Self-Consistent Energy Bands and Cohesive Energy of Potassium Chloride

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The valence and conduction bands of potassium chloride were determined by the augmented-plane-wave method from a potential of a more general functional form than that usually assumed in this method. With a few iterations of the band calculation within the Hartree-Fock-Slater (HFS) approximation, a good degree of self-consistency was obtained. The calculation of the cohesive energy of the crystal from the energy-band results was simplified considerably by using Slater's approximation to the exchange potential in the exchange-energy terms, and the resulting cohesive energy is in excellent agreement with experiment. The self-consistent HFS values of the Cl $3p$ bandwidth and the band gap were found to be 0.82 eV and 6.3 eV, respectively.

I. INTRODUCTION—THE APW METHOD

AS originally proposed,[1] the augmented-plane-wave (APW) method yields the eigenstates of a periodic one-electron potential of a rather restricted form. Within spheres centered at the atomic sites, the potential is required to be spherically symmetric, while outside these spheres (referred to as APW spheres) the potential is taken to be a constant. If, however, one requires accurate eigenstates of a potential of a more general form, as for example in the case of an iterative self-consistent-field calculation, the averaging of the potential necessary to satisfy the above restrictions may not be justified. It is therefore desirable to remove these restrictions insofar as is possible. In view of the extensive use of the APW method in recent years, it is also of interest to obtain an accurate assessment of the effects of these restrictions upon the calculated band structure.

It is convenient to express the potential to be treated, $V(\mathbf{r})$, as a "muffin tin" part, $V_m(\mathbf{r})$, which is spherically symmetric within the APW spheres and constant outside, plus a remainder:

$$V(\mathbf{r}) = V_m(\mathbf{r}) + V_1(\mathbf{r}) + V_2(\mathbf{r}), \qquad (1)$$

where $V_1(\mathbf{r}) = 0$ inside the spheres and $V_2(\mathbf{r}) = 0$ outside. If $V_2(\mathbf{r})$ is omitted, the problem remaining may be solved exactly by the APW method, as has been noted previously.[2] All that is required is the addition of the matrix element of $V_1(\mathbf{r})$ between the APW's ϕ_i and ϕ_j to the original matrix element of the Hamiltonian minus the trial value of the energy, $(H-E)_{ij}$.[1] Since the APW ϕ_i equals $\Omega^{-1/2} \exp[i(\mathbf{k}+\mathbf{K}_i)\cdot\mathbf{r}]$ in the region where $V_1(\mathbf{r})$ is nonzero,

$$(V_1)_{ij} = \frac{1}{\Omega}\int_{cell} \exp[-i(\mathbf{k}+\mathbf{K}_i)\cdot\mathbf{r}]$$
$$\times V_1(\mathbf{r})\exp[i(\mathbf{k}+\mathbf{K}_j)\cdot\mathbf{r}]d^3r = c(\mathbf{K}_i-\mathbf{K}_j), \quad (2)$$

[1] J. C. Slater, Phys. Rev. **51**, 846 (1937).
[2] H. Schlosser and P. M. Marcus, Phys. Rev. **131**, 2529 (1963).

where $\mathbf{k}$ is the vector in the first Brillouin zone labeling the translational symmetry of the eigenstate, Ω is the volume of the unit cell, $\mathbf{K}_i$ and $\mathbf{K}_j$ are reciprocal lattice vectors, and $c(\mathbf{K})$ is the Fourier coefficient of $V_1(\mathbf{r})$ corresponding to the reciprocal vector $\mathbf{K}$. Since within each sphere the APW's are made up of solutions of Schrödinger's equation for the appropriate spherically symmetric potential and therefore depend on E, the eigenvalue $E(\mathbf{k})$ is then determined by the customary procedure of varying E numerically to satisfy the condition,

$$\det[(H-E)_{ij}] = 0. \qquad (3)$$

Since the degree of convergence of a given eigenvalue is found to vary directly with the product $k_{\max}R_s$, where R_s is an APW sphere radius and $k_{\max}$ is the magnitude of the smallest wave vector omitted from the APW basis set, it is customary to choose the sphere radii so that nearest neighboring spheres touch. If the radii of these spheres are reduced, the dimensionality of the secular equation must increase in proportion to $(1/R_s)^3$ in order to maintain a given degree of convergence and thus it is not feasible to make $V_2(\mathbf{r})$ negligibly small by reducing the size of the APW spheres. Since the APW's do not form a complete set, the inclusion of matrix elements of V_2 in the secular equation would not be an exact procedure although it would at least give the first-order effect of V_2 upon the band energies. The main reason for not including the matrix elements of V_2 is that they would increase substantially the computational effort required to carry out the band calculation. However, it should usually be possible to treat V_2 as a first-order perturbation using the wave functions of the unperturbed APW eigenstates. If greater accuracy should be needed, one could use the eigenfunctions of the APW problem without V_2 as a basis set and diagonalize the resulting Hamiltonian matrix as has been done for relativistic corrections.[3]

It is also possible to estimate the effect of V_2 upon the energy bands by including approximate matrix elements of V_2 in the secular equation. One way to

[3] J. B. Conklin, Jr., L. E. Johnson, and G. W. Pratt, Jr., Phys. Rev. **137**, A1282 (1965).

approximate the matrix elements of V_2 is to replace the APW's by the corresponding plane waves in the expression for these matrix elements. The approximate value of $(V_2)_{ij}$ is then the Fourier coefficient of $V_2(\mathbf{r})$ corresponding to the reciprocal lattice vector $(\mathbf{K}_i - \mathbf{K}_j)$ as in Eq. (2). This approximation is justified if the major part of the true matrix element of V_2 comes from the regions close to the surfaces of the APW spheres where the interior parts of the APW's join continuously onto the plane-wave exterior part.

