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# Electronic Energy Bands in Potassium*

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The orthogonalized plane-wave method and the cellular method were applied to a calculation of electronic energy levels in potassium, using a potential obtained from a self-consistent field. The energies of twenty-four states at four symmetry points in the Brillouin zone have been obtained. The lowest band has been studied in detail and the qualitative features of the density of states were determined. Departures of the lowest band from free-electron behavior were found. A comparison of higher bands with the results of some other calculations suggests that certain features of band schemes may be reasonably independent of the potential used.

## I. INTRODUCTION

ELECTRONIC energy levels in the alkali metals have been studied for many years. The majority of the work has concerned the lighter elements, lithium and sodium.[1]

Principal attention has been devoted to the cohesive energy and to related properties such as the equilibrium lattice constant and the compressibility. The heavier alkali metals: potassium, rubidium, and cesium have been studied less extensively.[2–7] The work here reported concerns an application of the method of orthogonalized plane waves[8] and of the cellular method[9–10] to a calculation of electronic energy bands in potassium.

Gorin made a calculation of the cohesive energy of potassium[2] using the cellular method and a potential obtained from a self-consistent field for the $K^+$ ion. The results of his work were in marked disagreement with experiment, in that too little binding was obtained. This failure gave rise to the belief that an energy level calculation based on a self-consistent field would be very inaccurate for the heavier alkali metals. The quantum defect method was developed by Kuhn and Van Vleck[3] and extended by Brooks[4] and Ham[6] to avoid this difficulty by using observed spectroscopic data to circumvent the construction of an explicit potential. It has recently been shown, however, by Berman, Callaway, and Woods[5] that if proper account is taken of exchange interactions, a calculation based on a self-consistent field gives a result of reasonable accuracy for the cohesive energy of potassium. It then becomes interesting to extend their work to a calculation of higher electronic states.

The method of orthogonalized plane waves (OPW) was chosen in preference to the cellular method for a study of the higher states because in the OPW method it is not necessary to satisfy boundary conditions explicitly. The problem of accurately satisfying the boundary conditions is quite serious and difficult in the cellular method,[11] and it was felt that with the cellular method, it would have been impractical to study more than a small number of energy states. The cellular method was used, however, to study states near the bottom of the lowest band. The OPW method has the disadvantage that an explicit potential must be used, and more important, that the electron states in the atomic core must be known.[12] There are reasons why the OPW method should be expected to work well for metallic potassium. As in the other alkali metals, one has one electron moving outside of a relatively compact ion core. Consequently, overlapping of core wave functions will be negligible. The self-consistency problem, also, should not be serious since it is reasonable to expect that the average distribution of electrons in the core should not be significantly affected by the valence electron. This is supported by a calculation of Hartree and Hartree for the $K^-$ ion in which it was found that the wave function of the $3P$ electron differed only slightly from that for the $K^+$ ion.[13] The approximation of Wigner and Seitz is also made: that there is only one valence electron in an atomic cell. It moves in the potential of the positive ion, all other cells being neutral. The crystal potential and core wave functions used here were obtained from a self-consistent field with exchange for the $K^+$ ion.[14]

Because of the simplicity of the physical situation potassium should be a very favorable system for an energy band study. Such a study should furnish information concerning: (1) Validity of the free-electron approximation. There are three aspects here: (a) Departures of effective mass values from one, (b)

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presence of $k^4$ and higher terms in the $E(k)$ expansion near $\mathbf{k}=0$, and (c) departures of energy surfaces from spherical symmetry. It is not justified to assume that if the effective mass in the lowest band is nearly equal to unity, that the free-electron approximation holds in the other respects. Because of the possibilities of degereracies at symmetry points and band crossings, higher bands may be expected to show more complicated behavior than the lowest band. (2) Comparison of energy bands in potassium with those calculated for other elements having the body-centered cubic structure is particularly interesting since one of the most important problems in energy band theory is the question of how sensitive are the general features of an energy band to details of the potential. Comparison of energy bands in different elements of the same crystal structure should furnish information on this question. In addition, the effect of changes in the potential on the bands in potassium can also be examined.

