss the problems in the procedure that need to be resolved so that the results can be physically meaningful.

The procedures used to determine the energy differences due to atomic preparation and renormalization on the intermetallic compounds are similar to the procedures used on the pure metals. The difference arises in the step which describes the broadening of the s, p, and d electrons into bands, and their subsequent hybridization. Hybridization and charge transfer may now occur between the inequivalent metal and nonmetal sites. This information, which is found from the band calculation and is given in the angular momentum resolved density of states, ADOS, is not exactly the same as that found from the RAA because the sphere radii are different in the two methods. The band calculation

uses nonoverlapping muffin-tin spheres and the RAA uses WS spheres, which do overlap. In order to see whether the RAA will lead to results in good correspondence with the band calculation, it is necessary to recalculate or recast the results from the band calculation, i.e., the populations and the crystal potential, in terms of WS radii.

We begin by determining the Wigner-Seitz radii. In pure elemental solids, the WS radius is uniquely determined. The volume of the WS sphere is equal to the unit cell volume. For compounds the WS radii are not unique; the only restriction is that the total volume in the WS spheres which enclose a single set of basis atoms, be equal to the unit cell volume. This leaves a considerable degree of freedom in choosing the radii. One reasonable choice is to choose the WS radii such that the change in the total energy resulting from the renormalization procedure or the total binding energy be a minimum. This approach has the advantage of incorporating some energy or charge dependence on the radii. Alternatively, one may assume subjectively, as we did in this prototype study, that the ratio of the ideal WS radii is the same as that for the muffin-tin radii. For convenience the actual radii used in the calculation were located on the Waber mesh nearest to and smaller than the ideal WS radii. The effect of this is small since the mesh is quite fine. The WS radii were 1.967 Å for Zr and 1.395 Å for Cl.

Consider next the potentials. The crystal potential from the band calculation is defined only within the muffin-tin sphere. The renormalized atom potential is defined out to the WS radius which is larger than the muffin-tin radius. These two potentials may be compared to a

limited extent by comparing their potential parameters, such as the mean band positions and bandwidths for the s, p, and d electrons. Because these parameters are defined by conditions on the radial wavefunctions, it is necessary to extend the muffin-tin potential out to the WS radius. How this is done is, again, not unique. Recall that in compact metals, the crystal potential in the interstitial region outside the muffin-tin spheres tends to be relatively smooth and slowly varying, while in more open structures it varies more. Guided by such reasoning, it was assumed that the crystal potential between the muffin-tin and WS spheres were equal to the average value of the muffin-tin potential in the interstitial region, and it was hoped that the effects of this approximation would not be so severe as to provide unreasonable estimates of the potential parameters. This kind of potential is discontinuous at the muffin-tin radius and constant between the muffin-tin and WS radius. This will be called the extended muffin-tin potential, EMTP. The potential parameters were then determined at the WS radii.

We found that the RAA did not reproduce the correct Cl-p bandwidth. The WS condition on the renormalized atom potential for neutral chlorine with unit exchange gives a bandwidth of 13.26 eV, while on the EMTP, the bandwidth is 12.37 eV. These compare poorly with the 3 eV bandwidth found from the band calculation, which is shown by the angular momentum decomposed density of states, ADOS, in Figure 8. The small contribution of Cl-p admixing with the Zr-d above -3 eV is not included.

As a result of this large discrepancy in bandwidth, we found it impossible to locate the mean position of the Cl-p band unambiguously.

Using the band calculation result as a guide, we positioned the Cl-p band, between -6 and -3 eV, found from the band calculation, between the band extrema, -9.68 and 2.69 eV, found from the EMTP. This may be viewed as constructing a modified ADOS for the p band, where only the relative positions of the band extrema due to the WS condition and the shape of the ADOS from the band calculation are important. The mean p band position, ϵ , is then determined with respect to the WS band extrema, ϵ_1 and ϵ_2 , and is given by

$$\epsilon = \epsilon_1(1 - \gamma) + \epsilon_2\gamma, \quad \epsilon_1 < \epsilon_2$$

where γ determines the positioning. For the modified ADOS with a WS bandwidth of 12.37 eV, γ is .4195. For the renormalized atom potential using unit exchange parameter on the neutral atom, the WS bandwidth is 13.26 eV and γ is .506. The mean position of the p band is given by

$$\begin{aligned} \epsilon &= \langle \phi_p^{RA} | -\nabla^2 + V^{RA} | \phi_p^{RA} \rangle \\ &= \epsilon_p^{at} + \langle \phi_p^{RA} | V^{RA} - V^{at} | \phi_p^{RA} \rangle \end{aligned}$$

where ϕ_p^{RA} is the renormalized atomic 3p wavefunction and ϵ_p^{at} is the atomic energy level of the p electrons.

