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Energy Bands in Copper*

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The general method of obtaining energy bands and wave functions for a face-centered lattice has been outlined. The method has been applied to a copper lattice using a corrected Hartree potential field. The energy bands as a function of the internuclear distance have been calculated. The strong overlapping of the 3*d* band and the 4*s* band is shown. The assignment of electrons to the lowest energy bands leads to a satisfactory explanation of the well-known fact that copper is a good conductor. The various energy bands of the three directions 100, 110 and 111 have been correlated.

WIGNER and Seitz[1] recently introduced the cellular method and applied it to the calculation of the lowest energy state of the conducting electron in a sodium lattice and to the corresponding wave function. Slater[2, 3] extended their ideas to the calculation of higher energy states and wave functions in a body-centered lattice and, in particular, to the higher states of sodium. In this report, the ideas of Wigner, Seitz, and Slater will be extended to a face-centered lattice, in particular to copper.

Wigner and Seitz observed that the potential field acting on an electron in a metal is very approximately spherically symmetric in the neighborhood of a nucleus, so that the Schrödinger equation can be solved by the separation of variables, and numerical integration of the equation for the radial function, as in problems of isolated atoms. They then imagined the crystal to be made up of close-packed cells, one surrounding each nucleus, approximating spheres, but bounded by planes so that they fill all space. If the Schrödinger equation is solved for the electron in one of these cells, subject to certain boundary conditions, then the wave function for the whole lattice can be obtained.

To form the cell for an atom in a face-centered lattice, construct planes which perpendicularly bisect the lines drawn from the nucleus in consideration to its twelve nearest neighbors. The resulting polyhedral cell is a rhombic dodecahedron, as shown in Fig. 1. Each of the twelve faces is a rhombus, and the midpoints of all of the faces are at the same distance from the center.

To solve the Schrödinger equation exactly for the lattice, assuming that the correct potential is given, the procedure would be the following one. The wave equation is solved within the cell, subject to the boundary conditions that the wave function and its normal derivative be continuous in passing across the faces of the cell and satisfy the Bloch[4] condition in passing from one cell to another.

As the exact solution of this problem is impractical at present, it is necessary to proceed by satisfying these conditions approximately. The method actually used will be to solve the Schrödinger equation within the cell, requiring

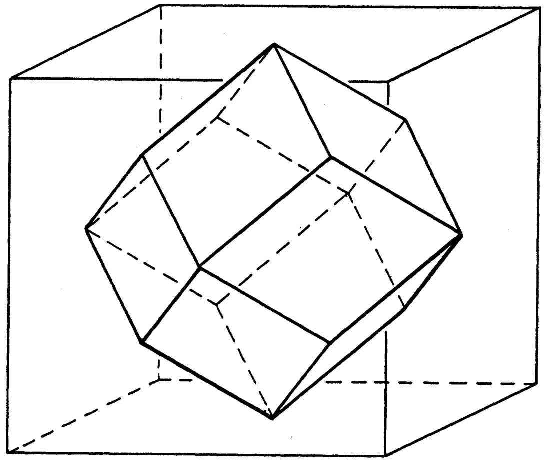

FIG. 1. Polyhedral cell for a face-centered lattice.

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* A preliminary report of these results is given in an abstract, Krutter, Phys. Rev. **47**, 810 (1935).

[1] Wigner and Seitz, Phys. Rev. **43**, 804 (1933).

[2] Slater, Phys. Rev. **45**, 794 (1934).

[3] Slater, Rev. Mod. Phys. **6**, 209 (1934).

[4] For discussion, see Sommerfeld and Bethe, "Electronen theorie der Metalle," *Handbuch der Physik*, Vol. 24, second edition.

continuity of the wave function and its normal derivative at the midpoints of the faces of the cell and taking into account the Bloch condition. In a face-centered lattice, this means fitting boundary conditions at twelve points, all at the same distance from the nucleus.

SECTION 1. STATEMENT OF BOUNDARY CONDITIONS

The distance between an atom and a nearest neighbor is also the perpendicular distance between opposite faces of the cell. Accordingly, the boundary condition is that in going from a point on one of the faces of the cell to a perpendicularly opposite point on the opposite face, the wave function is multiplied by $e^{ik\cdot r}$ where $|r|$ represents the perpendicular distance between faces. The normal derivative is multiplied by $-e^{ik\cdot r}$ in the same process.