Unfortunately, there is little accurate experimental information pertaining to energy bands in potassium, so that a detailed comparison of theory and experiment is not possible. Qualitative comparisons and predictions can be made in some cases. It is hoped this theoretical discussion will stimulate experimental effort.

## II. THE CRYSTAL POTENTIAL

We assume that each electron experiences only the potential of the corresponding positive ion. This potential consists of two parts: (1) The Coulomb potential of the atomic nucleus and the average distribution of the core electrons, and (2) the exchange interaction between the valence electrons and the core. The Coulomb potential is obtained in the obvious way from the core electron distribution. The exchange interaction is apparently quite important in obtaining quantitative results in a cohesive energy calculation.

We can define an effective exchange potential for the state $\psi_{\mathbf{k}}{}^i$ ($i$th irreducible representation of wave vector $\mathbf{k}$) in the following way:

$$V_{\mathbf{k}}{}^i(\mathbf{r}_1)=\frac{\sum_{nlm}\left[\int \psi_{nlm}{}^*(\mathbf{r}_2)(2/r_{12})\psi_{\mathbf{k}}{}^i(\mathbf{r}_2)d\mathbf{r}_2\right]\psi_{nlm}(\mathbf{r}_1)}{\psi_{\mathbf{k}}{}^i(\mathbf{r}_1)}, \tag{1}$$

where $\psi_{nlm}$ represents a core wave function. The exchange potential computed according to (1) will differ from state to state, and obviously depends on the wave function of the state considered. This means that a self-consistent solution of the Hartree-Fock equation is required. Slater has proposed two methods of averaging the exchange potential[15] which allow one to use one exchange potential for all states. It is doubtful that such procedures will have quantitative success.[16–17] It probably would be more accurate to assume that the exchange potential for a given state depends primarily on the angular momentum of the state considered, or in the case of the solid, on the predominant angular momentum in the decomposition of $\psi_{\mathbf{k}}{}^i$ into spherical harmonics.[16] In obtaining the exchange potential for a state of angular momentum $L$ of a valence electron, it is questionable whether it is desirable to average the exchange potentials of the core electron states of angular momentum $L$, since these have energy values in general far below that of the state we are considering. It seems more reasonable to construct an exchange potential for a given $L$ from an approximate wave function for a valence electron state of that $L$.

Such a procedure was followed in this calculation. An $S$-state exchange potential was constructed from the self-consistent field core wave functions and the lowest orthogonalized plane wave for the state $\Gamma_1$. This potential was used for the states $\Gamma_1$, $H_1$, $P_1$ and $N_1$. It is to be noted that the state $N_1$ will contain an admixture of $D$ functions. A $P$-state exchange potential was similarly obtained from the lowest OPW for the state $H_{15}$, and used in the calculations for $\Gamma_{15}$, $H_{15}$, $P_4$, $N_1'$, $N_3'$, and $N_4'$. $P_4$ will also have some $D$ character. A $D$-state exchange potential was obtained from a $D$ function calculated without exchange in a prior calculation of $k^4$ terms in the $E(\mathbf{k})$ relation. This potential

TABLE I. The quantity $rV$ is given in atomic units for $S$, $P$, and $D$ states, and for the Coulomb potential.