To gain better agreement with the width of the p band, it may be more appropriate to use an alternative approach such as redefining the WS radius to be larger for chlorine. Nevertheless, our construction

of the modified ADOS was an attempt to place the p band more realistically since the WS condition gave too large a bandwidth.

The determination of the Zr-s band was more difficult because of the extensive hybridization with the Cl-p and Zr-d bands. The characteristic free electron parabola is not evident in the bands. The WS condition on the EMTP places the bottom of the s band at -5.28 eV and a bandwidth of 12.37 eV. This agrees well with the contribution which mixes with the Cl-p band. These results are shown in Table 6.

Table 6. Potential parameters using the self-consistent muffin-tin potential from the last iteration extended out to the WS radius

ϵ_T	Δ_s	ϵ_d	Δ_d	ϵ_p	Δ_p
-5.28	16.43	1.36	4.95	-3.84	12.37

The determination of the Zr-4d bandwidth involved problems different from that for the chlorine p band. The WS condition determined the bandwidth to be 4.95 eV (between -2.3 and 2.6 eV the band extrema) for the EMTP and 5.33 eV for the renormalized atom potential arising from the neutral atom configuration with 3.664 e^- in the d band and unit exchange parameter. The determination of the bandwidth from the band calculation was based on the following considerations. Only the top five bands in Figure 6 could be attributed directly to the d bands. In order to obtain the upper limit of the d bands, the next six higher bands were calculated at the high symmetry points where hybridization is

weakest and the d character is most easily seen. The bandwidth was 6.1 eV, lying between the band extrema of -2.3 and 3.8 eV. Compared with Δ_d from Table 6, we see that the WS condition gives a realistic determination of the bandwidth but is too small by 1.15 eV. This suggests that unlike the chlorine case, the Zr WS radius is too large.

We have discussed how the WS sphere radii were determined and how the muffin-tin potential was modified so that comparison with the results from applying the RAA, was possible. We will now discuss how the population of the bands (ADOS) is modified when WS sphere radii are involved. Again, the construction is nonunique.

The ADOS is the distribution of the angular momentum character of the bands within each muffin-tin sphere as a function of the energy. Integrating the ADOS up to the Fermi level, determined the charge associated with each ℓ -character, the populations. Summing the populations over the angular momenta yields the total charge in each sphere. The normalization of the distribution assumes that each band contributes two electrons to the sum total density of states. The ADOS does not include any interstitial charge. The WS method includes the interstitial charge by using larger spheres. In order to make the proper correspondence between the MT and WS spheres, a modified ADOS must be defined to yield the charges in the WS spheres so that integrating the modified ADOS up to the Fermi level recovers the total charges in the bands.

The determination of the modified ADOS involved finding the charge in the WS spheres restricted to only certain types of electrons. This was accomplished in a three step procedure. The first step involved

using the wavefunctions found from the band calculation, except now the radial wavefunctions were defined out to the WS radius by solving Schrodinger's equation with the EMTP at the eigenvalue energies. Only the Zr-s, Zr-d, and Cl-p electrons were included. The second step maintained charge neutrality by renormalizing or linearly scaling the charges so that each band contributed two electrons. The third step determined the modified ADOS, by Kopp's technique, as was done for the muffin-tin case. These procedures allowed the wavefunctions which have their maximum in the neighborhood of the WS radius to contribute relatively more electrons than if a linear rescaling of the muffin-tin ADOS would have been used. This procedure determined the populations of the bands in the WS picture, but lead to unrealistic results. Chlorine is positively ionized, i.e., $4.674 e^-$, as is shown in Table 7.

Table 7. Comparison of charges in the WS spheres arising from using EMTP and linear scaling of the muffin-tin charges

	-5.9<E<-3.0		-2.25<E<-1.62		-1.56<E<1.25		total charge in WS sphere	
	MT	EMTP	MT	EMTP	MT	EMTP	MT	EMTP
Zr-s	.257	.454	.068	.120	.153	.243	.454	.784
Zr-d	.902	1.172	.699	.753	3.810	3.453	3.207	3.542
Cl-p	5.000	4.375	.142	.127	.364	.304	5.339	4.674

Charge transfer is closely related to the band populations. It may be revealed by comparing the total charge within the muffin-tin spheres in the first and last iteration from a self-consistent band

structure calculation. But, when a substantial amount of charge enters the interstitial region during the iteration procedure to reflect the metallic bonding in a metal, the concept of charge transfer becomes more difficult to define. The WS method involves no interstitial charges and defines charge transfer as the ionicity of the WS sphere. We want to determine whether the RAA can provide an estimate of charge transfer in compounds.

