PHYSICAL REVIEW VOLUME 108, NUMBER 2 OCTOBER 15, 1957

Electron Energy Bands in Cesium*

JOSEPH CALLAWAY AND ERNST L. HAASE
Department of Physics, University of Miami, Coral Gables, Florida

(Received June 10, 1957)

The orthogonalized plane wave method and the cellular method have been applied to a calculation of electronic energy levels in cesium. The same crystal potential was used for all states. Wave functions of core electrons, required in the application of the orthogonalized plane wave method, were determined for this potential. The cohesive energy was calculated according to a simple model. The magnitude at a nucleus of the wave function of an electron on the Fermi surface was estimated by perturbation theory. The energies of twenty-four states at four symmetry points of the Brillouin zone have been obtained. The bands inferred from these results are compared with those in other alkali metals.

I. INTRODUCTION

ONE of the principal problems in the theory of electronic energy bands in solids is to determine to what extent calculated bands are sensitive to details of the assumed crystal potential. A comparison of bands calculated for metals of the same crystal structure but differing in lattice constant and number of electrons should contribute to an answer to this question. The alkali metals are a useful system for this comparison since there have been a number of studies of their energy bands.[1–6] Most of this work has concerned the lighter alkali metals; there is little reliable information on the heavier ones. In addition, it would be of interest to determine the variation of energy bands from element to element throughout the alkali metals. There is some evidence to indicate that in the heavier alkali metals, the bands depart from the free-electron form.

Previous calculations of energy levels in cesium have been made by Gombas[7] and Sternheimer.[8]

The work of Gombas was based on perturbation theory applied to free-electron wave functions. He replaced, in lowest order, the actual potential in the exterior of the atomic cell by a constant: its average value. The difference between the average of the potential and the potential itself was treated by perturbation theory. This procedure may be reasonably valid since the potential is slowly varying over most of the volume of the cell. He obtained a value of -0.407 ry for the energy of the lowest state of a valence electron (Γ_1), which is in reasonable agreement with our result of -0.146 ry. The potentials used are slightly different. He attempted to locate the state H_1 in the same way, but used incorrect boundary conditions which give an energy apparently much too low. (He obtained -0.154 ry as compared to our result $+0.144$ ry.)

The calculation of Sternheimer was designed to test the hypothesis that an observed discontinuity in the compressibility of cesium at high pressures is due to a crossing of the 6*s* and 5*d* bands. He tried to locate the positions of those bands as a function of interatomic distance. The choice of potential will be discussed in the next section. Unfortunately, Sternheimer used inappropriate boundary conditions for the *d* bands. Our calculation is in reasonable agreement with his results for the location of the bottom of the 6*s* band and for the effective mass in this band. We do not, however, find the band to be almost parabolic. The shape of the *d* band calculated in this work is in disagreement with that determined by Sternheimer, in that the *d* band we obtain resembles much more closely that found in potassium[6] than the simple parabolic form he predicted. His calculation of the effective masses in the *d* band is not valid because of improper treatment of the degeneracies in this band. We also find that *p* levels lie quite close to the occupied band so that there is presumably a considerable degree of mixing of *s* and *p* states as well as *s* and *d* states. Our calculation does not attempt to test the validity of the hypothesis of crossing of *s* and *d* bands since we have used the observed lattice constant only.

We believed, however, that the potential used by Sternheimer for *s* states, was reasonably accurate, and could serve as a basis for a more careful study of the energy bands. His potential was adapted for use in this work. The cellular method was employed to study the bottom of the lowest band: the energy of the lowest state of a valence electron in the solid and the effective mass were determined. The cohesive energy was calculated on a simple model. The wave function was calculated to second order in k, and a crude estimate of the Knight shift was compared with the experimental result. The orthogonalized plane wave (OPW) method was applied to study the higher states. It was necessary to calculate wave functions for some of the core electrons using Sternheimer's potential. Energies of twenty-four states at four symmetry points of the Brillouin zone: Γ, H, P, and N were calculated.

---

* Supported by the Office of Naval Research.

[1] W. Kohn and N. Rostoker, Phys. Rev. **94**, 1111 (1954).

