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Theoretical X-Ray Scattering Factors Based on Energy-Band Structure

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The energy bands for the $3d$ and $4s$ states of copper and the $2p$ states of aluminum are calculated by the augmented-plane-wave method. The crystal charge density is calculated for copper and aluminum and is used to find the scattering factors. For copper these factors are in better agreement with experiment than are those determined from Hartree-Fock atomic calculations. This improvement is shown to be due to the fact that the copper valence-electron charge density is more spread out in the solid than in the atom. The calculated scattering factors are sensitive to the starting crystal potential because of the difficulty of handling exchange in the solid. For aluminum, no improvement over Hartree-Fock scattering factors is realized by performing an energy-band calculation.

I. INTRODUCTION

THE intensity of elastically scattered x rays is proportional to the square of the "scattering factor," which is defined as the Fourier transform of the electronic charge density

$$F(\mathbf{K})=\int_{\text{cell}}\rho(\mathbf{r})e^{i\mathbf{K}\cdot\mathbf{r}}d\mathbf{r}. \qquad (1)$$

Calculations of x-ray scattering factors in solids have always been based on the assumption that the total charge density can be approximated as a sum of *atomic* charge distributions on each lattice site. The total scattering factor F is then a sum of atomic scattering factors f_n multiplied by appropriate phase factors:

$$F\cong\sum_n f_n e^{i\mathbf{K}\cdot\mathbf{r}_n}, \qquad (2)$$

where $\mathbf{K}$ is a reciprocal lattice vector and $\mathbf{r}_n$ the position of the nth atom in the unit cell. This approximation was sufficiently accurate to give good agreement with experiment in most cases.

Recently, however, a good deal of evidence has accumulated to indicate that scattering factors calculated in this approximation, using the most accurate Hartree-Fock atomic scattering factors,[1] are significantly larger than the experimental values in a number of cases, particularly the transition metals.[2-7] The approximation of superposing atomic scattering factors, which is exact for nonoverlapping atomic charge densities, may be quite inaccurate when the atomic charge densities overlap and distort appreciably, as indeed they must in a solid.

The most likely explanation for the discrepancies between theory and experiment in the cases where they are found would seem to be that the outer electronic charge distribution around an atomic site is somewhat more spread out in the solid than in the free atom. The results of Wood[8] and Stern[9] on the band structure of iron indicate such an effect.

The purpose of the present work is to examine the solid-state effects which seem to invalidate the simple approximation for calculating scattering factors. In order to take specific account of the nature of a solid, a scattering factor calculation was performed using solid-state wave functions obtained from an augmented-plane-wave calculation of the energy bands.

II. THE APW METHOD

Wave functions are readily available within the context of the augmented-plane-wave (APW) method, making it especially appropriate for calculating scattering factors. The method was originally proposed by Slater[10] and programmed for the IBM-704 computer by Wood and others.

The basic idea behind the method is that the one-electron wave function in a crystal resembles an atomic function near the atomic sites, but resembles a plane wave in the region far from any nucleus. Therefore, nonoverlapping spheres are chosen, centered on each nucleus in the crystal. The wave function within each sphere is expanded in a series of radial functions times spherical harmonics of angle; in the region outside the spheres the expansion is in terms of plane waves. The function is required to be continuous across the surfaces of the spheres. The potential used is spherically symmetric within each sphere and equal to a constant in the region outside the spheres.

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[1] J. A. Hoerni and J. A. Ibers, Acta Cryst. **7**, 744 (1954); J. Berghius, IJ. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendahl, *ibid.* **8**, 478 (1955); A. J. Freeman, *ibid.* **12**, 261 (1959); L. H. Thomas and K. Umeda, J. Chem. Phys. **26**, 293 (1957); R. E. Watson and A. J. Freeman, Acta Cryst. **14**, 27 (1961); A. J. Freeman and R. E. Watson, *ibid.* **14**, 231 (1961).

[2] B. W. Batterman, D. R. Chipman, and J. J. DeMarco, Phys. Rev. **122**, 68 (1961).

[3] H. Bensch, H. Witte, and E. Wölfel, Z. Physik. Chem. **4**, 65 (1955).

[4] Y. Komura, Y. Tomiie, and R. Nathans, Phys. Rev. Letters **3**, 268 (1959); J. Phys. Soc. Japan **15**, 1434 (1960).

[5] M. J. Cooper, Phil. Mag. **7**, 2059 (1962).

[6] L. D. Jennings, D. R. Chipman, and J. J. DeMarco, Phys. Rev. **135**, A1612 (1964).

[7] D. R. Chipman and L. D. Jennings, Phys. Rev. **132**, 728 (1963).

[8] J. H. Wood, Phys. Rev. **117**, 714 (1960).

[9] F. Stern, Phys. Rev. **116**, 1399 (1959); Bull. Am. Phys. Soc. **5**, 456 (1960).

[10] J. C. Slater, Phys. Rev. **51**, 846 (1937).