U, the wave function, can be split up into an even part U_g and an odd part U_u. U_g is unchanged on going from one point to a diametrically opposite point, whereas U_u changes sign in this process. It is convenient to write U in the form $U=U_g+iU_u$. Then if the function is U_g+iU_u at the midpoint of one face, it is U_g-iU_u at the opposite point. Likewise, if the normal derivative is $U_g'+iU_u'$ at the midpoint of one face, then it is $U_g'-iU_u'$ at the other. It should be noticed that in the case of midpoints, perpendicularly opposite and diametrically opposite denote the same thing.

More explicitly the boundary conditions are:

$$U_g+iU_u=e^{ik\cdot r}(U_g-iU_u),$$
$$U_g'+iU_u'=-e^{ik\cdot r}(U_g'-iU_u'),$$

where the U's are computed at the midpoints of the faces. There are six such pairs of conditions for the six pairs of opposite faces. If the terms U_u, U_u', U_g, U_g' are combined, these equations reduce very conveniently to

$$-U_g'/U_u'=U_u/U_g=\tan(k\cdot r/2).$$

Six pairs of equations of this sort give in all twelve equations to be satisfied.

To satisfy these conditions at the midpoints, it is necessary to build up U_g as a sum of six independent functions and similarly six independent functions for U_u. Now this could be done by the use of any number of spherical harmonics, but we select only the twelve lowest spherical harmonics which should reproduce most correctly the energy bands originating from s, p and d levels in the atomic case. The f band will probably not be obtained correctly, since we are not using all of the f functions. The functions which are chosen are: (1) an s function; (2) three p functions with spherical harmonics x/r, y/r, z/r; (3) the five d functions with spherical harmonics xy/r^2, yz/r^2, zx/r^2, $(3z^2-r^2)/r^2$, $(x^2-y^2)/r^2$; and (4) only three of the seven possible f functions, namely, $x(y^2-z^2)/r^3$, $y(x^2-z^2)/r^3$, $z(x^2-y^2)/r^3$.

Let $R=r/2$ be the distance from the nucleus to the midpoint where the boundary conditions are to be satisfied. This distance is the same for all midpoints in a face-centered lattice, i.e., all the faces are at the same distance from the nucleus. We denote the radial part of the wave functions by s, p, d and f. The wave function built up in this manner is $U=U_g+iU_u$, where

$$U_g=As+2[Bxy+Cz(y-x)+Dz(x+y)+E(3z^2-r^2)+F(x^2-y^2)]d/r^2,$$
$$\begin{aligned}U_u=\sqrt{2}[G(x+y)+H(x-y)+Iz]p/r+2\sqrt{2}[Qz(x^2-y^2)+S\{x(y^2-z^2)+y(x^2-z^2)\}\\ +T\{x(y^2-z^2)-y(x^2-z^2)\}]f/r^3,\end{aligned}$$

x, y, z are the Cartesian coordinates, and $x^2+y^2+z^2=r^2$.

Boundary conditions are to be satisfied at the midpoints corresponding to values of $\sqrt{2}(x/R)$, $\sqrt{2}(y/R)$, $\sqrt{2}(z/R)$ equal to 110, 1–10, 101, 10–1, 011, 01–1. The corresponding values of $\tan(k\cdot R)$ are denoted by K, L, M, N, O, P where $K=\tan(k_x+k_y)R/\sqrt{2}$, $L=\tan(k_x-k_y)R/\sqrt{2}$, etc.

The twelve equations obtained from the boundary conditions are:

$$K[As+(B-2E)d]-2[Gp+Sf]=0, \tag{1}$$
$$L[As-(B+2E)d]-2[Hp+Tf]=0, \tag{2}$$
$$M[As+(-C+D+E+F)d]-[(G+H+I)p+(Q-S-T)f]=0, \tag{3}$$