[2] F. C. Von der Lage and H. A. Bethe, Phys. Rev. **71**, 612 (1947).

[3] D. J. Howarth and H. Jones, Proc. Phys. Soc. (London) **A65**, 355 (1952).

[4] H. Brooks, Phys. Rev. **91**, 1027 (1953).

[5] F. S. Ham, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 127.

[6] J. Callaway, Phys. Rev. **103**, 1219 (1956).

[7] P. Gombas, Z. Physik **113**, 150 (1939).

[8] R. M. Sternheimer, Phys. Rev. **78**, 235 (1950).

II. CRYSTAL POTENTIAL

The choice of crystal potential is of crucial importance in an energy-band calculation. In the alkali metals, it is usual to adopt the model of Wigner and Seitz in which an electron sees the field of one positive spherically symmetry ion, the rest of the cells being neutral. This model seems to give quite good results for the cohesive energies of the alkali metals. The potential within the cell is based, in this calculation, on the Hartree-Fock equation. According to the Hartree-Fock equations, the effective potential varies from state to state through the Brillouin zone. It is not possible to take this into account exactly. It is perhaps a reasonable approximation for states of not too high excitation to use an exchange potential determined by the predominant angular momentum in the expansion of the wave function for the state of interest in spherical harmonics.[6] This was done by Sternheimer for the 6*s* and 5*d* levels. In order to reduce the calculational problem somewhat, we have made the further and worse approximation that the potential is the same for all states in the Brillouin zone. The potential is essentially that for 6*s* states given by Sternheimer. It was observed that this potential is not a smooth function of position, and since no physical reason could be found for the fluctuations, they were smoothed out. The resulting potential is given in Table I. It yields an energy for the lowest state of a valence electron in the free atom in reasonable agreement with but slightly lower than the spectroscopic value -0.2862 ry. The Fourier coefficients of the crystal potential are given in Table II.

TABLE I. The function rV, where V is the crystal potential. V is in Rydbergs and r is in atomic units.

r	rV	r	rV
0.000	110.00	0.9	14.40
0.005	107.00	1.0	12.45
0.010	104.15	1.1	10.85
0.015	101.50	1.2	9.70
0.020	99.00	1.3	8.80
0.025	96.60	1.4	8.00
0.030	94.40	1.5	7.32
0.035	92.40	1.6	6.71
0.040	90.50	1.8	5.62
		2.0	4.77
0.05	87.00	2.2	4.07
0.06	83.85	2.4	3.56
0.07	80.90	2.6	3.220
0.08	78.15	2.8	2.985
0.09	75.55	3.0	2.800
0.10	73.05	3.2	2.655
0.11	70.65	3.4	2.568
0.12	68.30	3.6	2.498
		3.8	2.440
0.14	63.90	4.0	2.386
0.16	60.15		
0.18	56.70	4.5	2.287
0.20	53.70	5.0	2.216
0.22	50.90	5.5	2.172
0.24	48.40	6.0	2.132
0.26	46.10	6.5	2.096
0.28	43.90	7.0	2.066
0.30	41.80	7.5	2.041
0.32	39.80	8.0	2.020
0.34	37.95	8.5	2.005
0.36	36.20	9.0	2.000
0.38	34.55	10.0	2.000
0.40	33.00	11.0	2.000
		12.0	2.000
0.45	29.75	13.0	2.000
0.50	27.00		
0.55	24.60		
0.60	22.75		
0.65	21.00		
0.70	19.45		
0.75	18.00		
0.80	16.70		

TABLE II. Fourier coefficients of the crystal potential defined by $V(\mathbf{k})=\Omega_0^{-1}\int e^{i\mathbf{k}\cdot\mathbf{r}}V(r)d^3r$. The coefficients are given as functions of $n^2=[(a/2\pi)\mathbf{k}]^2$.

n^2	V_{n^2}	n^2	V_{n^2}
0	0.97031	30	0.09470
2	0.38561	32	0.08831
4	0.25191	34	0.08510
6	0.23107	36	0.08189
8	0.21579	38	0.07868
10	0.19613	40	0.07547
12	0.17080	42	0.07389
14	0.14724	44	0.07231
16	0.13276	46	0.07073
18	0.12465	48	0.06915
20	0.12004	50	0.06757
22	0.11585	52	0.06599
24	0.11167	54	0.06441
26	0.10748	56	0.06283

Adoption of a single potential for all states greatly simplifies the application of the OPW method. It is necessary, however, to have wave functions for core electrons which pertain to this potential. For the very tightly bound states: 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, and 3*d*, the wave functions were taken from Hartree's calculation[9] (a self-consistent field without exchange for Cs^+). For the higher states: 4*s*, 4*p*, 4*d*, 5*s*, and 5*p*, core wave functions were found by numerical integration of the appropriate wave equation.