The hope in proceeding in this fashion is that since the functions of the expansion are chosen so as to display as closely as possible the actual physical behavior, the convergence of the expansion will be fairly rapid. This is important, since otherwise larger secular equations must be solved, making the calculation rather impractical even on a very large computer.

The true wave function is expanded in a series of these "augmented plane waves":

$$\psi_i=e^{i\mathbf{k}\cdot\mathbf{r}_n}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}(2l+1)i^l\frac{j_l(k_iR_n)}{u_{nl}(R_n)}u_{nl}(|\mathbf{r}-\mathbf{r}_n|)$$
$$\times\frac{(l-|m|)!}{(l+|m|)!}P_l^m(\cos\theta)P_l^m(\cos\theta_i)e^{im(\phi-\phi_i)}$$

inside the nth sphere in the unit cell; here R_n is the radius of the nth sphere, $\mathbf{r}_n$ the position of the nth atom in the unit cell. Outside the spheres

$$\psi_i=e^{i\mathbf{k}_i\cdot\mathbf{r}}.$$

These expressions are derived in Slater's original paper[10]; the functions ψ_i are not orthogonal nor normalized. They do satisfy Bloch's theorem. The matrix elements of the Hamiltonian with respect to these functions are also derived by Slater:

$$\langle\psi_i|H-E|\psi_j\rangle$$
$$=(\mathbf{k}_i\cdot\mathbf{k}_j-E)\delta_{ij}+\frac{1}{\Omega}\sum_n e^{i(\mathbf{k}_j-\mathbf{k}_i)\cdot\mathbf{r}_n}$$
$$\times4\pi R_n^2\left[-(\mathbf{k}_i\cdot\mathbf{k}_j-E)\frac{j_1(|\mathbf{k}_j-\mathbf{k}_i|R_n)}{|\mathbf{k}_j-\mathbf{k}_i|}+\sum_{l=0}^{\infty}(2l+1)\right.$$
$$\left.\times P_l\left(\frac{\mathbf{k}_i\cdot\mathbf{k}_j}{|\mathbf{k}_i||\mathbf{k}_j|}\right)j_l(k_iR_n)j_l(k_jR_n)\frac{u_{nl}'(R_n,E)}{u_{nl}(R_n,E)}\right],$$

where Ω is the volume of the unit cell, P_l the l-order Legendre polynomial, and u_{nl}' the first derivative of u_{nl} with respect to r. Where the wave vector $\mathbf{k}$ is located at a symmetry point in the Brillouin zone, group theory can be used to reduce the size of the secular equation.

In order to calculate scattering factors, it is necessary to find the charge density in the crystal. It is a simple matter to calculate the spherically averaged charge density for a crystal within the framework of the APW method. After the eigenvalues have been obtained, the eigenvectors for the problem can be determined by diagonalizing the coefficient matrix. Thus, the wave function is

$$\Psi=\textstyle\sum_i a_i\psi_i,$$

where the coefficients a_i are now known and the ψ_i are the APW basis functions. From the APW solutions, the following expressions for the charge within the nth sphere and the charge outside the spheres in the plane-wave region may be derived in a straightforward manner[11]:

$$Q_{\mathrm{PW}}^{\mathbf{k},\alpha}=\sum_{i,j}a_ia_j\left[\Omega\delta_{ij}-4\pi\sum_u R_n^2e^{i(\mathbf{k}_j-\mathbf{k}_i)\cdot\mathbf{r}_n}\right.$$
$$\left.\times\frac{j_1(|\mathbf{k}_j-\mathbf{k}_i|R_n)}{|\mathbf{k}_j-\mathbf{k}_i|}\right],$$

$$Q_n^{\mathbf{k},\alpha}=\sum_{i,j}a_ia_je^{i(\mathbf{k}_j-\mathbf{k}_i)\cdot\mathbf{r}_n}\sum_{l=0}^{\infty}(2l+1)j_l(k_iR_n)j_l(k_jR_n)$$
$$\times P_l\left(\frac{\mathbf{k}_i\cdot\mathbf{k}_j}{|\mathbf{k}_i||\mathbf{k}_j|}\right)\frac{1}{u_{nl}^2(R_n)}$$
$$\times\int_0^{R_n}P_{nl}^2(|\mathbf{r}-\mathbf{r}_n|)d(|\mathbf{r}-\mathbf{r}_n|),$$

where $P_{nl}^2=4\pi r^2u_{nl}^2$ and the functions u_{nl} have been determined by numerical integration of Schrödinger's equation for the APW energy eigenvalue. To normalize the radial charge density to one in a unit cell, it is necessary only to divide by the total charge, which is just the sum of Q_{PW} and all the Q_n. Thus, the radial charge density in a given sphere corresponding to a given l value, and for the given irreducible representation at given $\mathbf{k}$, is

$$P_{nl}^2(|\mathbf{r}-\mathbf{r}_n|)$$
$$=4\pi\sum_{i,j}a_ia_je^{i(\mathbf{k}_j-\mathbf{k}_i)\cdot\mathbf{r}_n}P_l\left(\frac{\mathbf{k}_i\cdot\mathbf{k}_j}{|\mathbf{k}_i||\mathbf{k}_j|}\right)$$
$$\times\frac{(2l+1)j_l(k_iR_n)j_l(k_jR_n)}{u_{nl}^2(R_n)Q^{\mathbf{k},\alpha}}|\mathbf{r}-\mathbf{r}_n|^2u_{nl}^2(|\mathbf{r}-\mathbf{r}_n|).$$

