

Electronic Energy Bands in Metallic Calcium

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Theoretical studies of electronic energy bands in metallic calcium have been carried out by the Wigner-Seitz-Slater cellular method. The conductivity is found to be due to an overlap between the lowest "s" band and the "d" band. This overlap leaves a small number of vacant states near the points in the momentum cell whose coordinates are: 0 , $\pi/\sqrt{2}R$, $\pi/2\sqrt{2}R$. In terms of the computed results, interpretations of the binding energy, pressure coefficient of resistance, and paramagnetic susceptibility are made. Predictions are made about the Hall coefficient and about optical properties.

THE Wigner-Seitz-Slater cellular method¹⁻⁴ of calculating energy bands in metals has so far been applied only to monovalent metals, for which there is little difficulty in understanding the fundamentals of the process of electrical conduction. For the case of a divalent metal some general conclusions have been drawn, but the authors believe that a more detailed study of a particular divalent metal is worthwhile. On account of the particular interest in the behavior of the first group of transition elements, and because Hartree's results for the calcium atom were available, metallic calcium has been chosen for this more detailed study.

The application of the cellular method to a face-centered lattice has been given in previous papers.^{4, 5} Relations are given there which determine the energy of an electronic state in a metal as a function of the wave vector k . The relations between E and k can be handled easily only for particular directions. The special cases of propagation along 100, 110, and 111 directions were treated in detail in a previous paper.⁴ Other special directions have been treated by Shockley.⁵ The relations between E and k involve the values of the s , p , d , f functions and their derivatives at

the half-distance between nearest neighbors. These values have been found by numerical integration, as in the Hartree method of finding the self-consistent field for an isolated atom. The potential used was found by taking Hartree's results⁶ for the core and adding to this the potential of a valence electron of energy somewhat less than the eigenvalue and with the charge density normalized to the atomic volume.

For a particular interatomic distance, the lowest band will begin at the energy for which $s'=0$ at half of this distance. The next higher band will begin at the energy for which $d'=0$ at the same radius. For different interatomic distances, these conditions are fulfilled for different energies. In Fig. 1 a graph of the energies for which $s'=0$, $p'=0$, $d'=0$, $s=0$, $p=0$ are plotted as functions of the half-distance between neighbors.

The filled levels extend from $s'=0$ to about $d'=0$. As the interatomic distance is changed, the energy of the lowest filled levels depends upon the behavior of the $s'=0$ curve. The behavior of the upper filled levels depends upon the $d'=0$ curve. Since this curve is quite flat, most of the variation of energy with interatomic distance is due to the change of energy of the lower levels. This argument leads to the prediction that the actual interatomic distance would correspond to the minimum of the $s'=0$ curve. However, this argument neglects correlation effects. Qualitatively, correlation effects lead to the expecta-

* Work started at Purdue University.

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

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

³ Millman, *Phys. Rev.* **47**, 286 (1935).

⁴ Krutter, *Phys. Rev.* **48**, 664 (1935).

⁵ W. Shockley, *Phys. Rev.* **51**, 129 (1937). The authors wish to express their appreciation to Dr. Shockley for the privilege of seeing this paper in manuscript form, and for interesting discussions with him on the subject of electronic energy bands in solids.

⁶ Hartree, *Proc. Roy. Soc.* **A149**, 210 (1935).

potential and of a greater number of spherical harmonics in the expansion of the wave function, might make an appreciable difference in the magnitude of this energy overlap.⁹ It seems less likely that its dependence upon interatomic distance should be in the opposite direction from that given in Fig. 3.

Fig. 4 shows approximate contours in the plane $k_z=0$. Similar contours were also drawn in the plane $k_y=k_x$. From these special planes, energy surfaces in k space were interpolated and by a combination of graphical and numerical methods, the volume in k space inclosed by a given energy surface was found. This volume is proportional to the number of states with energy less than the energy considered. From a plot of the volume in k space as a function of energy, the number of states between E and $E+dE$ was found by graphical differentiation. The results are shown in Fig. 5.

A better estimate of the shape of the $n(E)$ curve could be obtained by using more of the special directions which have been worked out by Shockley⁵ and by obtaining an expansion of the large determinant which is valid in the region near $0, \pi/\sqrt{2}R, \pi/2\sqrt{2}R$. The high density of states near the bottom of the d band seems to be real

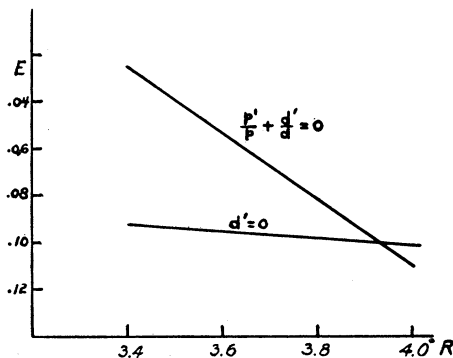


FIG. 3. Energy overlap at $k_z=0, k_x=\pi/\sqrt{2}R, k_y=\pi/2\sqrt{2}R$. $R=3.80$.

⁹ This pessimism is caused mostly by results obtained for the body-centered lattice. When fourteen boundary conditions are used instead of eight, a considerable change in the relations between E and k is found. (Manning and Chodorow, Phys. Rev. 50, 399 (1936), and unpublished work on potassium and tungsten.) However, the next state of improvement for the face-centered lattice would probably not involve such a drastic change. Shockley (Atlantic City Meeting, December, 1936) has attempted to justify Slater's method of fitting boundary conditions by showing that for the extreme case of a constant potential, the agreement within the lowest band is satisfactory.