II. SUPERPOSED-FREE-ION HFS POTENTIAL

To obtain a potential of a realistic form for the purpose of carrying out a numerical example of the above discussion, the Hartree-Fock-Slater (HFS) prescription was applied to an assumed charge density for KCl. This crystal charge density was obtained by superposing free-ion charge densities centered on the ionic sites of the crystal which has NaCl structure. Thus the superposed-free-ion (SFI) charge density may be written

$$\rho_{\rm SFI}(\mathbf{r}) = \sum_g \sum_{n=1}^2 \rho_n(|\mathbf{r} - \mathbf{R}_g - \mathbf{r}_n|), \qquad (4)$$

where the index g runs over all the points $\mathbf{R}_g$ of the fcc lattice and ρ_n is the free-ion charge density of the nth ion in the unit cell, located at $\mathbf{r}_n$ relative to $\mathbf{R}_g$. The Coulomb part of the HFS potential is then a lattice sum of the Coulomb parts $V_{cn}(r)$ of the free-ion HFS potentials and the exchange part is the averaged free-electron or "$\rho^{1/3}$" potential,[4,5]

$$V(\mathbf{r}) = \sum_g \sum_n V_{cn}(|\mathbf{r} - \mathbf{R}_g - \mathbf{r}_n|) - 6[3\rho_{\rm SFI}(\mathbf{r})/8\pi]^{1/3}. \quad (5)$$

In order that $V(\mathbf{r})$ might be reasonably close to the self-consistent HFS potential for the crystal, the free-ion charge densities were obtained from the HFS atomic program of Herman and Skillman.[6]

The Coulomb part of the potential in Eq. (5) may be expressed in the form given in Eq. (1), with the remainder terms V_1 and V_2 in Fourier-series form, by performing the appropriate radial integrations. For example, the spherical average of the Coulomb potential about the K^+ ($n=1$) ionic site, chosen to be at the origin, is

$$\bar{V}_{c1}(r) = V_{c1}(r) + \frac{4\alpha}{a} + \sum_{g,n} \frac{1}{2r|\mathbf{R}_g + \mathbf{r}_n|}$$
$$\times \int_{|\mathbf{R}_g + \mathbf{r}_n| - r}^{|\mathbf{R}_g + \mathbf{r}_n| + r} \left[V_{cn}(r') \pm \frac{2}{r'} \right] r' dr', \quad (6)$$

where the second term is the sum of the contributions of all neighboring ions, in the point-ion approximation. The Madelung constant[7] α is 1.747558 and the cube edge a was chosen to be 11.8014 a.u. following Howland.[8] The last term contains the departures of the Coulomb potentials of the near neighbors from the asymptotic forms, $\pm 2/r$, averaged by Löwdin's method.[9] The APW sphere radii were chosen to be $a/4$ which seemed to make V_2 as small as possible for the case of touching spheres. The average of the Coulomb potential in the region outside the APW spheres is obtained from the volume integrals of $\bar{V}_{c1}$ and $\bar{V}_{c2}$ inside the APW spheres and the volume integral over the entire cell of the Coulomb potential which is just the volume integral of $V_{c1} + V_{c2}$ over all space. Since the Coulomb part of $V(\mathbf{r}) - V_m(\mathbf{r})$ is, apart from an additive constant, a lattice sum of spherically symmetric functions, the Fourier coefficients of the Coulomb part of $V_1(\mathbf{r}) + V_2(\mathbf{r})$ are also easily obtained by radial integration.

The exchange part of the potential is not as easily treated because it is not linearly related to the charge density. However, the method applied above to the Coulomb potential can be used to express the total charge density in the form

$$\rho_{\rm SFI}(\mathbf{r}) = \rho_m(\mathbf{r}) + \rho_f(\mathbf{r}), \qquad (7)$$

where $\rho_m(\mathbf{r})$ equals the spherical average of the charge density within each APW sphere and the average of the charge density outside. It is then convenient to choose the exchange part of $V_m(\mathbf{r})$ to be

$$V_{m\,\rm exch}(\mathbf{r}) = -6[3\rho_m(\mathbf{r})/8\pi]^{1/3}. \qquad (8)$$

To obtain a Fourier series for the remainder of the exchange potential, this remainder was tabulated on a cubic grid of points in 1/48 of the unit cell and the Fourier coefficients were calculated by triple numerical integration. Similarly, $V_1(\mathbf{r})$ was tabulated, using Ewald's method[10] for the point-ion part of the Coulomb potential, and its Fourier coefficients were obtained numerically.

In Table I, the values of $V_1(\mathbf{r})$ are given at three points on the plane bisecting the line from the K^+ ion at the origin to the Cl^- ion at $a/2(001)$. The values of V_1 at $a/4(001)$ and $a/4(111)$ turn out to be the ex-

TABLE I. $V_1(\mathbf{r})$ and the exchange contribution to $V_1(\mathbf{r})$ in units of Ry/electron.

$\mathbf{r}$	$V_1(\mathbf{r})$	$V_{1\,\rm exch}(\mathbf{r})$
$(001)a/4$	0.281	0.205
$(011)a/4$	−0.083	−0.069
$(111)a/4$	−0.189	−0.156

[4] J. C. Slater, Phys. Rev. **81**, 385 (1951).