| $r$ | $rV_S$ | $rV_P$ | $rV_D$ | $rV_C$ |
|---|---|---|---|---|
| 0.00 | 38.00 | 38.00 | 38.00 | 38.00 |
| 0.01 | 36.78 | 36.76 | 36.70 | 36.52 |
| 0.02 | 35.61 | 35.57 | 35.49 | 35.12 |
| 0.03 | 34.51 | 34.39 | 34.30 | 33.82 |
| 0.04 | 33.46 | 33.30 | 33.19 | 32.63 |
| 0.05 | 32.53 | 32.27 | 32.15 | 31.54 |
| 0.06 | 31.64 | 31.32 | 31.19 | 30.54 |
| 0.07 | 30.83 | 30.41 | 30.29 | 29.61 |
| 0.08 | 30.12 | 29.58 | 29.46 | 28.75 |
| 0.09 | 29.60 | 28.77 | 28.67 | 27.93 |
| 0.10 | 28.42 | 28.02 | 27.93 | 27.15 |
| 0.15 | 24.78 | 24.77 | 24.70 | 23.74 |
| 0.20 | 22.22 | 22.12 | 21.92 | 20.86 |
| 0.25 | 20.10 | 20.00 | 19.62 | 18.50 |
| 0.30 | 18.33 | 18.29 | 17.67 | 16.57 |
| 0.35 | 16.99 | 16.82 | 16.00 | 15.02 |
| 0.40 | 16.08 | 15.64 | 14.64 | 13.76 |
| 0.50 | 13.41 | 13.73 | 12.56 | 11.81 |
| 0.60 | 10.91 | 12.08 | 11.06 | 10.29 |
| 0.70 | 9.86 | 10.48 | 9.87 | 8.98 |
| 0.80 | 8.85 | 8.84 | 8.88 | 7.83 |
| 0.90 | 7.93 | 7.94 | 8.02 | 6.81 |
| 1.00 | 7.15 | 7.17 | 7.26 | 5.93 |
| 1.10 | 6.47 | 6.50 | 6.56 | 5.17 |
| 1.20 | 5.93 | 5.95 | 5.94 | 4.54 |
| 1.40 | 5.321 | 5.093 | 4.887 | 3.598 |
| 1.60 | 4.262 | 4.526 | 4.054 | 2.982 |
| 1.80 | 3.090 | 3.462 | 3.428 | 2.595 |
| 2.00 | 2.545 | 2.839 | 2.971 | 2.357 |
| 2.50 | 2.286 | 2.199 | 2.350 | 2.099 |
| 3.00 | 2.130 | 2.049 | 2.141 | 2.025 |
| 3.50 | 2.055 | 2.020 | 2.076 | 2.006 |
| 4.00 | 2.025 | 2.009 | 2.035 | 2.001 |
| 4.50 | 2.009 | 2.005 | 2.013 | 2.000 |

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[15] J. C. Slater, Phys. Rev. **81**, 385 (1951).
[16] Herman, Callaway, and Acton, Phys. Rev. **95**, 371 (1954).
[17] J. Callaway, Phys. Rev. **99**, 500 (1955).

was used for the $D$-like states $\Gamma_{25}'$, $\Gamma_{12}$, $H_{25}'$, $H_{12}$, $P_3$, $N_2$, $N_3$, and $N_4$; and also for the $F$-like states $\Gamma_{25}$, $\Gamma_2'$, $H_{25}$, $H_2'$, $P_5$ and $N_2'$. It was assumed in using the OPW method that the core states could, with sufficient accuracy, be considered as eigenfunction in these potentials.[18]

One unsatisfactory feature of this procedure is that in the case of the $S$ and $P$ states the exchange potential according to (1) will have infinities where the approximate $\psi_k{}^i$ has zeros. These were removed in such a way as to give a reasonably smooth exchange potential. This smoothing is necessary in the OPW method but not in the cellular method, since there the exchange interaction can be treated as an inhomogeneous term in the wave equation. The Coulomb potential and the potential for $S$, $P$, and $D$ states are tabulated in Table I. Uncertainty as to the exact form of the exchange interaction is significant near $r=2$ for the $S$- and $P$-state potentials.

## III. CALCULATION OF THE ENERGY LEVELS

The OPW method leads to a secular equation of the form

$$\det[(X_{\mathbf{k}},HX_{\mathbf{h}})-E(X_{\mathbf{k}},X_{\mathbf{h}})]=0, \tag{2}$$

where $H$ is the crystal Hamiltonian and $X_{\mathbf{k}}$ is an orthogonalized plane wave

$$X_{\mathbf{k}}=e^{i\mathbf{k}\cdot\mathbf{r}}-\textstyle\sum_j\mu_{\mathbf{k}j}\sum_\nu \exp(i\mathbf{k}\cdot\mathbf{r}_\nu)\phi_j(\mathbf{r}-\mathbf{r}_\nu). \tag{3}$$

Here $\phi_j$ is a core function for the core state $j$, $\mathbf{r}_\nu$ is a lattice vector and $\mu_{\mathbf{k}j}=(1/\Omega_0^{\frac{1}{2}})\int\phi_j{}^*(r)e^{i\mathbf{k}\cdot\mathbf{r}}d\mathbf{r}$, with $\Omega_0=$ the volume of the atomic cell.[19] In practice we use linear combinations of orthogonalized plane waves which transform according to particular irreducible representations in setting up Eq. (2).