$$N[As+(C-D+E+F)d]-[(G+H-I)p-(Q+S+T)f]=0, \tag{4}$$
$$O[As+(C+D+E-F)d]-[(G-H+I)p+(-Q-S+T)f]=0, \tag{5}$$
$$P[As+(-C-D+E-F)d]-[(G-H-I)p+(Q-S+T)f]=0, \tag{6}$$
$$As'+(B-2E)d'+2K[Gp'+Sf']=0, \tag{7}$$
$$As'-(B+2E)d'+2L[Hp'+Tf']=0, \tag{8}$$
$$As'+(-C+D+E+F)d'+M[(G+H+I)p'+(Q-S-T)f']=0, \tag{9}$$
$$As'+(C-D+E+F)d'+N[(G+H-I)p'+(-Q-S-T)f']=0, \tag{10}$$
$$As'+(C+D+E-F)d'+O[(G-H+I)p'+(-Q-S+T)f']=0, \tag{11}$$
$$As'+(-C-D+E-F)d'+P[(G-H-I)p'+(Q-S+T)f']=0. \tag{12}$$

There are twelve simultaneous linear homogeneous equations for the twelve coefficients A, B, $\cdots T$ and, as such, they have nonvanishing solutions only when the determinant of the coefficients is zero. This gives a single relation between the six quantities K, L, M, N, O and P in terms of s, s', p, etc., which are obtained from numerical integration of the Schrödinger equation. Other relations arise because of the fact that they are derived from only three independent quantities, the three components of k (k_x, k_y, k_z). If a definite energy and a definite R are chosen, then the values s, p, d and f at the midpoints are fixed. So, if two variables determining the direction of k are arbitrarily assumed, then for each energy, internuclear distance, and wave normal, these equations will determine the electronic momentum k.

The task is then to look for solutions for which K, L, M, N, O, P are real, or, in other words, for real values of k_x, k_y, k_z. Complex values of k would correspond to damped waves in which we are not interested. The regions of energy and internuclear distance where this condition is satisfied will then correspond to the allowed energy bands. Complex values of k will then correspond to forbidden bands.

SECTION 2. SOLUTIONS OF THE EQUATIONS

If we consider propagation in the xy plane, i.e., $k_z=0$, the equations split up into two sets, one containing four equations and the other containing eight equations. The four equation set contains only the constants C, D, I, Q and the corresponding wave function changes sign on reflection through the xy plane. The set of eight equations contains the remaining eight constants, and its corresponding wave function is unchanged on reflection through the xy plane. These two sets of equations can in principle be solved separately. But, for all twelve coefficients to be different from zero demands that the determinant of each of the two sets of equations be zero. This, however, gives one more condition than before. As a result, the equation must be satisfied by letting the coefficients of one of the two sets be zero and satisfying the determinantal equations connected with the other set.

Set I

Let us consider the first set of equations in which C, D, I, $Q\neq 0$ and all the other coefficients are zero.

$$(-C+D)d'+M[Ip'+Qf']=0,$$
$$(C+D)d'+P[Ip'-Qf']=0,$$
$$M(-C+D)d-(Ip+Qf)=0,$$
$$P(C+D)d-(Ip-Qf)=0.$$

$C+D$ and $D-C$ are chosen as new constants. The determinantal equation then becomes

$$\begin{vmatrix} d' & 0 & Mp' & Mf' \\ 0 & d' & Pp' & -Pf' \\ Md & 0 & -p & -f \\ 0 & Pd & -p & -f \end{vmatrix}=0.$$

Solving this, the relation

$$\left[M^2+\frac{1}{2}\frac{d'}{d}\left(\frac{p}{p'}+\frac{f}{f'}\right)\right]\left[P^2+\frac{1}{2}\frac{d'}{d}\left(\frac{p}{p'}+\frac{f}{f'}\right)\right]=\left[\frac{1}{2}\frac{d'}{d}\left(\frac{p}{p'}-\frac{f}{f'}\right)\right]^2$$

is obtained.

This equation can be solved for any direction in the $k_z=0$ plane, so that the electronic momentum can be obtained as a function of the energy. The mechanics of this type of calculation have been given in detail by Slater[2] and will therefore not be repeated.

In the special directions 100 and 110 these equations break down into even simpler ones.

100 direction, $P=O=0$.

Class I: $C=D$; all other coefficients are zero. We obtain the condition $d'=0$. This is a so-called zero width band. In this particular direction, for the energy for which $d'=0$, the electron can have any value of k. The wave function which fits the boundary conditions is then $U=Dyzd/r^2$.