[5] Unless otherwise indicated, the potentials referred to here will have the units of Ry/electron, so that the potential due to a nucleus of atomic number Z located at the origin is $-2Z/r$ and the Coulomb part of the potential satisfies the equation $\nabla^2 V_c(\mathbf{r}) = -8\pi\rho(\mathbf{r})$, where the electronic-charge density $\rho(\mathbf{r})$ is a positive function having the units of electrons/cubic Bohr radius.

[6] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

[7] C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1956), 2nd ed., p. 77.

[8] L. P. Howland, Phys. Rev. **109**, 1927 (1958).

[9] P.-O. Löwdin, Advan. Phys. **5**, 96 (1956).

[10] P. P. Ewald, Ann. Physik **64**, 253 (1921); Ref. 7, Appendix A.

tremal values, while the dominance of the exchange part of V_1 is apparent from the table. Just inside each APW sphere, $V_2(\mathbf{r})$ undergoes angular variation with an amplitude of about 0.1 Ry, which is the same order of magnitude as the nonspherical part of the point-ion potential. About a given ionic center, the part of $V_2(\mathbf{r})$ produced by charges outside the corresponding APW sphere satisfies Laplace's equation and is therefore represented by an expansion in $r^l Y_l^m(\theta,\phi)$, where the lowest nonzero value of l is 4 because of the cubic symmetry about each ionic site. The rest of $V_2(\mathbf{r})$ is produced by the tails of the charge densities of neighboring ions and thus $V_2(\mathbf{r})$ falls off fairly rapidly as the distance from the center of an APW sphere decreases.

III. ACCURACY OF THE APW METHOD APPLIED TO KCl

To assess the effects upon the calculated band structure of the remainder terms in the potential of Eq. (1), the bands were calculated at several inequivalent points in the Brillouin zone for the potentials $V_m(\mathbf{r})$, $V_m(\mathbf{r})+V_1(\mathbf{r})$, and $V_m(\mathbf{r})+V_1(\mathbf{r})+V_2(\mathbf{r})$ For the last of these, the approximate matrix elements of $V_2(\mathbf{r})$ described above were used. The resulting bands were similar to those shown in Fig. 1, where the lowest band shown is the Cl $3p$ band which is the highest occupied band. By taking differences between these sets of re-
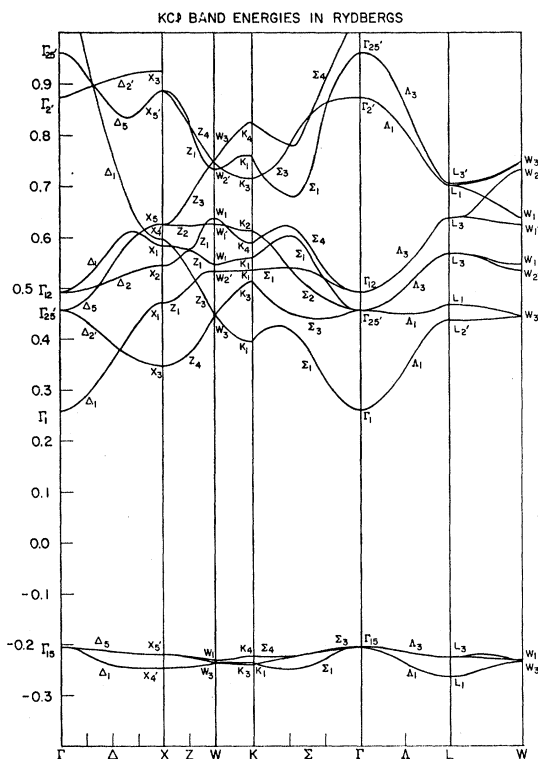

KCl BAND ENERGIES IN RYDBERGS

FIG. 1. The conduction bands and the highest valence band for KCl determined by the APW method at 12 inequivalent points in the first Brillouin zone using the self-consistent HFS potential.

sults, the effects of $V_1(\mathbf{r})$ and $V_2(\mathbf{r})$ on the bands were determined. The various states in the Cl $3p$ band were found to be shifted by amounts from -0.001 to -0.004 Ry by including $V_1(\mathbf{r})$, while the estimated effect of $V_2(\mathbf{r})$ on these states was typically 10 times smaller. These results were to be expected from the fact that the part of the Cl $3p$ charge density in the interstitial volume is concentrated close to the APW spheres and the fact that the energies of p states are not affected to first order by the nonspherical part of a potential of cubic symmetry. The effects of V_1 and V_2 on the K $3p$ and Cl $3s$ bands, both of which were found to be about 0.9 Ry below the Cl $3p$ band, were somewhat smaller. The estimated contributions of V_2 to the energies of the conduction bands were found to be less than 0.005 Ry in magnitude and typically $\sim\pm0.002$ Ry. The contributions of V_1 to these band energies, with one exception, ranged between -0.017 Ry and 0.039 Ry, the predominance of positive values being due to the positive average value (0.016 Ry) of the exchange part of V_1. However, in the case of the $\Gamma_{2'}$ state, the potential V_1+V_2 contributed 0.0689 Ry or 0.94 eV to the energy. The gap between the Cl $3p$ band and the lowest conduction state was 6.7 with the SFI potential of Eq. (1) as compared with a gap of 6.4 eV obtained from V_m alone, and with the experimental value of about 7.5 eV.[11] Thus the effect of V_1, the remainder term in the potential outside the APW spheres, is not negligibly small in comparison with the discrepancy between theory and experiment, while it would seem that the nonspherical potential inside the spheres may safely be neglected in KCl.