TABLE II. Fourier coefficients of potential are given in rydbergs as functions of the number $m^2=(a\mathbf{k}/2\pi)^2$. Only even intergal values of $m^2$ occur for the body-centered cubic structure.

| $m^2$ | $V_S(m)$ | $V_P(m)$ | $V_D(m)$ | $V_C(m)$ |
|---|---|---|---|---|
| 0 | 0.8677 | 0.8692 | 0.8748 | 0.7924 |
| 2 | 0.2841 | 0.2900 | 0.2843 | 0.2346 |
| 4 | 0.2314 | 0.2369 | 0.2281 | 0.1965 |
| 6 | 0.1865 | 0.1913 | 0.1824 | 0.1612 |
| 8 | 0.1489 | 0.1525 | 0.1439 | 0.1298 |
| 10 | 0.1249 | 0.1266 | 0.1192 | 0.1106 |
| 12 | 0.1143 | 0.1143 | 0.1097 | 0.1035 |
| 14 | 0.1000 | 0.0996 | 0.0973 | 0.0922 |
| 16 | 0.0879 | 0.0875 | 0.0864 | 0.0821 |
| 18 | 0.0775 | 0.0772 | 0.0769 | 0.0733 |
| 20 | 0.0686 | 0.0685 | 0.0688 | 0.0657 |
| 22 | 0.0631 | 0.0632 | 0.0636 | 0.0610 |
| 24 | 0.0585 | 0.0596 | 0.0594 | 0.0572 |
| 26 | 0.0540 | 0.0552 | 0.0562 | 0.0558 |

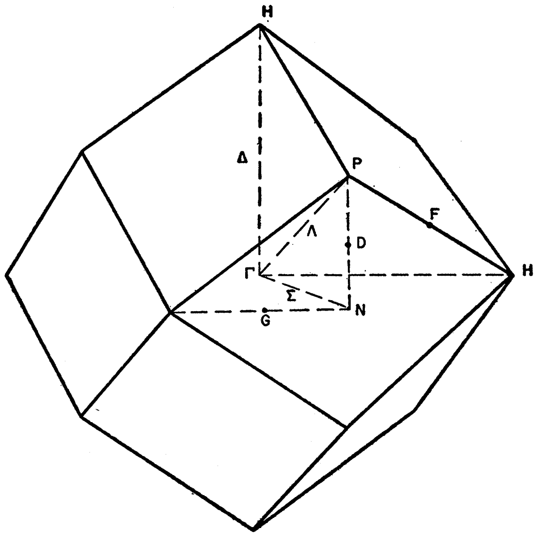

FIG. 1. Brillouin zone for the body-centered cubic lattice.

We assume that the core states $\phi_j$ are eigenfunctions of the crystal Hamiltonian.[18] In this case, the matrix elements in (2) are

$$(X_{\mathbf{k}},HX_{\mathbf{h}})=k^2\delta_{\mathbf{kh}}+V(\mathbf{k}-\mathbf{h})-\textstyle\sum_j E_j\mu_{\mathbf{k}j}{}^*\mu_{\mathbf{h}j}, \tag{4}$$

and

$$(X_{\mathbf{k}},X_{\mathbf{h}})=\delta_{\mathbf{kh}}-\textstyle\sum_j \mu_{\mathbf{k}j}{}^*\mu_{\mathbf{h}j},$$

where $E_j$ is the energy value of the core state $j$ and $V(\mathbf{k})$ is a Fourier coefficient of potential

$$V(\mathbf{k})=\Omega_0{}^{-1}\int e^{i\mathbf{k}\cdot\mathbf{r}}V(\mathbf{r})d\mathbf{r}. \tag{5}$$

The Fourier coefficients $V(k)$ are given in Table II as functions of $m^2=(a\mathbf{k}/2\pi)^2$ for $S$, $P$, and $D$ states ($a$ is the lattice parameter).