Class II: $C=-D$; $I, Q, C, D\neq 0$; all other coefficients are zero. The condition

$$K^2=-(2d'pf/dp'f')/(p/p'+f/f')$$

is obtained with the corresponding wave function

$$U=4Dxzd/r^2+i\{\sqrt{2}I(z/r)p+2\sqrt{2}Qz(x^2-y^2)f/r^3\}.$$

110 direction, $M=P$.

Class I: $D=I=0$. The relation $M^2=-d'f/df'$ is obtained with a corresponding wave function

$$U=C(y-x)zd/r^2+i\sqrt{2}Qz(x^2-y^2)f/r^3.$$

Class II: $C=Q=0$. The relation is

$$M^2=-pd'/p'd$$

with the wave function

$$U=2Dz(x+y)d/r^2+i\sqrt{2}I(z/r)p.$$

Set II

Although it is possible to solve set I for any direction in the $k_z=0$ plane, the set of eight equations cannot be solved as easily. However, they can be solved in the particular directions 100 and 110. Since this process is simply algebraic manipulation, only the results will be recorded.

100 direction.

Class III: $B\neq 0$, $G=-H$, $S=-T$; all other coefficients are zero.

$$K^2=-(2pd'f/p'df')/(p/p'+f/f'),$$
$$U=Bxyd/r^2+i\{\sqrt{2}Gyp/r+2\sqrt{2}Sy(x^2-z^2)f/r^3\}.$$

Class IV: $S=T$, $F=E$; all other coefficients are zero.

$$K^2=-d'f/df',$$
$$U=E(z^2-y^2)d/r^2+i\sqrt{2}Sx(y^2-z^2)f/r^3.$$

Class V: $3E=-F$, $G=H$; all other coefficients except A are zero.

$$K^2=-(3s'pd'/Sp'd)/(s'/s+d'/d),$$
$$U=As+2E(y^2+z^2-2x^2)d/r^2+i2\sqrt{2}Gxp/r.$$

110 direction. The 110 direction simplifies considerably, but not so completely as the 100 direction. The eight equation set breaks up into two groups.

Class III: H, F, $T\neq 0$; all other coefficients are zero.

$$M^2=-(2pd'f/p'df')/(p/p'+f/f'),$$
$$U=2F(x^2-y^2)d/r^2+i\{\sqrt{2}H(x-y)p/r+2\sqrt{2}T(y-x)(z^2+xy)f/r^3\}.$$

Classes IV and V will be discussed more completely since they are more complicated. Although we will give only one set of equations, it turns out that there are two cases contained in it. Since $M=P$ in the 110 direction, our original eight equations now become five after splitting off Class III. In this set only A, B, E, G and S are different from zero. The equations reduce to

$$\begin{aligned}
As'+(-B-2E)d'&=0,\\
K[As+(B-2E)d]-2(Gp+Sf)&=0,\\
M[As+Ed]-(Gp-Sf)&=0,\\
As'+(B-2E)d'+2K(Gp'+Sf')&=0,\\
As'+Ed'+M(Gp'-Sf')&=0.
\end{aligned}$$

The determinantal equation of this is

$$\begin{vmatrix}
s' & -d' & -2d' & 0 & 0\\
s' & d' & -2d' & 2Kp' & 2Kf'\\
s' & 0 & d' & Mp' & -Mf'\\
Ks & Kd & -2Kd & -2p & -2f\\
Ms & 0 & Md & -p & f
\end{vmatrix}=0.$$

Solving this, the following equation is obtained:

$$\begin{aligned}
&2K^2M^2p'df'(5sd'+s'd)\\
&\quad+K^2d'(pf'+p'f)(5s'd+sd')\\
&\quad+4KMd'(pf'-p'f)(s'd-sd')\\
&\qquad+2M^2d'(pf'+p'f)(2sd'+s'd)+12s'pd'^2f=0.
\end{aligned}$$

This equation is to be solved in conjunction with the relation $K=2M/(1-M^2)$. This is best done graphically as follows: K is plotted as a function of M using the equation $K=2M/(1-M^2)$. The biquadratic equation is then plotted. The intersections of these two curves determine the allowed K and M values, which in turn define k. This is repeated for various energies, which means different coefficients for the biquadratic in K and M since the values of s, s', p, p', etc. depend on the energy.