Also

$$Q_{\mathrm{PW}}^{\mathbf{k},\alpha}+\sum_{n,l}Q_{nl}^{\mathbf{k},\alpha}=1,$$

where

$$Q_{nl}^{\mathbf{k},\alpha}=\int_0^{R_n}P_{nl}^2(|\mathbf{r}-\mathbf{r}_n|)d(|\mathbf{r}-\mathbf{r}_n|).$$

These expressions involve various terms and summations which also occur in the expression for the APW matrix elements. Hence the charge density is readily calculated without extensive additional computation.

The above expressions give charge densities for a given eigenstate. What is needed, however, is the total charge density in the crystal, taking account of all occupied eigenstates. This can be found by calculating eigenvalues and charge densities on a regular mesh in the Brillouin zone and then averaging over all points in the zone which correspond to occupied eigenstates. For

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[11] D. J. Howarth, Phys. Rev. 99, 469 (1955).

a cubic crystal, the obvious choice is to calculate at points on a regular cubic mesh.

The formula for the scattering factor takes a very simple form in the case of a "muffin-tin" charge density, where we have a spherically symmetric charge density within each APW sphere and a constant density in the region outside the spheres. The scattering factor is defined by Eq. (1) as the Fourier transform of the charge density. The "muffin-tin" charge density is the sum of two charge densities with well-known Fourier transforms, the first a constant throughout the unit cell, the other radial in each APW sphere and zero outside the spheres.

The Fourier transform of a constant is a delta function; the transform of the radial densities is just a sum of phase factors times integrals which are analogous to atomic scattering factor integrals. Combining these two results, we obtain this formula for the scattering factors due to a "muffin-tin" charge density:

$$F(\mathbf{K})=\Omega\frac{Q_{\mathrm{pw}}}{V_{\mathrm{pw}}}\delta_{\mathbf{K}}+\sum_n e^{i\mathbf{K}\cdot\mathbf{r}_n}\int_0^{R_n}\Bigg[P_n{}^2(|\mathbf{r}-\mathbf{r}_n|)$$

$$-4\pi|\mathbf{r}-\mathbf{r}_n|^2\frac{Q_{\mathrm{pw}}}{V_{\mathrm{pw}}}\Bigg]j_0(K|\mathbf{r}-\mathbf{r}_n|)d(|\mathbf{r}-\mathbf{r}_n|).$$

Here V_{pw} is the volume outside the APW spheres, P_n is the total radial charge density in the nth sphere. This expression has been programmed for the IBM-7094 computer at the Massachusetts Institute of Technology and uses the charge density results from previous programs to calculate scattering factors.

III. RESULTS

Actual calculations were made on two substances, copper and aluminum. The results of Batterman, Chipman, and DeMarco[2] indicate a discrepancy between experiment and Hartree-Fock theory for copper, iron, and aluminum; Cooper's results[5] indicate a similar discrepancy for chromium. Copper, iron, and chromium are similar metals, distinguished by the number of $3d$ electrons they contain; aluminum is an element of much lower atomic number. Therefore, it seems reasonable to choose a metal from the $3d$ transition group for a calculation, along with aluminum, which presents a somewhat different problem from the others, as is discussed later on.

Of the transition group elements, copper seems the best choice for three reasons. First of all, its $3d^{10}4s^1$ electronic configuration gives a spherically symmetric charge density, so that the use of only the spherically averaged charge density is more acceptable than for an open-shell atom like iron, where the actual charge density is not spherically symmetric.

Second, the band theory has had its most striking success with copper. The band calculations of Segall[12] by the Green's-function method, and of Burdick[13] by the APW method, are in excellent agreement. Furthermore, the theoretical bands agree very well with experiment, particularly with regard to the prediction of the Fermi surface.

Finally, one problem with band calculations is that they are not usually carried to self-consistency, because of the enormous computational effort required. Because of the good agreement of the copper bands with experiment, it can be hoped that the calculation is reasonably self-consistent, even without carrying out several iterations.

The copper bands were recalculated, using a different potential from that of Segall and Burdick. Details of this calculation are presented in Appendix I. The results are almost identical with Burdick's, but the eigenvalues are much better converged, an important point when accurate wave functions are needed. The charge density corresponding to each eigenstate was calculated (calculations were made at the equivalent of 256 points on a cubic mesh throughout the Brillouin zone), and the total charge density calculated by averaging over the occupied states. The scattering factors were calculated or the first eleven Bragg reflections. The values thus computed appear to be no better than the Hartree-Fock values.