III. COHESIVE ENERGY

According to the standard theory of the cohesion of the alkali metals[10] the cohesive energy is the difference of two quantities: the boundary correction and the Fermi energy. The boundary correction is the difference in energy between the lowest state of a valence electron in the solid and in the free atom. The Fermi energy takes account of the spread in energy of electrons in the band. If the band is parabolic, it can be determined from the effective mass. The average binding energy E_B of an electron is

$$E_B=E_0+2.21E_2/r_s^2-E_a, \tag{1}$$

where E_0 is the energy of the lowest state of a valence electron in the solid; E_2 is the reciprocal of the effective mass ratio: $E_2=m/m^*$, and E_a is the energy of the

---

[9] D. R. Hartree, Proc. Roy. Soc. (London) **A143**, 506 (1934).

[10] E. Wigner and F. Seitz, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 97.

lowest state of a valence electron in the free atom, -0.2862 ry. To this must be added E_I, the interaction energy (including correlation) of the valence-electron distribution. If Wigner's formula is used for the correlation energy,[11] we have for E_I:

$$E_I = 0.284/r_s - 0.88/(r_s + 7.79). \tag{2}$$

The calculated values of E_0, E_2, and E_I are given in Table III as is the cohesive energy computed from these quantities. The values obtained by Sternheimer[8] and by Brooks[4] are also given. The quantity r_s was taken as 5.64 (in atomic units a_{H}). Small differences between these results and those of Sternheimer will be noted. The difference in the energy of the lowest state is largely unexplained, but may be due to the smoothing of Sternheimer's potential. (The fluctuations of Sternheimer's original potential are sufficiently large as to render numerical integration of the wave equation with it somewhat unreliable.) In this calculation, E_2 was obtained by Bardeen's method[12] which makes calculation of matrix elements unnecessary.

It is interesting that such a simple model gives a reasonable value for the cohesive energy. There is, of course, considerable uncertainty in the value of E_I, and it is inadequate to determine the Fermi energy from E_2 only. The calculations presented in Sec. V show that the lowest band is far from parabolic.

IV. THE KNIGHT SHIFT

The shift of the nuclear magnetic resonance line in metallic cesium (as compared with nonmetallic cesium) has been measured.[13] This shift gives a value for $\langle |\psi_F(0)|^2 \rangle$ where ψ_F is the wave function of an electron on the Fermi surface; and $\langle\ \rangle$ symbolizes an average over the Fermi surface; if the spin paramagnetic susceptibility per unit mass, χ_p, is known:

$$\frac{\Delta H}{H} = \frac{8\pi}{3} \chi_p M \langle |\psi_F(0)|^2 \rangle, \tag{3}$$

where M is the atomic mass. It is convenient to compare $\langle |\psi_F(0)|^2 \rangle$ with $|\psi_A(0)|^2$, where ψ_A is the wave function for the valence electron in the free atom. The latter quantity can be obtained from the observed hyperfine splitting in cesium,[14] according to the formula of Fermi[15]:

$$\Delta W = \frac{8\pi}{3} \left(\frac{2I+1}{I} \right) \mu \mu_N \mu_B |\psi_A(0)|^2, \tag{4}$$

where ΔW is the hyperfine splitting in energy units, μ is the nuclear magnetic moment in units of the nuclear magneton, μ_B is the Bohr magneton, μ_N is the nuclear magneton, and I is the nuclear spin. From this we obtain $|\psi_A(0)|^2 = 3.9$ in atomic units.