OPW expansions were constructed for 24 states mentioned in Sec. II at the symmetry points $\Gamma$, $H$, $P$, and $N$ in the Brillouin zone. The Brillouin zone for the body-centered cubic lattice is shown in Fig. 1. Linear combinations of orthogonalized plane waves were employed which transformed according to the irreducible representations of interest (see appendix of reference 17). Because high-speed electronic computing equipment is not available at the University of Miami, the computations did not in general involve higher than fourth order determinants. Fifth-order determinants were solved for two states: $N_1$ and $P_4$. Third- and second-order determinants were used for the states in the $F$ band where only a qualitative indication of the energy is required. Such highly excited states can probably be reasonably well represented by small numbers of plane waves. The lowest two eigenvalues (in one case, three) of all the representations calculated are given in Table III. The order of the levels at the four symmetry points is shown in Fig. 2.

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[18] The last statement is not strictly accurate. One should use a procedure essentially similar to that of reference 12 to allow for fact that the effective exchange potential for the core states will deviate from that of the valence electron. It was felt, however, that the resultant gain in accuracy was not sufficient to justify the rather considerable labor involved.

[19] This calculation was made for a lattice parameter of 5.20 A, or $r_s=4.84$ atomic units.

TABLE III. Lowest energy states in potassium (energies in rydbergs).

| Representation | Order of determinant | No. of waves | Energies | |
|---|---|---|---|---|
| | | *S*-like states | | |
| $\Gamma_1$ | 8 | 135 | −0.4304 | +0.8346 |
| $H_1$ | 4 | 62 | +0.2651 | +0.9760 |
| $P_1$ | 4 | 40 | +0.0544 | +1.1445 |
| $N_1$ | 5 | 22 | −0.2239 | +0.2682<br>+0.6274 |
| | | *P*-like states | | |
| $\Gamma_{15}$ | 4 | 42 | +0.6986 | 1.3277 |
| $H_{15}$ | 4 | 38 | +0.0621 | +0.9057 |
| $P_4$ | 4 | 18 | −0.1262 | +0.9340 |
| $N_{1'}$ | 4 | 18 | −0.1902 | +0.5561 |
| $N_{3'}$ | 4 | 20 | +0.1765 | 0.7813 |
| $N_{4'}$ | 4 | 20 | +0.3561 | 1.0721 |
| | | *D*-like states | | |
| $\Gamma_{25'}$ | 4 | 48 | +0.2200 | +1.4814 |
| $\Gamma_{12}$ | 4 | 54 | +0.2640 | +0.9263 |
| $H_{25'}$ | 4 | 56 | +0.5372 | +1.2726 |
| $H_{12}$ | 4 | 54 | −0.1322 | +1.1224 |
| $P_3$ | 3 | 36 | +0.4856 | +1.3603 |
| $N_2$ | 4 | 24 | +0.0552 | +0.8447 |
| $N_3$ | 4 | 28 | +0.6939 | +1.2785 |
| $N_4$ | 4 | 24 | +0.4363 | 0.8300 |
| | | *F*-like states | | |
| $\Gamma_{25}$ | 3 | 48 | +0.2897 | +1.8382 |
| $\Gamma_{2'}$ | 2 | 32 | +1.7401 | 4.1990 |
| $H_{25}$ | 3 | 48 | 1.4246 | 1.5285 |
| $H_{2'}$ | 3 | 56 | +0.7046 | +2.8097 |
| $P_5$ | 3 | 36 | +0.5967 | +1.3760 |
| $N_{2'}$ | 3 | 24 | +0.8945 | 2.0873 |

In order to study the convergence of the OPW expansion, an eighth order secular determinant for the state $\Gamma_1$ was solved on the Whirlwind Computer at the Massachusetts Institute of Technology through the courtesy of Professor J. C. Slater and Mr. F. J. Corbato. Convergence of the eigenvalue to the value $-0.447$ found by the cellular method for this state for the potential $V_s$ appeared to be slow. (The best value of the energy of the lowest state is $-0.453$ rydberg found from the Hartree-Fock equations directly without the approximation of an exchange potential.) Table IV shows the lowest eigenvalue in each order: from first to eighth, and the lowest six eigenvalues in eighth order. It is interesting to note that the major change occurs between first and second order (where there are 13 waves). There also seems to be a clustering of eigenvalues in a region near $E=+1.25$. A small eigenvalue change in each order is necessary, but not sufficient to ensure convergence.