We are now prepared to perform a self-consistent calculation on the renormalized atom. The self-consistent procedure is outlined as follows. An atomic configuration is assumed, the renormalized atom is constructed, the renormalized atom potential is created so that the potential parameter can be determined. The potential parameters position the ADOS. The ADOS is integrated up to the Fermi level which is determined by charge neutrality in the unit cell. The integrated ADOS yields a new occupation of the atomic orbitals of the renormalized atom. This closed the procedure. We then iterate until the configuration reaches equilibrium. The relative position of the Zr-d and Cl-p bands is revealed when charge transfer is allowed between the two elements.

One motivation for using the RAA to determine charge transfer and the relative position of the bands when only a rough or simple shape to the ADOS is assumed or known, i.e., to bypass the necessary band calculation. In the spirit of the WS approximation, the modified ADOS were renormalized to the neutral atom configurations to find the relative positions of the bands with no charge transfer. Five electrons were placed in the narrow Cl-p band. The Zr-s electrons were treated as a free electron band. The shape of the Zr-d ADOS was altered by first

dropping the contribution which hybridizes with the Cl-p band because it was positioned outside the d band, and then compensated by renormalizing the d ADOS found between -2.25 and 1.62 eV to two electrons and between -1.56 and 1.25 eV to four electrons. The ADOS from 1.25 to 2.6 eV, the top of the band, was assumed to be a constant holding four electrons. This fixed the area under the ADOS. With these fixed areas for the ADOS, the renormalized atom was solved self-consistently. The Cl-p ADOS containing five electrons was positioned below the Fermi level. No charge transfer to or from the chlorine was allowed. Charge was transferred between the s and d bands at the zirconium site. The results are shown in Table 8.

The area under the Cl-p ADOS was increased by .1 e and solved to self-consistency again. The Cl-p ADOS was fully occupied but now was positioned closer to the Fermi level. If the area under the Cl-p ADOS is increased further, say as much as .3 e the Cl-p band shifts up to the Fermi level and begins to depopulate. It is possible to reach self-consistency by iterating on the charge transfer but the resulting mean Cl-p band position will be near the Fermi level, which is contrary to that found from the band calculation. This may be expected when the nature of the algorithm or self-consistent procedure is considered. Unoccupied bands cannot exist below the Fermi level; the p band is expected to raise, as charge is transferred toward chlorine. The shape of the ADOS found from the band calculation cannot be altered. We may expect this type of problem to arise whenever the bandwidth found from the band calculation differs significantly from that found from imposing

Table 8. Results from the renormalized atom method for various charge transfers

ionization on Zr		Zr-s	Zr-d	Cl-p	ϵ_T	Δ_s	ϵ_d	Δ_d	ϵ_p	Δ_p
initial	final									
0	0	.336	3.664	5.0	-5.17 eV	16.96 eV	1.11 eV	5.33 eV	-7.58 eV	13.26 eV
.1	.1	.317	3.583	5.1	-4.92	16.79	1.11	5.15	-5.19	13.46
.2	.2	.3	3.5	5.2	-4.69	16.63	1.11	4.98	-2.82	13.65
.3	.259	.290	3.451	5.259	-4.56	16.53	1.11	4.88	-1.44	13.76

the WS boundary condition. If the Cl-p ADOS is assumed to be narrow, i.e., 3 eV, a different procedure than the one used here must be used.

From the results from Table 8, when the relative position of the Zr-d and Cl-p bands is compared with that found from the band calculation, we find a charge transfer near $.1 e^-$ toward chlorine. But this is outside the WS approximation. The question then arises as to whether some boundary condition may be applied so that meaningful results may be found. One simple idea that was tried was to determine the quantity of charge that would force the renormalized atom potentials on the WS surface to have a common value. It was found that a charge transfer of .225 electrons was necessary, and consequently the relative positions of the p and d bands were unrealistically close together.

In summary, it was not possible to determine the charge transfer self-consistently with the present construction of fitting the bands in the RAA formalism. It is also realized that hybridization energy was neglected throughout this work. This involves a net lowering of the energy due to the bandwidth and causes some rearrangement of the charge. The hybridization energy is difficult to evaluate, and in pure metals good agreement for the cohesive energies have been found by treating on-site hybridization as a constant and fitting it to experiment. It may be possible that when hybridization between inequivalent sites is properly accounted for in the RAA, more realistic estimates of the charge transfer may be obtained. But, we do not know how to treat this problem at this time.

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