Table I compares the valence-electron scattering factors obtained in various ways. The third column contains the values computed from the analytic Hartree-Fock atomic wave functions of Synek,[14] the fourth the band result using the Slater $\rho^{1/3}$ exchange potential.[15] The $\rho^{1/3}$ band scattering factors are slightly lower than the Hartree-Fock for the (111) and (200) reflections, but are generally about 0.1 electron higher for the remaining reflections. The difference between the two is small. The last column contains the experimental values for those reflections measured, along with the probable error limits. The numbers actually listed are the experimental values less the Hartree-Fock core scattering factors, since calculations were done only on

TABLE I. Scattering factors for copper $3d$ and $4s$ electrons.

Vector	HFS	Hartree-Fock	$\rho^{1/3}$ band	Chodorow	Experiment
111	6.43	6.20	6.01	5.67	5.65±0.10
200	5.68	5.43	5.34	4.97	4.47±0.34
220	3.70	3.44	3.49	3.06	3.05±0.30
311	2.79	2.54	2.63	2.22	
222	2.56	2.31	2.40	2.01	2.12±0.10
400	1.81	1.60	1.71	1.38	
331	1.42	1.23	1.34	1.07	
420	1.31	1.13	1.24	0.99	
422	0.95	0.79	0.90	0.71	0.35±0.38
511	0.74	0.61	0.70	0.56	
333	0.74	0.61	0.70	0.56	0.46±0.10

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[12] B. Segall, Phys. Rev. **125**, 109 (1962).

[13] G. A. Burdick, Phys. Rev. **129**, 138 (1963).

[14] M. Synek, Phys. Rev. **131**, 1572 (1963).

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

3*d* and 4*s* bands. The core part can be eliminated, since it should not be seriously affected by the presence of the other atoms in the solid. It is assumed that the Hartree-Fock value is the best for the core, since the core orbitals should remain very much atom-like in the solid.

The experimental values are those of Batterman, Chipman, and DeMarco[2] for the (200), (220), and (422) reflections. The (111), (222), and (333) reflections were measured more precisely by Jennings, Chipman, and DeMarco.[6] It is quite evident that the $\rho^{1/3}$ band scattering factors are no better than the Hartree-Fock atomic values—slightly better for the first two reflections, but slightly worse for the other four experimentally measured reflections. This result is disappointing and somewhat surprising, since it had been thought that the discrepancy between theory and experiment was due to solid-state effects. In an effort to explain this result, some further computations were done.

Because the potential for the copper crystal was derived from a Hartree-Fock-Slater (HFS) atomic potential, using Slater's $\rho^{1/3}$ exchange approximation,[15] it is interesting to compare the above results with scattering factors obtained from such an *atomic* charge density. The HFS values for core scattering factors are slightly higher than the HF values, but not significantly so.

The valence scattering factors are shown in the second column of Table I. They are considerably larger than the corresponding HF values, and the $\rho^{1/3}$ energy band values would represent a considerable improvement over these numbers.

This leads to an interesting conjecture about the disappointing results first obtained. It is well known that one major problem with energy-band calculations is the proper treatment of exchange. The $\rho^{1/3}$ approximation is really rather crude. However, both the HFS and the band calculations make use of it. It can be hoped that to some extent the errors involved in using the approximation are the same in both cases, so that a more realistic estimate of the correction due to the solid-state effects can be realized by comparing the band results with the HFS atomic calculation. It can be seen in Table I that if this difference were subtracted from the Hartree-Fock values, the result would be in considerably better agreement with experiment.

The preceding argument is an attempt to retain the good exchange treatment of the Hartree-Fock method, while still treating the Coulomb potential by the energy-band approach. Although it explains away the disappointing results, this argument may well be subject to question. However, it does serve to point up the problem of the proper treatment of exchange.

Further studies were made of various factors which might affect the results, but none seemed to do so appreciably. Relativistic effects, inaccuracy of the finite (256 points) sum over the Brillouin zone, possible errors in the eigenvalues, and lack of self-consistency—all these possibilities were examined and discarded as being unable to account for the fact that the calculated scattering factors are still much too large.

It seems necessary to fall back on the idea of difficulties with the treatment of exchange. As previously stated, the rather crude $\rho^{1/3}$ exchange approximation is used only because it is so difficult to consider exchange in any exact manner. This would also restrict the validity of any iterative scheme to achieve self-consistency in which the $\rho^{1/3}$ approximation was used. It is well known that this method overestimates the exchange, especially at small and large distances from the nuclei.[16] Since the effect of exchange is to cause the wave function to contract, this will give scattering factors which are too large. This could well be the source of the difficulty. Some better way of handling exchange in the solid is needed. Even if such a method is not available, it would be desirable at least to show that it is in fact the exchange problem which makes it impossible to obtain agreement with experiment.

There is a different method available for handling exchange, at least for copper, in the form of the Chodorow potential, first used by Chodorow[17] in calculating copper bands at several points of high symmetry in the zone. This is in fact the potential used by Burdick[13] in doing the copper bands; it was not used in this calculation because a better method seemed to be available for constructing a potential (see Appendix I). It is a semiempirical potential which gives Hartree-Fock 3*d* wave functions when used in a simple Hartree atomic calculation. As such it takes account of exchange in a semiempirical way, since it is designed to give the right atomic wave function. Practically all the contribution to the valence scattering is due to 3*d* bands, so this is an appropriate choice.