IV. THE SELF-CONSISTENT ENERGY-BAND CALCULATION

In the course of an iterative HFS energy-band calculation, a crystal charge density $\rho(\mathbf{r})$ is obtained by summing the charge densities of all occupied Bloch states, and the potential for the next iteration is obtained by solving Poisson's equation for this crystal charge density and adding the exchange correction which is proportional to $\rho^{1/3}(\mathbf{r})$. From the crystal charge density given by the Bloch states of this potential, a new potential is derived by the same prescription and a comparison of these two potentials indicates the degree of self-consistency which has been achieved. Since $\rho(\mathbf{r})$ is not in general a lattice sum of spherically symmetric functions, the calculation of the Coulomb part of the potential in the iterative calculation is a little more involved than above. If we write

$$\rho(\mathbf{r})=\rho_m(\mathbf{r})+\rho_f(\mathbf{r}), \tag{9}$$

where $\rho_m(\mathbf{r})$ is the spherical average of $\rho(\mathbf{r})$ inside each APW sphere and equals the average ρ_0 of $\rho(\mathbf{r})$ in the

[11] G. Kuwabara and K. Aoyagi, J. Phys. Chem. Solids **22**, 333 (1961).

region outside, then the exchange part of the potential is conveniently handled as described in Sec. II. The contributions of ρ_m and ρ_f to the Coulomb potential are conveniently treated separately, using Ewald's method to obtain the solution of Poisson's equation for ρ_m and a Fourier-series solution for the Coulomb potential from ρ_f.[12]

A considerable simplification of the iterative calculation was obtained by neglecting $\rho_f(\mathbf{r})$ when calculating the potential. With this approximation, the difficulty in treating the exchange potential was removed and it was only necessary to calculate the spherical average within each APW sphere of the charge density from the Bloch functions. As a check on this approximation, the potential from $\rho_m(\mathbf{r})$ alone in the SFI case was used to recalculate charge densities of a few occupied states. The discrepancies thereby introduced in these charge densities suggested a discrepancy in the total charge density five or ten times smaller than the difference between $\rho_{SFI}(\mathbf{r})$ and the final charge density of the iterative calculation. The contributions of $\rho_m(\mathbf{r})$ to the remainder terms V_1 and V_2 were also neglected since they seemed less important than those of ρ_f in the SFI case.

The potential for each iteration was derived from an average of the charge density from the previous iteration and the charge density used to obtain the potential for the previous iteration.[13] For the $3s$ and $3p$ valence bands, the charge densities of the Bloch states were summed on a cubic grid of 32 points in the first Brillouin zone. The $1s$, $2s$, and $2p$ charge densities of both ions were assumed to remain the same as in the free ions. This assumption was later checked by calculating the core states of the self-consistent KCl potential and was found to be justified. In the third and last iteration, the contributions to the potential neglected in the previous iterations were included approximately and the resulting band structure is shown in Fig. 1. The degree of self-consistency of these results is characterized by the differences of less than 0.01 Ry between the contributions of $\rho_m(\mathbf{r})$ to the potentials for the second and third iterations.

TABLE II. SFI and self-consistent (SC) charge densities outside APW spheres.

r	$\rho_{SFI}(\mathbf{r})$	$\rho_{SC}(\mathbf{r})$
$(002)a/8$	0.0114	0.0105
$(012)a/8$	0.0058	0.0055
$(112)a/8$	0.0033	0.0029
$(022)a/8$	0.0023	0.0016
$(122)a/8$	0.0017	0.0010
$(222)a/8$	0.0011	0.0006
average charge density (ρ_0)	0.00378	0.00335

[12] J. C. Slater and P. DeCicco, MIT Solid-State and Molecular Theory Group Quarterly Progress Report No. 50, 1963 (unpublished).
[13] This procedure has also been used to speed the convergence of self-consistent atomic HFS calculations. See Ref. 6.

A comparison of the charge density from the second iteration of the band calculation with $\rho_{SFI}(\mathbf{r})$ indicates that a good choice of the starting potential was made. The increase of 0.1 electrons in the charge within the Cl sphere suggests that the Cl⁻ ion in KCl is slightly compressed as compared with the free Cl⁻ ion. The similarity between the SFI and self-consistent charge density in the interstitial region, shown in Table II, suggests that a better restricted iterative procedure, at least for KCl, would involve holding $\rho_f(\mathbf{r})$ fixed rather than neglecting it during the iterative calculation.

V. DISCUSSION OF THE BAND STRUCTURE OF KCl

A. Valence-Band Width

In Fig. 1 the energy bands from the third iteration described above are plotted on the APW scale, on which zero corresponds to the value of $V_m(\mathbf{r})$ in the region outside the APW spheres. The Cl $3p$ band has a width of 0.0601 Ry as compared with a width of 0.0549 Ry obtained from the SFI potential. These values differ significantly from the width of 0.112 Ry or 1.52 eV found by Howland. Since Howland treated the exchange correction exactly within the tight-binding approximation, the Cl $3p$ band which he calculated, results in effect, from a k-dependent potential. However, it is not certain that the discrepancy in band widths is to be attributed principally to the k dependence of the Hartree-Fock (HF) potential since the tight-binding approximation used by Howland may also contribute. Furthermore, a k-averaged HF potential might yield a Cl $3p$ band differing substantially from that obtained in the HFS approximation.