111 direction

$K=M=O$; $L=N=P=$ zero. It is also possible to treat the original twelve equations for an electron moving in the 111 direction. The equations break down into six groups; the results of the algebraic manipulation are recorded below.

Class I: $C=F$; all other coefficients are zero.

$$d'=\text{zero (zero width band)},$$

while

$$U=C(y-x)(z-x-y)d/r^2.$$

Class II: $B=-2D$, $D=E$, $2G=-I$; all other coefficients except S are zero.

$$\begin{aligned}K^2&=-(4pd'f/p'df')/(3p/p'+f/f'),\\ U&=2D(3z^2-r^2+z(x+y)-2xy)d/r^2\\ &\quad+i\{\sqrt{2}G(x+y-2z)p/r\\ &\qquad+2\sqrt{2}S[x(y^2-z^2)+y(x^2-z^2)]f/r^3\}.\end{aligned}$$

Class III: $Q=-2T$, $C=-F$; all other coefficients except H are zero

$$\begin{aligned}K^2&=-(4pd'f/p'df')/(3p/p'+f/f'),\\ U&=2C(y-x)(x+y+z)d/r^2\\ &\quad+i\{\sqrt{2}H(x-y)p/r\\ &\qquad+2\sqrt{2}T(y-x)(z^2+xy+2z(x+y))f/r^3\}.\end{aligned}$$

Class IV: $D=-E$, $B=-2D$; all other coefficients are zero. $d'=$ zero, while

$$U=D(r^2-3z^2+z(x+y)-2xy)d/r^2.$$

Class V: $B=D$, $G=I$; all other coefficients except A are zero.

$$\begin{aligned}K^2&=-(2s'pd'/sp'd)/(s'/s+d'/d),\\ U&=As+2B(xy+xz+yz)d/r^2\\ &\qquad+i\sqrt{2}G(x+y+z)p/r.\end{aligned}$$

Class VI: $Q=T$; all other coefficients are zero. $f=$ zero.

$$U=iQ\{z(x^2-y^2)+x(y^2-z^2)-y(x^2-z^2)\}f/r^3.$$

Although the twelve equations have been solved for these special cases, it turns out to be simpler, especially for the 100 direction and the 111 direction, to set up our original equations to take into account the symmetry properties of these special directions. Solving with the symmetry property gives very good clues as to how the classes in the various directions are connected to one another.

SECTION 3. APPLICATION TO COPPER LATTICE

Everything, thus far, is applicable to any face-centered lattice. However, to proceed further, it is necessary to confine the discussion to a particular metal. Then given a potential field, it is possible to calculate s, p, d and f, and so be able to determine how the energy varies as a function of k.

In obtaining radial solutions of the Schrödinger equation for a free atom, it is necessary to find solutions which remain finite at infinity. However, in the cellular method, any solution can be used, since only the wave function as far as the cell boundaries is used. The wave function is continued in the next cell in accordance with the Bloch theorem.

Since the correct potential is unknown in the case of copper, it is necessary to take as an approximation a potential field having the correct general characteristics. As a first approximation to the potential field, it seemed advisable to use the Cu^+ field of Hartree.[5] This should be accurate enough to give a general idea of the manner in which the atomic $4s$, $4p$, and higher levels spread into energy bands as the lattice is compressed. In studying the splitting up of the $3d$ level, a slight correction was made. The $4s$ wave function in the field of Cu^+ was calculated, and its contribution to the potential field was determined. The contribution was added to Cu^+ and the contribution of one of the $3d$ electrons, as given by Hartree, was subtracted. This was the potential field used in the calculation of the $3d$ wave functions in the lattice. It is essentially the potential field due to the nucleus and to the $1s^2\cdots 3d^9 4s$ electrons.

Using the potential field discussed, the wave functions were calculated by numerical integration for a set of energy values. In Fig. 2 the energy is plotted as a function of internuclear distance for $s'=0$, $s=0$, $p'=0$, etc. To discuss the energy bands, it is really necessary to plot different sets of energy *versus* internuclear distance curves for different directions of k. The broad features can, however, be discussed by means of this diagram. The $4s$ level at infinite separation spreads into a band, limited by $s'=0$ and $s=0$ as the lattice is compressed. As the

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[5] Hartree, Proc. Roy. Soc. **A141**, 282 (1933); **A143**, 506 (1934).