This potential was therefore used for a calculation of the copper energy bands. The calculation is not identical with Burdick's, mainly because better convergence of the eigenvalues was demanded, to within 0.0002 Ry. The bands were calculated at only 32 points in the zone, since tests on the $\rho^{1/3}$ band calculation showed that the difference in scattering factors is negligible if only 32 instead of 256 points in the zone are used. The eigenvalues are almost identical with Burdick's, none differing by as much as 0.01 Ry. Charge density and scattering factors were calculated as before. The results in this case are considerably better than the Hartree-Fock atomic values and are in excellent agreement with experiment.

The Chodorow-potential scattering factors are tabulated in column five of Table I, where they may be compared with those calculated by other methods. The values are everywhere better than the atomic Hartree-

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[16] D. R. Hartree, Phys. Rev. **109**, 840 (1958).

[17] M. I. Chodorow, Ph.D. thesis, Massachusetts Institute of Technology, 1939 (unpublished).

TABLE II. Scattering factors for aluminum.

Vector	Experiment	Hartree-Fock core	Hartree-Fock total
111	8.63±0.14	8.87	8.97
200	8.25±0.14	8.54	8.51
220	7.09±0.13	7.39	7.34
311	6.42±0.12	6.68	6.67
222	6.19±0.13	6.47	6.47
400	5.48±0.15	5.72	5.76
331	4.96±0.14	5.25	5.31
420	4.67±0.13	5.11	5.18
422	4.38±0.15	4.61	4.68
511	4.00±0.16	4.28	4.35
333	4.00±0.16	4.28	4.35

Fock and the other energy band values. Of the six experimental values, the Chodorow values lie within experimental error of four and barely miss the other two. For the higher order reflections the difference between Chodorow and Hartree-Fock values is small, as would be expected since the factors for these reflections are affected only by the charge density close to the nuclei where the wave functions are very much atom-like.

The other substance for which calculations have been made is aluminum. The problem in aluminum is a special one as can be seen in Table II. Not only are the Hartree-Fock scattering factors[18] larger than the experimental factors, but even the Hartree-Fock values for the neon core *alone* are larger than the *total* experimental scattering factor. No band calculation for the $3s$ and $3p$ valence electrons alone could account for the sizable discrepancy, since the valence electrons contribute almost nothing (<0.1 electron) to the scattering factors. The only possibility seems to be a sizable redistribution of the atomic core electrons on passing into the solid. This is not likely, but perhaps more likely than in elements of higher atomic number. Therefore, the core bands might be calculated to find such a redistribution.

Therefore, the aluminum $2p$ bands were calculated, the $2p$ atomic state being the highest in energy of the core states. The bands are extremely narrow, since they lie about 5 Ry below the Fermi energy. The charge density and scattering factors were calculated, but there was no appreciable difference between these values and the atomic Hartree-Fock or HFS values, a result which is not surprising, of course.

IV. DISCUSSION

From the results presented here, it is clear that it is possible to get reasonable agreement with the experimental scattering factors in copper by calculating them on the basis of an energy-band calculation for the outer electrons. There are several difficulties with this treatment, however, and this discussion attempts to show that the difficulties do not negate the value of the results.

First of all, there is every reason for confidence in the experimental values of the scattering factors. The measurements of Batterman, Chipman, and DeMarco,[2] performed on powders, have been confirmed in a number of ways. Jennings, Chipman, and DeMarco[6] measured the scattering from single crystals of copper and confirmed those results. Bensch, Witte, and Wölfel[3] confirm the aluminum results, Komura *et al.*[4] confirm the iron results, and Cooper[5] reports a similar disagreement with Hartree-Fock values in the case of chromium. And finally, there is the evidence of Chipman and Jennings,[7] on rare gases, a case where free-atom results should be valid. Their results agree with Hartree-Fock calculations; moreover, the small-angle scattering factors extrapolate at zero angle to the atomic number, as they should. Thus there is good reason to believe that a real disagreement exists, well outside the experimental uncertainty, between the experimental x-ray scattering factors in copper, iron, aluminum, and chromium, and the best available atomic Hartree-Fock calculations of these factors.

Secondly, there is good reason to trust the energy-band eigenvalues, though there may be some question with regard to the wave functions. Calculations of Burdick[13] on copper, Wood[19] on iron, and numerous others, have demonstrated the validity of the APW method. Slater has discussed the method in detail.[20] In the present case, a standardized way of choosing the crystal potential, based on the $\rho^{1/3}$ method for exchange, reproduces Burdick's copper energy bands very closely. The use of the Chodorow potential, with more stringent convergence requirements than Burdick demanded, also reproduces his bands well. The copper and aluminum eigenvalues have been computed as accurately as possible, with convergence requirements far more stringent than usual, in order to minimize any errors in the wave function due to lack of convergence. The eigenvalues are therefore converged to within 0.0002 Ry.