Although there does not appear to be any clear-cut experimental value for the valence bandwidth, one interpretation of the K_β x-ray emission data of Parratt and Jossem is that the width at half-maximum of the Cl $3p$ band density of states is about 0.33 eV.[14] While the Cl $3p$ band of the APW calculation has not been evaluated at sufficiently many points to obtain an accurate density-of-states curve, the width at half-maximum of the density of states seems to lie between 0.3 and 0.5 eV, as compared with 0.87 eV found by Howland.[8]

B. Work Function and Band Gap

In the one-electron picture, the work function of the crystal is the negative of the energy of the highest occupied state on the energy scale for which the potential goes to zero outside the crystal, provided that a suitable final state for a transition of this energy exists. With the work function greater than the band gap, this restriction presents no difficulty if we assume phonon-assisted indirect transitions or consider the large col-

[14] L. G. Parratt and E. L. Jossem, Phys. Rev. 97, 916 (1955).

lection of states close to the top of the valence band. From the Cl $3p$ band obtained from the SFI potential of Eq. (5), the work function is 10.27 eV, as compared with experimental values ranging from 8.1 to 8.7 eV.[15,16] From a point-ion calculation of the **E** field at an ionic site in a (100) surface of a KCl crystal, and the ionic polarizabilities of K$^+$ and Cl$^-$,[17] a surface dipole layer producing a positive contribution of 0.5 eV to the one-electron potential inside the crystal was found. In addition, the Γ_{15}Cl $3p$ state went up in energy by 0.68 eV in going from the SFI to the self-consistent potential. With these two corrections, the theoretical value of the work function is lowered to about 9.1 eV.

The self-consistent band gap separating the Γ_{15}Cl $3p$ state and the Γ_1 conduction state is 6.3 eV, as compared with the gap of 6.7 eV from the starting potential and the experimental gap of 7.5 eV. One way to account for the discrepancy of 1.2 eV is to claim that the Cl $3p$ band is too high by roughly this amount as is the HFS $3p$ level of the free Cl$^-$ ion. This interpretation is supported by the close association between the free-ion one-electron energies and the positions of the occupied bands in KCl shown in Table III. A comparison of the

TABLE III. The free-ion valence energy levels are related to the approximate average energies of the valence bands by adding the Madelung shifts, $\pm 4\alpha/a = \pm 0.59232$ Ry, to the free-ion energies.

Orbital	HFS	HF
K$^+$ valence energies (Ry)		
$3s$	-3.4480^a	-3.930^b
$3p$	-2.2307^a	-2.341^b

K$^+$ ionization potential^c = 31.81 eV = 2.338 Ry

Cl$^-$ valence energies (Ry)		
$3s$	-1.062^a	-1.454^d
$3p$	-0.1909^a	-0.2971^d

Electron affinity of Cl^e (Cl$^-$ ionization potential) = 3.72 eV = 0.2735 Ry

Approximate positions of valence bands (in Ry) found by averaging the energies of the bands and by shifting the free-ion energies

Level	Shifted HFS	APW^f	Shifted HF	Howland^g
K$^+$3s	-2.856	-2.88	-3.338	-3.333
K$^+$3p	-1.639	-1.655	-1.749	-1.75
Cl$^-$3s	-1.654	-1.660	-2.046	-2.01
Cl$^-$3p	-0.782	-0.778	-0.887	-0.84

^{a} Calculated using the HFS program described in Ref. 6.
^{b} D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A166**, 450 (1938).
^{c} R. B. Leighton, *Principles of Modern Physics* (McGraw-Hill Book Company, Inc., New York, 1959).
^{d} D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A156**, 45 (1936).
^{e} M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1956), 1st ed.
^{f} From SFI potential which has $V_m(r) = -0.5152$ Ry outside the APW spheres.
^{g} Reference 8.

[15] J. W. Taylor and P. L. Hartman, Phys. Rev. **113**, 1421 (1959).
[16] E. A. Taft and H. R. Philipp, J. Phys. Chem. Solids **3**, 1 (1957).
[17] A. R. Ruffa, Phys. Rev. **130**, 1412 (1963).

valence energies from the Herman-Skillman HFS atomic program with the HF valence energies of the free ions reflects most of the difference between the spacing of the HFS valence bands and the spacing of Howland's valence bands. Thus if we "correct" the position of the Cl $3p$ band by the amount by which the HFS Cl$^-$ $3p$ energy differs from the experimental ionization potential of Cl$^-$ or the HF Cl$^-$ $3p$ energy, we obtain a band gap which is in excellent agreement with experiment.

If, however, we lower the Cl $3p$ band by the difference of 1.1 eV between the Cl$^-$ $3p$ HFS energy and the electron affinity of Cl,[18] the work function is increased to 10.2 eV. One can come close to resolving this difficulty by supposing that the final state of the crystal in the photoemission process involves a localized hole rather than a Bloch hole. The energy of the final state is then lower than the Bloch-hole state by the energy of interaction of a hole localized on a Cl$^-$ site with the electronic polarizability of the neighboring ions.[19] A value of 1.3 eV for this energy has been obtained assuming a point-charge hole and taking the induced polarizations to be point dipole moments.[20] The fact that 93% of the charge of the APW Γ_{15} Cl $3p$ state is within the Cl APW sphere lends some support to this model. If the same correction is to be applied to the energy of the system when an electron-hole pair is formed, it is then necessary to raise the bottom of the conduction band by the same amount to obtain the correct band gap.