TABLE III. The cohesive energy: the quantities E_0, E_2, E_B, E_I, and the cohesive energy as defined in Sec. III are given as calculated by us, by Sternheimer,[8] and by Brooks[4] using the quantum-defect method. Atomic units (Rydbergs) are used, except as indicated. Deviations of the band from parabolic form are not included.

Quantity	This calculation	Sternheimer	Brooks
E_0	-0.4156	-0.4258	-0.4266
E_2	1.401	1.366	1.202
$E_B - E_a$	-0.0321	-0.0447	-0.0569
E_i	-0.0152	-0.0152	-0.0152
Cohesive energy (kcal/mole)	14.8	18.7	22.6
Experimental cohesive energy (kcal/mole)	19.7		

Because of the inaccuracies of Hartree-type wave functions in the heavier elements, the principal quantity of theoretical interest is

$$\xi = \langle |\psi_F(0)|^2 \rangle / |\psi_A(0)|^2. \tag{5}$$

The value given by Knight[13] is $\xi = 1.3$.

A crude calculation of ξ has been attempted. The value of $|\psi_A(0)|^2$ can be taken from the work of Sternheimer[16]:

$$|\psi_A(0)|^2 = 2.6.$$

To obtain ψ_F is difficult. We assume that the Fermi surface is spherical and take the expansion of $\psi_{\mathbf{k}}$ as given by Silverman,[17]

$$\begin{aligned} \psi_{\mathbf{k}} &= e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}, \\ u_{\mathbf{k}} &= u_0 + ik \cos\theta u_1 + k^2 (u_2 P_2 + \phi_0), \end{aligned} \tag{6}$$

where

$$P_2 = (3\cos^2\theta - 1)/2.$$

In Eq. (6), the functions u_0, u_1, u_2, and ϕ_0 are essentially those given by Silverman. These functions have been calculated. For $k_F = 0.340$, we obtain

$$|\psi_F(0)|^2 = 3.0.$$

This yields

$$\xi = 1.2.$$

The agreement is remarkable considering the crudeness of the assumptions. In the first place, there is no reason why an expansion of $\psi_{\mathbf{k}}$ in powers of k should converge readily on the Fermi surface. Also, one would expect that relativistic effects would be particularly noticeable in a calculation of the wave function at the nucleus. This may be the explanation for the very considerable discrepancy between the observed and computed values of $|\psi_A(0)|^2$. There is also uncertainty in regard to the value of χ_p, the paramagnetic susceptibility. The value

---

[11] E. Wigner, Phys. Rev. **46**, 1002 (1934). There is an error in Wigner's formula in the low-density limit which has been corrected above.

[12] J. Bardeen, J. Chem. Phys. **6**, 367 (1938).

[13] W. D. Knight, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2, p. 93.

[14] P. Kusch and H. Taub, Phys. Rev. **75**, 1477 (1949).

[15] E. Fermi, Z. Physik **60**, 320 (1930).

[16] R. M. Sternheimer (private communication). We are indebted to Dr. Sternheimer for furnishing his wave function for the free atom.

[17] R. A. Silverman, Phys. Rev. **85**, 227 (1952).

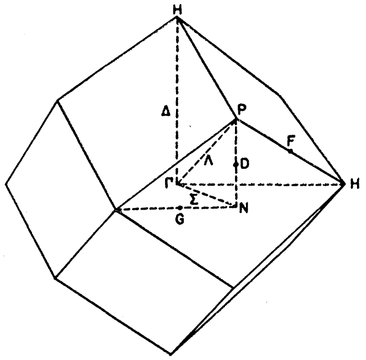

FIG. 1. Brillouin zone for the body-centered cubic lattice.

used by Knight was taken from a calculation by Pines for free electrons.[18]

V. CALCULATION OF THE HIGHER LEVELS

The orthogonalized plane wave method has been treated adequately in other papers,[19] and it is not necessary to repeat the discussion here. In this calculation, OPW expansions were constructed for twenty-four symmetry types at four symmetry points in the Brillouin zone at the points Γ, H, P, and N. The Brillouin zone for the body-centered cubic lattice is shown in Fig. 1. A lattice parameter of 6.06 A was used, corresponding to $r_s=5.64$ in atomic units.[20] Linear combinations of orthogonalized plane waves were employed which transform according to the irreducible representations of interest.[21]

