d electron in axial crystal fields.[6] Using this theory, it is possible to compute Δ, the splitting in the lower orbital triplet due to the axial field, from either $g_{\|}$ or $g_{\perp}$. However, the values thus obtained differ by a factor of $2\frac{1}{2}$. This large discrepancy indicates that either the small orthorhombic component of the crystal field makes the theory inapplicable to this case, or that the theory requires some modification.

ACKNOWLEDGMENT

The authors want to thank E. Sabisky and M. E. Heller for their help in making the measurements.

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PHYSICAL REVIEW VOLUME 119, NUMBER 3 AUGUST 1, 1960

Electron Wave Functions in Metallic Potassium

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(Received March 18, 1960)

Wave functions to order k^2 are presented for electrons in metallic potassium. The calculation is an application of the cellular method. The potential was derived from a self-consistent field and contains exchange effects.

INTRODUCTION

In previous calculations, the cohesive energy of potassium was determined, and some features of the energy band system were studied.[1,2] The present work presents wave functions determined according to the cellular method, together with an improved calculation of the cohesive energy.

The wave functions and energy of an electron of wave vector **k** are expanded in powers of k according to the method of Silverman.[3] We have:[4]

$$\psi_{\mathbf{k}}=e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}};\quad u_{\mathbf{k}}=u_0Y_{00}+iku_1Y_{10}+k^2(u_2Y_{20}+\phi_0Y_{00}),\tag{1}$$

$$E(k)=E_0+E_2k^2+E_4k^4+\cdots.\tag{2}$$

The Y_{lm} are normalized spherical harmonics.

$$Y_{00}=(4\pi)^{-\frac{1}{2}};\quad Y_{10}=(3/4\pi)^{\frac{1}{2}}\cos\theta;\quad Y_{20}=(5/4\pi)^{\frac{1}{2}}(3\cos^2\theta-1)/2.\tag{3}$$

The equations determining the functions u_0, u_1, etc., and the energy parameters E_0, E_2, E_4, are summarized in reference 4.

The functions which are tabulated are:

$$R_0=ru_0;\quad R_1=ru_1;\quad R_2=ru_2;\quad Q_2=r\phi_0.\tag{4}$$

The normalization integral for $\psi_{\mathbf{k}}$ is[5]

$$\int_\Omega|\psi_{\mathbf{k}}|^2d\tau=\int_\Omega|u_{\mathbf{k}}|^2d\tau=1+k^2(J_1+2J_2),\tag{5}$$

in which

$$J_1=\int_0^{r_s}R_1^2dr;\quad J_2=\int_0^{r_s}R_0Q_2dr.$$

In the original cohesive energy and band calculations, an attempt was made to take core valence exchange interactions into account by constructing separate exchange potentials for states of s, p, and d symmetry. The potentials given in reference 2 were used in this work for the basic s, p, and d functions incorporated in R_0, R_1, R_2, and Q_2. The exchange interaction is somewhat weaker for d functions than for s and p functions; this is the cause of the somewhat peculiar shape of the function R_2.

All calculations were made for a sphere radius $r_s=4.84$ (Bohr units), which is appropriate for 0°K.[6]

The band parameters computed in this way are $E_0=-0.452$ ry; $E_2=1.160$; $E_4=-0.85$. With the exception of E_4, the results are in good agreement with those previously reported. The E_4 given in reference 2 is in error. The cohesive energy, computed in the standard way[7] (but neglecting corrections due to core polarization) is 22.3 kcal/mole. A reasonable estimate of the core polarization effect is an increase of 2.6 kcal/mole in the cohesive energy. The experimental cohesive energy is 22.6 kcal/mole.

A quantity of interest in the theory of the Knight shift[8] is $\xi=|\psi_f(0)|^2/|\psi_A(0)|^2$ where $\psi_f(0)$ is the average over the Fermi surface of the value of the wave function

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TABLE I. The solid-state functions R_0, R_1, and Q_2 are given as functions of r for $E_0=-0.452$ ry. The normalization of these functions is given in Eq. (5) of the text. $\int_0^{r_s} R_1^2dr=0.193_3$, $\int_0^{r_s} R_0Q_2dr=2.486$, $\int_0^{r_s} R_2^2dr=1.385$, $\lim_{r\to 0}(R_0/r)=3.81$, and $\lim_{r\to 0}(Q_2/r)=4.27$.