C. Character of the Conduction Bands

In view of a recent attempt to identify certain features of the optical absorption and reflectivity spectra with direct optical transitions between band states, assuming nearly free-electron conduction bands,[21] it is appropriate to begin a discussion of the conduction bands by comparing them with the free-electron bands. The state at the bottom of the conduction band is of Γ_1 symmetry as in the free-electron case and in the neighborhood of Γ_1 the band is of the form

$$E(\mathbf{k}) = E(\Gamma_1) + k^2/m^*. \tag{10}$$

By fitting the energies of the Γ_1 and $\Delta_1(0\frac{1}{2}0)\pi/a$ states to this form, an approximate value of 0.58 electron masses is obtained for the effective mass m^* from the self-consistent bands of Fig. 1. A fourth-order fit including also the point $(010)\pi/a$ yielded a value of 0.55 for m^* at Γ_1, suggesting that this fitting procedure is reasonably reliable in this case. The value of m^* obtained in this way also seems insensitive to the differ-

[18] M. Born and K. Huang, *Dynamics of Crystal Lattices* (Oxford University Press, New York, 1956), 1st ed.
[19] T. I. Kucher and K. B. Tolpygo, Fiz. Tver. Tela **2**, 2301 (1960) [English transl.: Soviet Phys.—Solid State **2**, 2052 (1961)].
[20] T. I. Liberberg-Kucher, Zh. Eksperim. i Teor. Fiz. **30**, 724 (1956) [English transl.: Soviet Phys.—JETP **3**, 580 (1956)].
[21] J. C. Phillips, Phys. Rev. **136**, A1705 (1964).

ences among the potentials mentioned in Secs. III and IV.

Additional contrast between the conduction bands in KCl and the free-electron bands can be seen in Table IV, where the free-electron and APW band energies relative to the Γ_1 level are given at the three points of highest symmetry. Only for those states such as Γ_1, $\Gamma_{15'}$, $X_{4'}$, and $X_{5'}$, whose wave functions are dominantly s- or p-like, is there reasonable agreement between the free-electron and APW energies. This can be understood qualitatively in terms of a pseudopotential formalism[22] in which the conduction states having the same symmetry as occupied states experience a repulsive potential in place of the orthogonality requirement which forces the s and p parts of the wave functions of these states to have nodes inside the ionic spheres. In this formalism, the effective wave functions of such states are "smooth functions," perhaps similar to plane waves. From the fact that the energy of the Γ_1 state is 0.26 Ry on the APW scale, it would appear that the average over the unit cell of the pseudopotential for such states would be of the order of 0.26 Ry higher than the average HFS potential outside the APW spheres. For the states which are orthogonal to the occupied states by symmetry, the pseudopotential is just the HFS potential which has an average value of about -0.75 Ry on the APW scale. This suggests that the d-like states such as $\Gamma_{25'}$, Γ_{12}, and X_3 should be on the order of one rydberg below the corresponding free-electron states.

The lower conduction bands presented here are in qualitative agreement with those of a recent approximate OPW calculation although the band gap in the latter calculation was 9.8 eV.[23] Thus the proximity of the d-like bands to the bottom of the conduction band, made plausible by the above arguments, is established by direct calculation and is the essential difference between the band structure presented here and that assumed by Phillips.[21]

The complexity of the low-lying conduction bands is such that one can have little hope of identifying optical transitions between valence and conduction bands reliably. This difficulty is compounded by the fact that the dominant features of the optical data are attributed to excitons and other collective excitations[24] and by the sensitivity of the conduction bands to the potential used to calculate them. If, for example, the average potential outside the APW spheres were arbitrarily raised in order to bring the Γ_{15}-Γ_1 spacing up to 7.5 eV, the d-like states would move several tenths of an electron volt closer to the bottom of the conduction band since there is less probability density outside the spheres in the d states than in the Γ_1 state. Thus the rapid rise in the

[22] J. C. Phillips and L. Kleinman, Phys. Rev. 116, 287 (1959).
[23] S. Oyama and T. Miyakawa, J. Phys. Soc. Japan 20, 624 (1965); 21, 868 (1966).
[24] H. R. Philipp and H. Ehrenreich, Phys. Rev. 131, 2016 (1963).

TABLE IV. The free-electron energy, equal to k^2 in atomic units, and the APW band energies relative to the APW Γ_1 energy.

Symmetry	$\mathbf{k}a/\pi$			k^2	$E(\text{APW}) - E(\Gamma_1)$
Γ_1	0	0	0	0.0	0.0
$\Gamma_{25'}$	2	2	2	0.85	0.20
Γ_{12}	0	4	0	1.13	0.23
$\Gamma_{2'}$	2	2	2	0.85	0.61
$\Gamma_{25'}$	4	0	4	2.27	0.70
Γ_{15}	2	2	2	0.85	0.95
X_3	-2	0	2	0.57	0.09
X_1	0	2	0	0.28	0.21
X_2	-4	2	0	1.42	0.28
X_1	-2	0	2	0.57	0.32
$X_{4'}$	0	2	0	0.28	0.21
X_5	-4	2	0	1.42	0.36
$X_{5'}$	-2	0	2	0.57	0.63
X_3	2	4	2	1.70	0.66
$L_{2'}$	1	1	1	0.21	0.18
L_1	1	1	1	0.21	0.21
L_3	-1	-1	3	0.78	0.31
L_3	-1	3	3	1.35	0.38
L_1	-1	-1	3	0.78	0.44
$L_{3'}$	-1	-1	3	0.78	0.45

density of states at the transition from s-like states near Γ_1 to d-like states may correspond to the beginning of a rapid rise in the hole-electron recombination luminescence as a function of incident photon energy which is found to occur at 8.1 eV.[25]