The present results are somewhat unsatisfactory, even though good agreement with experiment has been obtained in the case of copper scattering, using the energy bands calculated from the Chodorow potential. The difficulty is the fact that the wave functions and hence the scattering appear to be rather sensitive to the potential used, even though the bands themselves are not. For aluminum the discrepancy between theory and experiment cannot be accounted for by band theory.

The copper results are summarized in Table I. It is apparent that the band calculation using the Chodorow potential leads to much better agreement with experiment than the calculation using the $\rho^{1/3}$-type potential. This sensitivity of the wave function to the assumed potential is rather discouraging at first sight. It is precisely the fact that the energy-band eigenvalues are not very sensitive to the potential that makes a band calcu-

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[18] A. J. Freeman, Acta Cryst. **12**, 261 (1959).

[19] J. H. Wood, Phys. Rev. **126**, 517 (1962).

[20] J. C. Slater, M.I.T. Solid-State and Molecular Theory Group Quarterly Progress Report No. 51, 1964, p. 14 (unpublished).

lation a reliable and useful procedure. This sensitivity of the wave function is, of course, an example of the general feature of variational calculations that a first-order error in the wave function gives rise to only a second-order error in the energy so that good eigenvalues may be obtained with somewhat poorer wave functions. It might be concluded that wave functions of the required accuracy cannot be obtained reliably from a band calculation, that the scattering factors are subject to an error larger than the discrepancy to be explained, and that therefore the procedure is essentially meaningless.

However, such a conclusion is rather too pessimistic. While the sensitivity of the wave function to the potential is somewhat dismaying, it does not negate the result that agreement between energy-band scattering factors and experiment can be found. The difficulty with the band calculation appears to be the question of choosing an exchange potential, as discussed previously. Careful consideration of the results leads to the encouraging conclusion that either potential leads to good agreement with experiment, if the exchange effect can be cancelled out and the effect of going from atom to solid isolated.

It has already been remarked that the band results using the $\rho^{1/3}$ potential show little improvement over the Hartree-Fock values. This point is further demonstrated in Fig. 1, where the radial charge densities for the valence electrons are compared. There is little difference between the two except at large distances, where the effect on the scattering factors is small. It is the contention of this discussion that this is not the comparison which should be made, that it is the least meaningful when exchange effects are uncertain.

In an attempt to cancel out the exchange effects, the $\rho^{1/3}$-type band calculation should be compared, not with Hartree-Fock results, but with an atomic calculation also based on the $\rho^{1/3}$ exchange approximation. The errors in using this approximation should be similar in both cases, making it likely that any differences will be due to the changed environment of the solid over the atom, which is of course the effect of interest. It is clear from Table I that the difference is sizable, and in the correct direction, though because of the exchange problem the actual values of the calculated scattering factors are still too high. In Fig. 2 it is shown that the charge density in the solid is more spread out than in the atom.

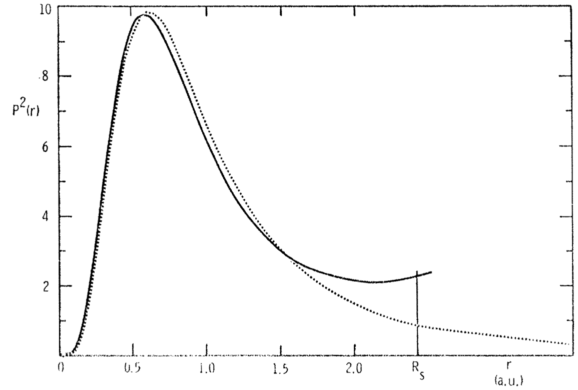

FIG. 1. Copper radial charge density (3*d* and 4*s*) (a.u. = atomic units). "Dotted curve is Hartree-Fock, solid curve $\rho^{1/3}$ band."

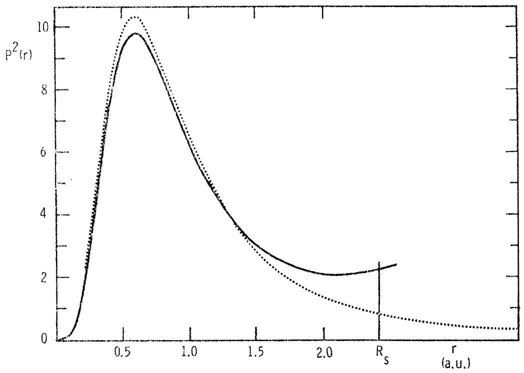

FIG. 2. Copper 3*d* and 4*s* radial charge density ($\rho^{1/3}$ comparison). "Dotted curve is HFS atomic, solid curve is $\rho^{1/3}$ band."

The comparison of the band scattering factors using the Chodorow potential with the Hartree-Fock atomic results is again appropriate. The Chodorow potential reproduces Hartree-Fock 3*d* wave functions, so it is a sort of Hartree-Fock potential. The comparison shown in Table I is again favorable, the absolute values also being good. Reference to Fig. 3 shows the considerably more spread-out charge density in the solid again in this case. Clearly then the difference in scattering factors is due to the spreading out of the charge upon entering the solid, with more charge concentrated at large distances from the nuclei where it makes a considerably smaller contribution to the scattering.