r	R_0	R_1	R_2	Q_2
0.000	0.0000	0.00000	0.00000	0.0000
0.005	0.0172	−0.00120	0.00000	0.0193
0.010	0.0313	−0.00459	−0.00001	0.0350
0.015	0.0424	−0.00984	−0.00004	0.0474
0.020	0.0510	−0.01663	−0.00009	0.0569
0.025	0.0573	−0.0247	−0.00017	0.0638
0.030	0.0616	−0.0339	−0.00027	0.0684
0.035	0.0641	−0.0440	−0.00040	0.0709
0.040	0.0651	−0.0547	−0.00057	0.0717
0.045	0.0647	−0.0660	−0.00076	0.0708
0.050	0.0631	−0.0776	−0.00097	0.0685
0.06	0.0570	−0.1016	−0.00146	0.0604
0.07	0.0479	−0.1257	−0.00202	0.0486
0.08	0.0367	−0.1493	−0.00262	0.0342
0.09	0.0241	−0.1719	−0.00322	0.0179
0.10	+0.0107	−0.193	−0.00378	+0.0006
0.11	−0.0031	−0.213	−0.00428	−0.0171
0.12	−0.0167	−0.230	−0.00467	−0.0349
0.13	−0.0300	−0.246	−0.00493	−0.0524
0.14	−0.0427	−0.259	−0.00503	−0.0692
0.15	−0.0547	−0.270	−0.00493	−0.0850
0.16	−0.0657	−0.279	−0.00462	−0.0999
0.17	−0.0757	−0.286	−0.00406	−0.1135
0.18	−0.0847	−0.291	−0.00325	−0.1258
0.19	−0.0926	−0.294	−0.00215	−0.1367
0.20	−0.0994	−0.296	−0.00077	−0.1462
0.22	−0.1098	−0.293	+0.00291	−0.1609
0.24	−0.1159	−0.283	0.00786	−0.1698
0.26	−0.1180	−0.268	0.01412	−0.1733
0.28	−0.1166	−0.249	0.0217	−0.1716
0.30	−0.1121	−0.225	0.0306	−0.1652
0.32	−0.1049	−0.199	0.0408	−0.1545
0.34	−0.0953	−0.170	0.0521	−0.1401
0.36	−0.0838	−0.139	0.0647	−0.1225
0.38	−0.0708	−0.107	0.0783	−0.1020
0.40	−0.0566	−0.074	0.0929	−0.0791
0.45	−0.0177	+0.009	0.1131	−0.0143
0.50	+0.0228	0.090	0.1775	+0.0566
0.55	0.0619	0.164	0.225	0.1288
0.60	0.0977	0.229	0.273	0.199
0.65	0.1293	0.285	0.321	0.264
0.70	0.1559	0.330	0.368	0.323
0.80	0.193	0.394	0.456	0.417
0.90	0.210	0.428	0.533	0.478
1.00	0.210	0.438	0.596	0.507
1.10	0.195	0.430	0.647	0.506
1.20	0.170	0.411	0.684	0.481
1.30	0.137	0.384	0.710	0.435
1.40	0.098	0.352	0.725	0.372
1.50	0.057	0.318	0.731	0.296
1.60	+0.014	0.284	0.730	0.210
1.70	−0.030	0.250	0.723	0.117
1.80	−0.073	0.218	0.712	+0.020
1.90	−0.115	0.188	0.698	−0.080
2.00	−0.156	0.162	0.682	−0.182
2.2	−0.234	0.119	0.647	−0.384
2.4	−0.306	0.087	0.613	−0.580
2.6	−0.371	0.064	0.582	−0.768
2.8	−0.431	0.048	0.554	−0.946
3.0	−0.485	0.037	0.529	−1.112
3.2	−0.533	0.030	0.509	−1.266
3.4	−0.578	0.024	0.493	−1.410
3.6	−0.618	0.020	0.482	−1.543
3.8	−0.656	0.017	0.474	−1.666
4.0	−0.692	0.014	0.472	−1.780
4.2	−0.726	0.011	0.473	−1.887
4.4	−0.760	0.007	0.480	−1.989
4.6	−0.793	0.004	0.491	−2.085
4.8	−0.827	0.001	0.509	−2.178
4.84	−0.834	0.000	0.513	−2.196

at a nucleus, and $\psi_A(0)$ is similarly the value of the wave function of an electron in the free atom at the nucleus. The technique of expanding the wave function in powers of k is apparently capable of yielding results for ξ in reasonable agreement with experiments in the cases of rubidium and cesium. We find from the expansion, using $k_f=0.396_6$, $|\psi_f(0)|^2=0.862$. A calculation of ψ_A, using the same potential that was used in the computation of R_0, gave $|\psi_A(0)|^2=0.743$. We then have $\xi=1.16$.

ACKNOWLEDGMENTS

Much of this work was done while the author was visiting professor in the department of mathematics, Queen Mary College, University of London. He also wishes to acknowledge his indebtedness to Mrs. J. Gordon for assistance with the calculations.