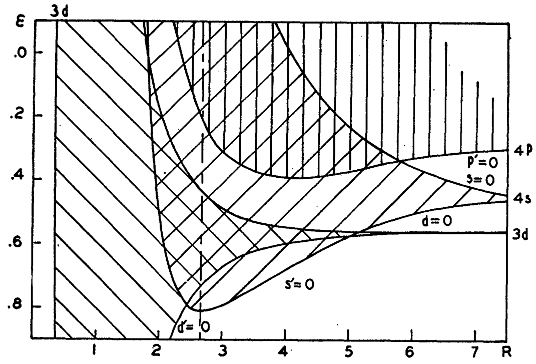

FIG. 2. Energy as a function of internuclear distance. (Energy measured in Rydberg units.)

lattice is compressed still further, the $3d$ band, limited by $d'=0$ and $d=0$, overlaps the $4s$ band, so that at normal separation, denoted by the vertical line in Fig. 2, the $3d$ band and the $4s$ band overlap considerably. Although the normal configuration of the free copper atom is $3d^{10}4s$, as the lattice is compressed the electrons can no longer be described by s or d wave functions, but instead it is necessary to build up the wave function by a combination of s and d wave functions with also a little p and f.

Higher energy bands arising from higher energy atomic levels, overlap in a very complicated fashion. But the approximations used in setting up the problem are not good enough to allow the discussion of the higher bands, even qualitatively. The discussion, will therefore be restricted to the lower energy bands.

The minimum of the $4s'=0$ curve is at $r=2.7$. This is in good agreement with the values of the actual effective internuclear distance obtained in the following manner. If the volume occupied by a copper atom in the actual lattice of spacing 3.61 Angstroms is calculated and from it the radius of the sphere having the same volume, then the radius obtained is 2.66 atomic units. The good agreement must mean that the minimum of the total energy curve must be tied up intimately with the minimum of the $4s'=0$ curve. Wigner and Seitz have pointed out the close connection in the case of sodium. The correlation in copper is not as clear.

The unhatched regions at large internuclear distance represent forbidden energy bands independent of the direction of k. These correspond to the well-known energy gaps in atomic levels. As the lattice is compressed to the actual internuclear distance, the energy gaps depend on the direction of k and are consequently not represented in this diagram.

More information can be obtained if the dependence of k on the energy is discussed. To do this, it is convenient to discuss a momentum space, in which certain zones are formed. If the energy contours are plotted in this space, the gaps in energy come at the boundary of the zones. For a detailed discussion of this, the reader is referred to Slater.[3] It is more convenient in the case of copper to cut through this zone along three particular lines. These are the 100, 110 and 111 directions. Quantitative calculations can be carried out only in the 100, 110 and 111 directions. But these are sufficient to give a general idea of all directions. The first problem that arises is that of accounting for the eleven electrons of the $3d^{10}4s$ normal configuration, when the lattice is compressed. This can be done if the energy *versus* k curves are studied. In Fig. 3, the energy is plotted as a function of k at $R=2.6$ for propagation in the 100 direction. Class V, for this direction, splits into two parts, so that for the range of energy shown, there are six different energy *versus* k curves. The vertical line denotes the boundary of the first momentum

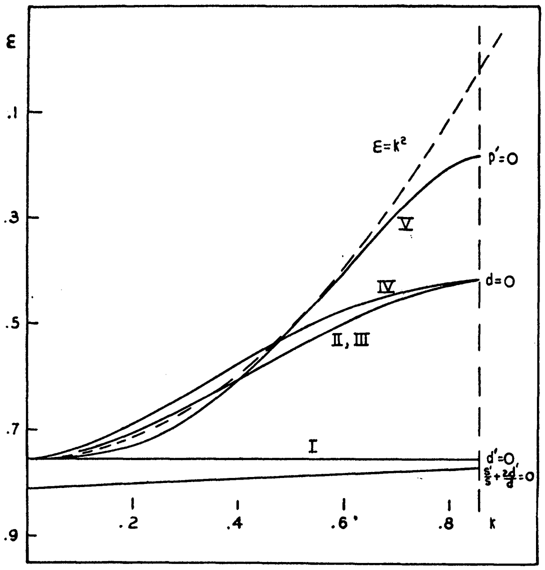

FIG. 3. Energy as a function of momentum for an electron moving in 100 direction. ($R=2.6$.)