VI. CALCULATION OF THE COHESIVE ENERGY

Within the HFS approximation it is possible to obtain an expression for the total energy of the system involving only the one-electron energies, one-electron potentials, and the total charge density. We begin by considering the expectation value of the Hamiltonian of the crystal with the nuclei fixed, for a state represented by a Slater determinant of the occupied Bloch states ϕ_s determined in the band calculation. Since all ϕ_s satisfy the equation

$$-\nabla^2\phi_s = [E_s - V(\mathbf{r})]\phi_s \qquad (11)$$

for the same potential $V(\mathbf{r})$, they are orthogonal and the total kinetic energy is therefore

$$\langle T \rangle = \sum_s E_s - \int \rho_e(\mathbf{r}) V(\mathbf{r}) d^3r, \qquad (12)$$

where

$$\rho_e(\mathbf{r}) \equiv \sum_s \phi_s^*(\mathbf{r})\phi_s(\mathbf{r}). \qquad (13)$$

The Coulomb terms in the total energy are

$$\frac{1}{2}\int \rho_e(\mathbf{r}) V_{\text{coul}}'(\mathbf{r}) d^3r + \frac{1}{2}\sum_\alpha V_\alpha' Z_\alpha,$$

where $V_{\text{coul}}'(\mathbf{r})$ is the Coulomb part of the HFS potential, $V'(\mathbf{r})$, derived from $\rho_e(\mathbf{r})$ and the nuclear charges,

[25] T. Timusk and W. Martienssen, Phys. Rev. 128, 1656 (1962).

and V_α' is the electrostatic potential at the site of the αth nucleus, of charge Z_α, produced by all other charges. The exchange term,[26]

$$-\tfrac{1}{2}\sum_s \int \phi_s^*(1)\phi_s(1)\left[\sum_{s'} \delta m_{\sigma s},m_{\sigma s'}\frac{\phi_{s'}(1)}{\phi_s(1)}\right.$$

$$\left.\times\int \phi_{s'}^*(2)\frac{2}{r_{12}}\phi_s(2)d^3r_2\right]d^3r_1,$$

involves the charge density of the state s multiplied by the s-dependent exchange potential which is replaced by the "$\rho^{1/3}$" potential to obtain the HFS approximation from the Hartree-Fock equations. If we make this same replacement in the above exchange energy, the sum on s may be performed and the total energy becomes

$$\langle H\rangle=\sum_s E_s-\int \rho_e(\mathbf{r})V(\mathbf{r})d^3r+\frac{1}{2}\int \rho_e(\mathbf{r})V'(\mathbf{r})d^3r$$

$$+\tfrac{1}{2}\sum_\alpha V_\alpha'Z_\alpha,\quad(14)$$

where $V'(\mathbf{r})$ is equal to $V(\mathbf{r})$ only if the band calculation is self-consistent in the HFS sense. Equation (14) can also be applied to obtain the total energy of a free ion, $\langle H\rangle_n$, provided that all the free-ion orbitals satisfy Schrödinger's equation with the same potential.[27] This condition is satisfied by the results of the Herman-Skillman program mentioned above. The cohesive energy per unit cell in the HFS approximation is then

$$U=\lim_{N_B\to\infty}\left\{\frac{\sum\limits_s E_s}{N_B}-\int \rho_e(\mathbf{r})V(\mathbf{r})d^3r\right.$$

$$\left.+\frac{1}{2}\int \rho_e(\mathbf{r})V'(\mathbf{r})d^3r+\tfrac{1}{2}\sum_n V_n'Z_n\right\}-\sum_n \langle H\rangle_n,\quad(15)$$

where the integrals and the sums on n are taken over the unit cell and N_B is the number of points in the Brillouin zone over which the one-electron energies and charge densities are summed. Since most of the terms in Eq. (15) are $\gg U$, it is appropriate to divide the region of integration into parts inside and outside the APW spheres and to make use of the similarity between the free-ion and crystal charge densities and potentials within the spheres. Making use also of the close relationship between the band energies and the free-ion one-electron energies shown in Table III, we can express U in terms of quantities which are $\lesssim U$ and thus the accuracy required for integrations involved is easily attained. A further simplification of the calcula-

[26] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. II.

[27] This has already been done in relativistic atomic HFS calculations. See E. C. Snow, J. M. Canfield, and J. T. Waber, Phys. Rev. **135**, A969 (1964).

TABLE V. Approximate corrections are added to the calculated cohesive energy and the estimated uncertainties in these corrections are given (in Ry).

Correction for replacing V' by V_m'	-0.0147 ± 0.002
Convergence correction	-0.0206 ± 0.005
Correction for summation on finite grid of points in Brillouin zone	$-0.019\ \pm0.008$
Uncorrected cohesive energy	-0.4600
Corrected cohesive energy	$-0.514\ \pm0.015$

tion is obtained by replacing $\rho_e(\mathbf{r})$, $V'(\mathbf{r})$, and $V(\mathbf{r})$ by their "muffin tin" averages $\rho_{em}(\mathbf{r})$, $V_m'(\mathbf{r})$, and $V_m(\mathbf{r})$ so that only radial integrations need by performed. An approximate correction of the error thereby introduced in the case of KCl is given in Table V.