This spreading out of the charge density is the expected result. The overlap of atomic potentials on neighboring lattice sites will certainly tend to lower the potential in the region near the sphere radius. This lowered potential will cause more charge to be found in this region, thus giving rise to a more spread-out charge density. Indeed, previous results of Wood[8] and Stern[9] point to just such a spreading of the wave function for solid iron.

In line with this argument, it is not surprising that it is the transition (and noble) metals which reveal a disagreement with the Hartree-Fock values, nor is it surprising that the attempt to explain the similar problem in aluminum fails completely: The real problem with aluminum is that one would not expect a discrepancy at all. The charge density of the outer valence electrons, such as the copper 4*s* or the aluminum 3*s* and 3*p*, is concentrated at large distances from the nuclei. It will be considerably modified in the solid, but at the distances in question its effect on the scattering factor is quite small, and the effect of the change is negligible.

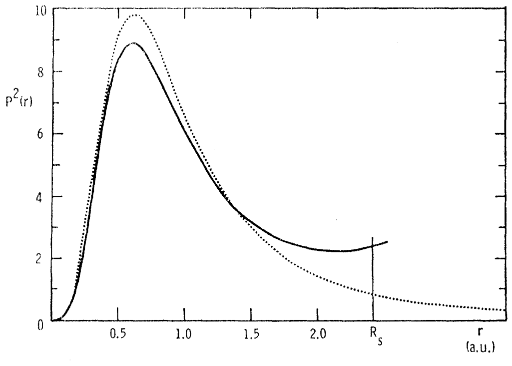

FIG. 3. Copper 3*d* and 4*s* radial charge density. Dotted curve is Hartree-Fock, solid curve is band (Chodorow potential).

On the other hand, core electrons, like the aluminum 2*p*, lie several rydbergs below the Fermi energy, and tend to be concentrated rather close to the nuclei. Thus, they see mainly the atomic potential, their wave functions not being appreciable in the outer region where the potential is modified in the solid. As a consequence their charge density and their contribution to the scattering are little changed on entering the solid.

The situation required for an appreciable difference in the scattering factors between free atom and solid is that of an orbital which extends out far enough from the nucleus to encounter the modified potential in the solid, but which has sufficient concentration near the nucleus so that it will affect the scattering factor. A *d* orbital fits this description very well, while other types do not. A *d* orbital is appreciable close to the nucleus, but tails off slowly and extends out some distance. Thus, the circumstances necessary to produce a discrepancy between free atom and solid scattering factors occur only in the transition series.

Thus the present results on copper are quite reasonable. The *d* electrons are expected to spread out in the solid, and the APW energy-band calculation, in taking account of the differences in the solid, naturally gives much better agreement with experiment than any atomic calculation. The aluminum 2*p* charge density does not spread out; this, too, is the reasonable result for core electrons, and the explanation of the aluminum scattering must lie elsewhere.

The necessity of postulating some as yet unknown mechanism to account for the aluminum discrepancy of course weakens the conclusions of this paper. Any mechanism operative in aluminum might very well also affect the copper results, thereby worsening the apparent agreement obtained in this paper. The spreading out of the 3*d*-electron charge density still seems to be a real effect, but the good agreement with experiment thereby obtained needs to be accepted with caution.

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APPENDIX I: COPPER ENERGY BANDS

Energy-band calculations on copper have been done previously by Burdick,[13] using the APW method, and Segall,[12] using the Green's-function method. Their results agree both with each other and with experiment. However, Burdick's eigenvalues are converged only to within about 0.003 Ry; it seemed best to have better convergence than that, in order to have an accurate wave function. Then, too, there is a more standardized method of choosing the potential[20] than Burdick used.

Copper is face-centered cubic with a lattice constant of 3.6147 Å or 6.83087 a.u.[21] The primitive unit cell contains only one atom. The APW spheres are chosen to be touching with radius 2.4151 a.u. An atomic potential was calculated by the Hartree-Fock-Slater method, which uses the Slater $\rho^{1/3}$ exchange approximation, by means of a computer program due to Herman and Skillman.[22]

The crystal potential is derived by superposing contributions from adjacent sites, using the Löwdin alpha-expansion technique[23] to express the spherically averaged contribution of the charge density on neighboring atoms to the charge density on the atom in question. Exchange was accounted for using the $\rho^{1/3}$ approximation. For copper the first six sets of nearest-neighbor atoms were taken into account. The average potential outside the spheres was calculated by solving the Ewald problem for the constant charge density between spheres, using the results of Slater and DeCicco.[24] This result was corrected for exchange, again using the $\rho^{1/3}$ approximation. A computer program due to DeCicco was used. The discontinuity in the potential at the sphere radius is 0.0897 Ry. This potential is quite different from Burdick's.

Energy eigenvalues for the 3*d* and 4*s* bands of copper

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[21] G. Frohnmeyer and R. Glocker, Acta Cryst. **6**, 19 (1953).