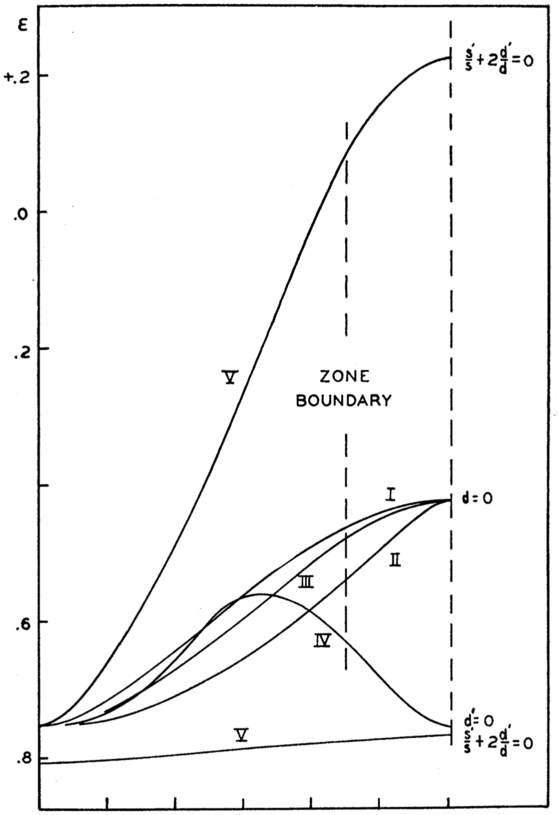

FIG. 4. Energy as a function of momentum for an electron moving in 110 direction. ($R=2.6$.)

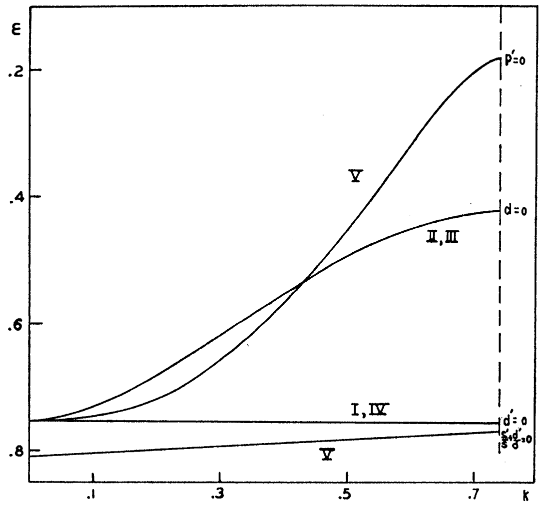

FIG. 5. Energy as a function of momentum for an electron moving in 111 direction. ($R=2.6$.)

zone. The diagram is repeated continuously as the value of k is increased. For higher energies there will be other bands, but these cannot be calculated accurately with the method used thus far.

Now the electrons will fill the bands, first filling the lower ones. Two electrons (degeneracy in spin) are assigned to each band. This leaves the Class V top band only half filled, so that there are 10 electrons filling 5 bands completely. The eleventh electron is in an unfilled band. This electron will play an important part in discussions on conductivity. Electrons in unfilled bands are the conduction electrons. Nonconductors have all filled bands.

In Figs. 4 and 5, the energy as a function of k at $R=2.6$ is plotted for propagation in the 110 and 111 directions. The vertical lines denoting the edge of the zone come at different values of k in each different direction. The assignment of electrons again leaves the bands denoted by Class V only half filled. And again, the Class V band is split in two. This indicates that the bands denoted by Class V in the three directions 100, 110 and 111 are slices of the same band.

The next point of interest is the correspondence between the energy *versus* k curve of the conducting electron and the free electron parabola $\epsilon=k^2$ in atomic units. In the 100 direction (see Fig. 3) the correspondence is very good. In Fig. 6, the top Class V bands are plotted on the same scale for the different directions. It is seen that the slope of the various energy *versus* k curves agree closely with the slope of the free electron

TABLE I.