One desirable property of a total energy formula is that the calculated energy be fairly insensitive to the assumed wave function of the system. In this case, the assumed wave function is determined by the potential $V(\mathbf{r})$. A change $\delta V(\mathbf{r})$ in this potential produces changes δE_s in the one-electron energies and a change $\delta\rho_e(\mathbf{r})$ in the total charge density which in turn produces a change $\delta V'(\mathbf{r})$ in $V'(\mathbf{r})$. From Eq. (14), the associated change in the total energy is

$$\delta\langle H\rangle=\delta\sum_s E_s-\int \rho_e(\mathbf{r})\delta V(\mathbf{r})d^3r$$

$$-\int \delta\rho_e(\mathbf{r})[V(\mathbf{r})-V'(\mathbf{r})]d^3r$$

$$+\frac{1}{2}\int [\rho_e(\mathbf{r})\delta V'(\mathbf{r})-\delta\rho_e(\mathbf{r})V'(\mathbf{r})]d^3r$$

$$+\tfrac{1}{2}\sum_\alpha \delta V_\alpha'Z_\alpha.\quad(16)$$

The first two terms in Eq. (16) cancel in first-order perturbation theory while the third is quite small if $V(\mathbf{r})$ is nearly self-consistent in the HFS sense. In the remaining terms, the Coulomb interactions of $\delta\rho_e(\mathbf{r})$ with $\rho_e(\mathbf{r})$ and the nuclear charges come in twice and with opposite signs. Therefore only the exchange terms remain and from the binomial expansion of $[\rho_e(\mathbf{r})+\delta\rho_e(\mathbf{r})]^{1/3}$ we have to first order

$$\delta V_{\text{exch}}'(\mathbf{r})=\frac{\delta\rho_e(\mathbf{r})}{3\rho_e(\mathbf{r})}V_{\text{exch}}'(\mathbf{r}),\quad(17)$$

so that

$$\delta\langle H\rangle\approx-\frac{1}{3}\int \delta\rho_e(\mathbf{r})V_{\text{exch}}'(\mathbf{r})d^3r.\quad(18)$$

Thus as self-consistency is approached, $\langle H\rangle$ does depend linearly on the charge density, but only through a term involving the exchange potential.

The two principal sources of uncertainty in the numerical calculation are the truncation of the APW basis set needed to obtain a finite secular equation, and the use of a sum over a finite grid of points in the

Brillouin zone to approximate the limit in Eq. (15). The error in U introduced by these approximations is given by Eq. (16) without the term involving $\delta V(\mathbf{r})$, and by the same arguments as were used to obtain Eq. (18) this error is

$$\delta U = \delta \sum_s E_s - \frac{1}{3} \int \delta \rho_e(\mathbf{r}) V_{\text{exch}}'(\mathbf{r}) d^3r$$

$$- \int \delta \rho_e(\mathbf{r}) [V(\mathbf{r}) - V'(\mathbf{r})] d^3r, \quad (19)$$

where the δ quantities are the errors introduced by the above approximations.

In the calculation on KCl, $V(\mathbf{r})$ was the "muffin tin" potential used for the second iteration of the band calculation. The error introduced by using $V_m'(\mathbf{r})$ and $\rho_{em}(\mathbf{r})$ in place of $V'(\mathbf{r})$ and $\rho_e(\mathbf{r})$ was corrected approximately using $V_1(\mathbf{r})$ from the SFI potential and a Fourier series for $\rho_e(\mathbf{r})$ in the region outside the spheres obtained from the APW wave functions. The summation over the Brillouin zone for the K^+ and Cl^- $3s$ and $3p$ valence bands was done on a cubic grid of 32 points weighted equally. The error introduced by this procedure was estimated by replacing the equal weights by a set of weights based on Simpson's rule. Since the wave functions of the core states are well represented by Bloch sums of nonoverlapping functions, only the integration of the radial Schrödinger equation inside the spheres was needed to obtain the core charge densities and one-electron energies. The error produced by cutting off the APW basis set at wave vectors having square magnitude equal to 55 in units of $(\pi/a)^2$ was estimated by recalculating some of the Bloch states with larger basis sets. In Table V, these corrections are listed together with their estimated uncertainties.

As a check on the sensitivity of the cohesive energy to the wave function assumed, the difference between the values of U from the first and second iterations was calculated from Eq. (18). This difference, $U(1) - U(2)$, was found to be 0.032 Ry or about 6% of the cohesive energy.

The value for the self-consistent-field part of the cohesive energy obtained in Table V is equivalent to -161 ± 5 kcal/mole and compares very favorably with the value of -160 ± 3 kcal/mole obtained by Howland's treating the exchange term exactly in the tight-binding approximation.[8] To compare with experiment, it is appropriate to add a zero-point energy of 1 kcal-mole obtained from the Debye model, and a van der Waals energy of attraction between the ions of -7.6 kcal/mole.[18] Thus the calculated cohesive energy becomes -168 ± 5 kcal/mole as compared with the value of -167.8 ± 2 from the Born-Haber cycle.[18]

VII. CONCLUSION

On the basis of the above investigation, it appears that no great enhancement of the accuracy of energy-band calculations is to be obtained by improving upon the APW method for solving the one-electron problem because of the uncertainty in the periodic potential used. If, however, a more reliable prescription for this potential were to be found, then the refinements of the APW method discussed here would be significant. We have also seen that the iteration of the band calculation to self-consistency and the calculation of the cohesive energy from the energy band results are feasible, at least within the HFS approximation. The comparison of the calculated band structure of KCl with experiment, while limited, is quite satisfactory in view of the intrinsic limitations of the theory.