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

[23] P. O. Löwdin, Advan. Phys. **5**, 95 (1956).

[24] J. C. Slater and P. D. DeCicco, M.I.T. Solid-State and Molecular Theory Group Quarterly Progress Report No. 50, 1963, p. 46 (unpublished).

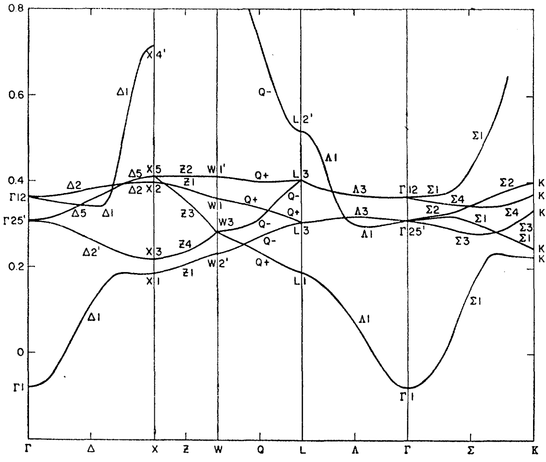

FIG. 4. Energy bands in copper.

were calculated at 20 symmetry points; a graph of the bands is shown in Fig. 4. The bands are practically identical with those of Burdick, differing at most by 0.02 Ry. The relative positions of the various points are quite similar; there seems to be little effect except that the new bands are slightly narrower. Agreement with Segall's bands is also very good, supporting Segall's contention[12] that the band structure is not as sensitive to the potential as was at one time believed.

The question of convergence is twofold. There is the problem of including enough basis functions ("augmented plane waves") in the expansion of the wave function. And there is the additional problem that the expressions for the APW wave functions and matrix elements involve a summation over all values of angular momentum, $l=0$ to $l=\infty$. So there is the second problem of when to terminate this sum. Tests at Γ and Σ points indicated that inclusion of all basis functions whose plane wave portions have $|\mathbf{k}|^2 \leq 54$ (corresponding to about 60 functions), and inclusion of all terms in the l summation up to $l=8$, gave eigenvalues converged within 0.0002 Ry. The Fermi energy was determined to be around 0.55 Ry on the APW scale, and all states of lower energy are occupied.

For the occupied eigenstates, the spherically averaged charge densities associated with each l value and with the plane waves were computed by the methods described. The total crystal charge density was calculated as a weighted average of the individual eigenstate charge densities.

APPENDIX II: THE CHODOROW POTENTIAL

The potential used in the second calculation of the copper energy bands was derived by Chodorow,[17] and was used previously by him and by Burdick[13] and Segall[12] in the calculation of copper energy bands. This is a semiempirical potential derived for the purpose of accounting for exchange in a simple way. It is defined as that potential which when used in a single Hartree equation gives the Hartree-Fock $3d$ wave functions; that is, it gives the right result including exchange correlation without the need of actually constructing an appropriate antisymmetric wave function. The potential is not a true one-electron potential but only a semiempirical one adjusted to make the answer turn out correctly. It will not give very accurate $4s$ eigenvalues, but these contribute very little to the copper scattering so this is unimportant.

Chodorow used the Hartree-Fock $3d$ wave functions and eigenvalue for the free Cu^+ ion as given by Hartree[25] to calculate the potential which reproduces the $3d$ wave function, using the formula

$$V(r)=\nabla^2\psi/\psi+E.$$

To this potential he added a contribution due to the $4s$ function in order to obtain a potential appropriate for neutral copper. The $4s$ function he used was that calculated by Krutter[26] in his early energy-band calculation.

This potential, which is essentially an atomic potential, is used in the present band calculation as the potential within each APW sphere. The value of this potential at the sphere radius is used as the constant potential between spheres.

APPENDIX III: ALUMINUM ENERGY BANDS

Aluminum is face-centered cubic with lattice constant 4.0318 Å or 7.6191 a.u.[27] The primitive unit cell contains one atom. The APW spheres are chosen to be touching, with radius 2.69375 a.u. The potential is chosen in the same way as that of copper, by superposition of Hartree-Fock-Slater atomic charge densities on each lattice site, the summation being taken to include the first six sets of nearest neighbors. The average potential outside the spheres was calculated by solving the Ewald problem.[24] The discontinuity in the potential at the sphere radius is 0.0941 Ry.

Energy eigenvalues for the aluminum $2p$ band were calculated at 20 symmetry points. The band is extremely narrow, over-all width only 0.001 Ry. Eigenvalues are converged to within 0.0001 Ry, using basis functions with plane-wave parts having $|\mathbf{k}|^2 \leq 40$ and terms in the l summation up to $l=8$. The $2p$ band lies well below the Fermi energy, so all states are occupied.

The spherically averaged charge densities associated with each l value and with the plane waves were computed as for copper. The total crystal charge density was taken as the weighted average of the individual eigenstate charge densities.

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[25] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **157**, 490 (1936).

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[27] B. F. Figgins, G. O. Jones, and D. P. Riley, Phil. Mag. **1**, 747 (1956).