CLASS	100	110	111
I	$d'=0$	$M^2=-d'f/df'$	$d'=0$
II	$K^2=-2pd'f/d(pf'+fp')$	$M^2=-pd'/p'd$	$K^2=-4pd'f/d(3pf'+fp')$
III	$K^2=-2pd'f/d(pf'+fp')$	$M^2=-pd'f/d(pf'+fp')$	$K^2=-4pd'f/d(3pf'+fp')$
IV	$K^2=-d'f/df'$	See Graph	$d'=0$
V	$K^2=-3s'pd'/p'(ds'+2d's)$	See Graph	$K^2=-2s'pd'/p'(s'd+sd')$

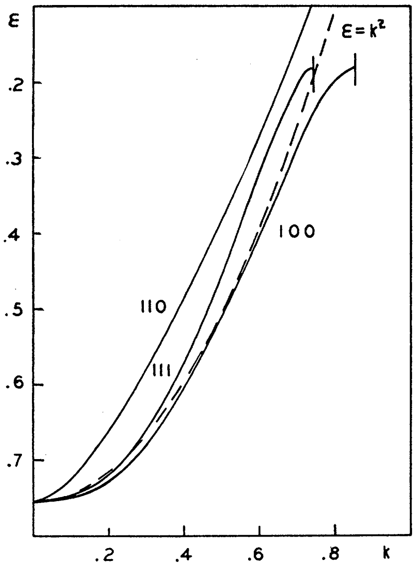

FIG. 6. Comparison of energy *versus* momentum curves for Class V. ($R=2.6$.)

curve for values of k corresponding to a half filled first momentum zone.

In Fig. 7, the energy contours for the conduction electron have been plotted in the $k_z=0$ section of the first zone. If the electron were exactly free electron-like, the contours would be exactly circles. For small values of k, the curves are decidedly not free electron curves. However, for larger values of k, the contours approximate circles.

The real part of the wave function for an electron moving in the 100 direction as seen by cutting through in the 110 direction was plotted for $k=0.596$ with $R=2.6$ for the distance between atoms. The correspondence between this curve and the real part of the $e^{ik\cdot R}$ of a free electron, i.e., cos $(k\cdot r)$, was found to be satisfactory. This concludes the various checks of the free electron behavior of the conduction electron.

It should also be mentioned that if a wave function is computed in any direction except those directions along which boundary conditions are satisfied, the wave functions will not fit exactly as we pass from cell to cell in ordinary space.

The final remaining point of interest is that of the correlation of the various classes for the three directions. This is necessary, as it is desirable at least to be able to take average values for example of dE/dk for various directions for a given energy. The various bands, although solved for different directions, have been correlated by consideration of the nodal properties of the wave functions of the various classes. This correlation is given in Table I.*

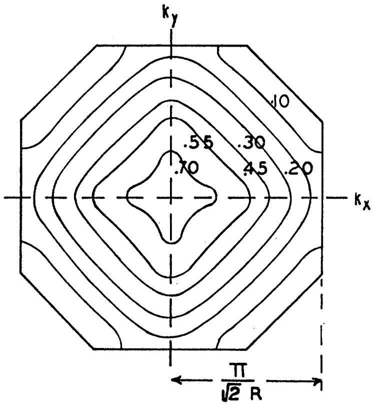

FIG. 7. Energy contours of Class V, $k_z=0$ and $R=2.6$, in the first zone of momentum space.

The general method of obtaining energy bands and wave functions for a face-centered lattice has been outlined. The method has been applied to a copper lattice using a corrected Hartree potential field. The energy bands as a function of the internuclear distance have been calculated. The strong overlapping of the $3d$ band and the $4s$ band is shown. The assignment of electrons to the various energy bands leads to the result that, theoretically, copper is a good conductor, a well-known experimental fact. The various energy bands of the three particular directions 100, 110, 111 have been correlated. For more quantitative results than those obtained, the approximations used in this report must be improved. The first and most important step in this direction is the task of obtaining a better potential field. This would take the form of a self-consistent Hartree problem for metals.

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**Note added in proof:* It appears from further study that these correlations must be revised. See a forthcoming paper by J. C. Slater.