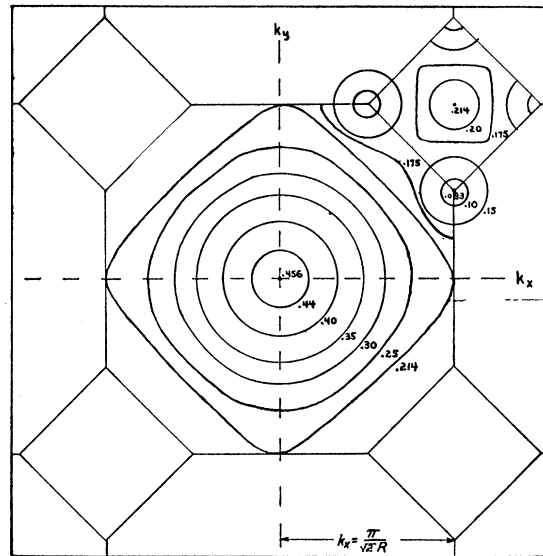


FIG. 4. Energy contours of lowest band in the $k_z=0$ plane for $R=3.80$.

and not the unfortunate consequence (as are zero width bands) of approximations in the theory. This point will be discussed in more detail in another paper.

In order to show the connection between these results and the electrical conductivity of metallic calcium, it is necessary to consider three important factors which effect the conductivity of a metal. They are:

1. Not all of the valence electrons can take part in the conduction process. Under the influence of the external field, some of the electrons in states near the top of the Fermi distribution will make transitions to other states of higher energy. These excited states are characterized by a mean momentum in the direction of the field, and hence by a current in that direction. For calcium at about the observed interatomic distance, all of the states, except those near $0, \pi/\sqrt{2}R, \pi/2\sqrt{2}R$ and the twenty-three equivilant points, will be separated from vacant states by a finite energy gap, and hence only a small number can actually make transitions under the influence of the field.

2. The momentum which is imparted to the stream of electrons in a given length of time depends upon the spacing of the energy contours near the top of the Fermi distribution. For the highest states in the lower band the energy contours in momentum space will be much closer

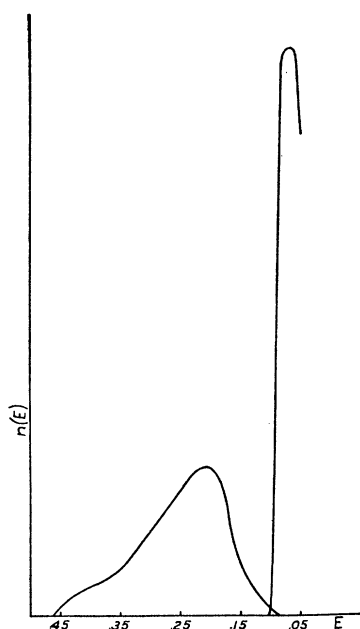


FIG. 5. $n(E)$ as a function of E . $n(E)dE$ is the number of states between E and $E+dE$. $R=3.80$.

together than for the states at the bottom of the upper band, and hence most of the conduction will be due to electrons in the lower band.

3. Electrons are scattered out of the beam by collision with ions. The probability of scattering will depend upon the amplitude of vibration of the scattering ions and upon the density of vacant states near the edge of the Fermi distribution. The first effect accounts for the ordinary change of resistance with temperature and has been discussed in detail by Mott and Jones.¹⁰ Since the vacant d states are effective in scattering but not in conduction, the effect of the high density of d states just above the highest occupied level is to make the conductivity of calcium less than for an element where electrons in only one band need be considered. The effect of

pressure on the conductivity can be understood by comparing Fig. 3 and Fig. 5. As the pressure is increased, the number of vacant d levels near the top of the Fermi distribution increases more rapidly than the number of vacant states in the lower band. This explains why the resistance of calcium increases with pressure.

The paramagnetic contribution to the susceptibility of a metal depends upon the number of vacant levels at the edge of the Fermi distribution. In calcium the density of vacant states is great enough so that the metal is paramagnetic. At higher pressures the number of vacant states is increased so much that it may be possible to detect experimentally a change of susceptibility with pressure.

As Mott and Jones¹¹ have pointed out, when the conduction is due to the holes in a nearly filled band, the Hall coefficient should be large and have the opposite sign from the case of free or nearly free electrons. No record has been found of an experimental determination of this coefficient.

There is a type of optical absorption by a metal which corresponds to a transition from an occupied state to a vacant state having the same coordinates in k space. From the E vs. k curves, it can be seen that when the end state is in one of the narrow bands near $d'=0$, the energy difference allowed by the selection rule can be equal to or less than 0.36 unit. This corresponds to an absorption of all wave-lengths greater than about 2500A. For wave-lengths less than this, there can be absorption to some of the other d bands. There may be a decreased absorption below 2500A but there does not seem to be any possibility of a transparent region between 4000A and 1000A.

The authors wish to thank Professor J. C. Slater and Professor N. H. Frank for helpful discussions about the subject matter of this paper.

¹⁰ Reference 7, page 243.

¹¹ Reference 7, page 283.