Using this example as a guide, we would expect that those solutions of fourth-order determinants based on forty or more waves should be convergent to about 0.04 rydberg. This estimate may be conservative, for some of the higher states may be better represented by a few orthogonalized plane waves than the lowest state. In particular, the convergence of the *D*-band states may be somewhat better. It is also reasonable to expect that the difference between energy levels found using approximately the same number of waves is stable. For this reason, it is likely that the state $N_1$ will continue to lie below $N_1'$. However, it is possible that in higher order, $P_4$ would be found to lie below $H_{12}$, since $H_{12}$ appears nearly convergent in fourth order with 54 waves while $P_4$ is farther from convergence in fifth order with 24 waves. (By a peculiarity of the group theory, each order of the secular determinant for $P_4$ only includes a small number of additional waves.) Many of the results of this work depend only on relative positions of the levels and are probably reliable even if the absolute value of the energies are somewhat uncertain. Nevertheless, the convergence appears to be much poorer than that of the augmented plane wave method.[20]

A very important question in the calculation of energy bands is the sensitivity of the electron energy levels to changes in the potential. One would hope that such features as the relative order of the levels at a symmetry point would be reasonably independent of details of the potential. Unfortunately, the contrary result seems to be indicated by some work of Howarth on copper.[20] Howarth found that the assumption that the potential is constant in the region outside the inscribed sphere in the atomic cell was sufficient to invert the triply degenerate and doubly degenerate *D*-band levels at the center of the Brillouin zone in comparison to an earlier calculation.[21] This modification of the potential is used not only in the augmented plane-wave method employed by Howarth[20] but also in the method of Kohn and Rostoker.[22] The effect of such a modification of the potential was examined in this case. Since the core wave functions do not extend into the region in which the potential is to be modified, it is necessary only to consider the effect of appropriate changes in the Fourier coefficients of potential. To sufficient accuracy, we may assume that the original potential is just the Coulomb potential $2/r$ of the positive ion. It is advantageous to choose the constant potential so that the $m^2=0$ coefficient of the difference vanishes. Since the Coulomb potential is reasonably flat in this region, the difference in the potentials is small, and the Fourier

TABLE IV. Lowest eigenvalues by order for $\Gamma_1$ (in rydbergs). The lowest six eighth-order eigenvalues are also given.

| Order | Lowest $E(\Gamma_1)$ | Order | Lowest $E(\Gamma_1)$ |
|---|---|---|---|
| 1 | −0.2371 | 5 | −0.4125 |
| 2 | −0.3834 | 6 | −0.4232 |
| 3 | −0.3900 | 7 | −0.4246 |
| 4 | −0.4049 | 8 | −0.4304 |
| Lowest 6 eigenvalues in eighth order | | | |
| | −0.4304 | | 1.2621 |
| | +0.8346 | | 1.3309 |
| | 1.1478 | | 1.4525 |

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

[21] D. J. Howarth, Proc. Roy. Soc. (London) **A220**, 513 (1953).

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coefficients of the difference in potential (which may be computed analytically) are so small that the effects on the energy levels are quite negligible. There may, however, be good reason why this modification is not so serious as in Howarth's case.[20]

## IV. DEPARTURES FROM THE EFFECTIVE MASS APPROXIMATION

The effective mass near $\mathbf{k}=0$ can be taken from the work of Berman, Callaway, and Woods as 85.6% of the free-electron mass. However, the proximity of $D$ band states at $N$, $H$, and $P$ to the ground state $\Gamma_1$ (note that $N_1$, and $P_4$ contain $D$ functions as well as $S$ and $P$, respectively) suggest that there may be appreciable $k^4$ terms in the expansion of $E(\mathbf{k})$ near $\mathbf{k}=0$. The coefficient of $k^4$ can be calculated according to the procedure of Silverman[23] within the framework of the cellular method.