Because high-speed electronic computing equipment was not readily available to us, the calculations did not involve higher than fourth-order determinants. The convergence of the expansions appears to be quite good for the state Γ_1 for which an eighth-order secular determinant was solved on the Whirlwind Computer at the Massachusetts Institute of Technology through the courtesy of Dr. L. C. Allen. The lowest eigenvalue in fourth order was -0.4258 ry and in eighth order it decreased to -0.4268. The energy of this state according to the cellular method was 0.4156 ry. The OPW method is expected to yield a slightly lower energy owing to a small error in the calculated 4s wave function. The very good convergence exhibited by Γ_1 may not hold, however, for all the other states. In particular, at the symmetry points N and P, fewer plane waves will be included in the OPW expansion for a fixed number of terms, so that the convergence is probably somewhat poorer. Also, the D-like states did not appear to converge as fast as the S and P states.

A conservative estimate would be that S and P states at Γ and H are convergent to within 0.02 Rydberg, D states within possibly 0.04 ry. The possible errors at P and N may be double these figures. The convergence of F-like states will probably be worse since smaller determinants were used: these states are relatively high. Except as discussed in the next section, the order of levels within a particular band is probably reliably given.

The lowest two eigenvalues of the representations calculated are given in Table IV. The states are classified as S, P, D, or F according to the lowest spherical harmonic which would appear in a cellular-method calculation. The states are arranged in order of increasing energy. The relation of the states at the symmetry points is shown in Fig. 2.

VI. DISCUSSION

Previous work on potassium led to the hypothesis that the order of levels at symmetry points in a band of one particular type (as an s, p, d band) is relatively independent of the crystal potential, and is determined by the square of the wave vector of the lowest OPW

TABLE IV. Energies of states at four symmetry points: states of a particular symmetry are arranged in order of increasing energy. The degeneracy, order of determinant solved, and number of waves included in the expansion for each representation are listed. The quantity $m^2=[(a/2\pi)\mathbf{h}]^2$, where $\mathbf{h}$ is the wave vector of the lowest OPW for the particular representation, is given. The energies of the lowest two states of each symmetry type are also given.

Representation	Degeneracy	Order of determinant	No. of waves	m^2	Energies (ry)	
S-like states						
Γ_1	1	8	135	0	−0.4268	0.6022
N_1	1	4	18	$\frac{1}{2}$	−0.2848	0.3449
P_1	1	4	40	$\frac{3}{4}$	−0.1181	0.6051
H_1	1	4	62	1	−0.1445	0.8163
P-like states						
$N_{1'}$	1	4	18	$\frac{1}{2}$	−0.3417	0.2758
P_4	3	4	18	$\frac{3}{4}$	−0.2591	0.4847
H_{15}	3	4	38	1	−0.1726	0.6522
$N_{3'}$	1	4	20	$\frac{3}{2}$	−0.0088	0.5255
$N_{4'}$	1	4	20	$\frac{3}{2}$	0.0687	0.4203
Γ_{15}	3	4	42	2	0.2691	0.7578
D-like states						
H_{12}	2	4	54	1	−0.2079	0.5349
N_2	1	4	28	$\frac{3}{2}$	−0.1666	0.5139
$\Gamma_{25'}$	3	4	48	2	−0.1162	0.8290
Γ_{12}	2	4	54	2	0.0421	0.5738
P_3	2	3	36	11/4	0.0976	0.8418
N_4	1	4	28	10/4	0.0995	0.5502
$H_{25'}$	3	4	56	3	0.1299	0.7548
N_3	1	4	28	14/4	0.2416	0.7931
F-like states						
Γ_{25}	3	3	48	1	0.1142	1.1293
$H_{2'}$	1	3	56	3	0.2036	1.6954
P_5	3	3	36	11/4	0.3545	0.9014
N_2	1	3	24	14/4	0.4702	1.3727
H_{25}	3	3	48	5	0.8014	1.0866
$\Gamma_{2'}$	1	2	32	6	0.9727	2.8687

---

[18] D. Pines, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), p. 367.

[19] C. Herring, Phys. Rev. **57**, 1169 (1940); J. Callaway, Phys. Rev. **97**, 933 (1955).

[20] C. S. Barrett, *Structure of Metals* (McGraw-Hill Book Company, Inc., New York, 1952), p. 646.

[21] Further details of the OPW calculation, including linear combinations of the plane waves and the wave functions for the core states, etc., may be found in the Master's thesis of E. L. Haase, University of Miami, 1957 (unpublished).

in the expansion of the wave function.[6] In Table IV, we give the value of $m^2=[(a/2\pi)\mathbf{h}]^2$, where $\mathbf{h}$ is the wave vector of the lowest OPW pertaining to the particular state for all of the states listed. With two exceptions, the ordering of levels according to increasing m^2 is the same as the ordering according to increasing energy. In the case of P_3 and N_4, the observed interchange of the expected order is probably the result of incomplete convergence of the levels. The reason for the interchange of H_2 and P_5 in the F band is not known. The agreement with the hypothesis is, however, quite good. The comments that were made in the calculation on potassium[6] in regard to the order of levels predicted by Wigner[10] apply here as well.

In comparing the bands with those calculated for potassium, we note a general tendency for the bands to be narrower. This tendency is particularly pronounced for the P band. Some tendency toward contraction would be expected because of the larger lattice constant.

The D band is of particular interest in view of the proposal of Sternheimer[8] in regard to a discontinuity in the compressibility. The energy Sternheimer obtains for the bottom of the D band corresponds approximately to the energy we have obtained for H_{12}, which is a low level. We have not attempted to verify his statements regarding the motion of the bands as the lattice constant is decreased. The general form of the D band is in good agreement with previous calculations for potassium[6] and iron.[22] In particular, we note that the separation of the triply and doubly degenerate levels at the center of the zone is smaller than at the corner H, and that the order is reversed at H. The maximum spread of the D levels occurs at N. The magnitude of the split between the triply and doubly degenerate D levels at the center of the zone in cesium is considerably greater than in potassium, in spite of the relative compression of the band.

The relative order of levels in the P and S bands separately corresponds to that in potassium. The P band appears to have been lowered quite considerably with respect to the S and D bands. This feature, however, may be sensitive to details of the potential. The choice of one potential for all states may be serious here. If this result is real, however, a nonspherical form for the Fermi surface is suggested, which would be elongated along the [110] axis in the Brillouin zone. At any rate, the low energy of the P levels indicates that the expansion of $E(k)$ in powers of k used previously does not converge readily.

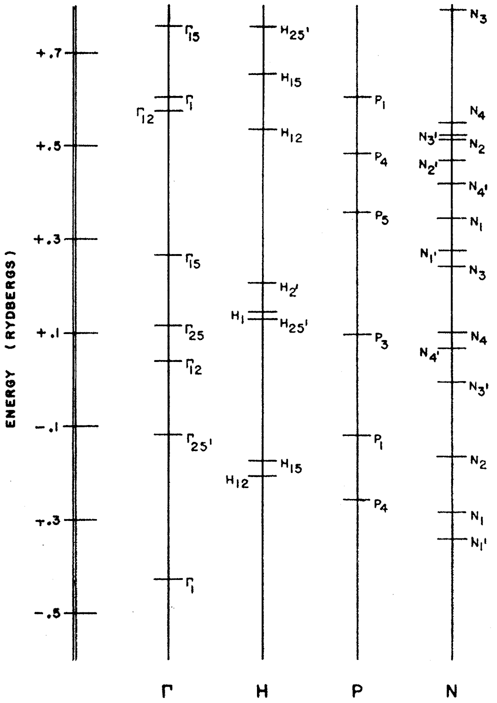

FIG. 2. Energy levels at four symmetry points up to 0.75 Rydberg.

ACKNOWLEDGMENTS

We are indebted to Dr. R. D. Woods for his aid in the early stages of this calculation. Mrs. P. Zwillinger, Mr. D. Jack, and Mr. J. Termine assisted with the very laborious computations. We wish to thank Dr. R. M. Sternheimer for furnishing unpublished material concerning his calculations.

---

[22] J. Callaway, Phys. Rev. 99, 500 (1955).