According to Silverman, if we write

$$E(\mathbf{k})=E_0+E_2k^2+E_4k^4, \tag{6}$$

then

$$E_4=\frac{2}{5}r_s^2E_2-\frac{4}{15}\frac{E_2^2}{\gamma}r_s^2\left(\frac{rf_d^1}{f_d}\right)^{-1}+\frac{\gamma E_2}{u_0(r_s)}\left[\gamma^{-1}E_2\left(\frac{\partial u_0}{\partial E}\right)_{r_s,E_0}-\frac{r_su_0(r_s)\int_0^{r_s}P_p^2dr}{P_p^2(r_s)}\right], \tag{7}$$

where $r_s$ is the radius of the atomic sphere, and

$$\gamma=r_s^3u_0^2(r_s)/3;$$

$u_0$ is the cellular method wave function for $k=0$, $f_d$ is a solution of the wave equation for a $D$ state of energy $E_0$, and $P_p$ is the $P$ function involved in the usual calculation of the effective mass. This expression was evaluated using the results for $u_0$, $E_0$, $E_2$, and $P_p$ of the previous calculation of Berman, Callaway, and Woods[5] plus a $D$ function calculated using the potential $V_d$ given in Table I for energy $E_0$. The quantity $(\partial u_0/\partial E)_{r_s,E_0}$ was evaluated by expressing $u_0$ for $r>4$ as a sum of regular and irregular Coulomb functions with coefficients that are known functions of energy according to the procedure of Ham[24] and then differentiating the expansion. The value of $E_4$ obtained was 1.64 in atomic units. Such a term would give a contribution to the cohesive energy in the cellular method of 5.81 $E_4/(r_s)^4$ or 5.4 kcal/mole (a repulsion), which, however, is probably canceled by the additional attractions resulting from polarization and relativistic effects.

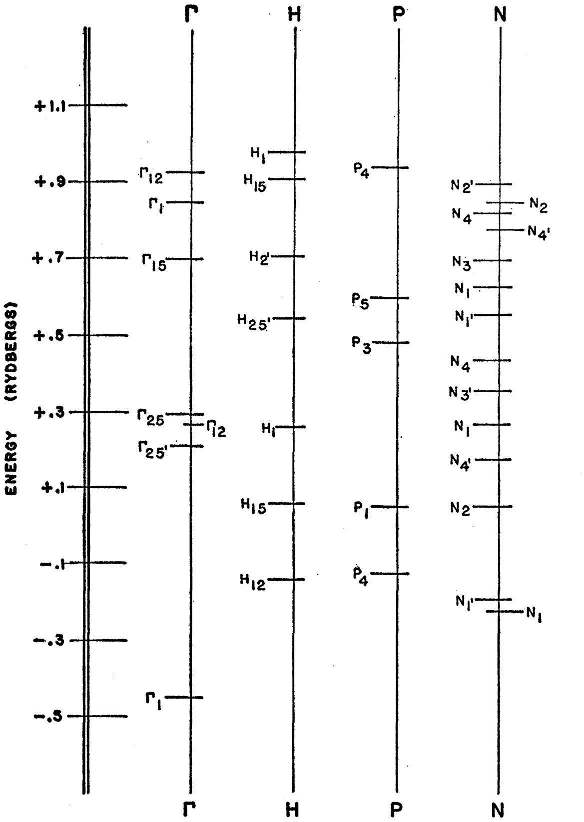

FIG. 2. Order of the energy levels at the four symmetry points $\Gamma$, $H$, $P$, and $N$. All levels with $E<1$ ry are shown.

This relatively large value of $E_4$ indicates that there will be marked deviations of the energy surfaces from the free-electron approximation. As pointed out by Cohen,[25] a large $E_4$ also suggests that there may be important deviations of the energy surfaces from spherical symmetry, since if expanded in powers of $\mathbf{k}$, the lowest such terms will be proportional to the fourth power of the wave vector.

## V. STRUCTURE OF THE LOWEST BAND

In order to determine the form of the lowest $E(\mathbf{k})$ surface, it is necessary to determine the energies of a large number of the states between the end points $\Gamma_1$, and $H_{12}$ of the band. This is very difficult because a very large number of terms in the OPW secular determinant would be required in order to include a reasonable number of waves, even along symmetry axes like (100). Accordingly, we have recourse to an interpolation scheme. It seems natural to expand $E(\mathbf{k})$ in a Fourier series, including only those terms which have the proper symmetry. An expansion in powers of $k$, i.e., Kubic Harmonics, about $k=0$ does not seem desirable because

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[25] M. H. Cohen (private communication).

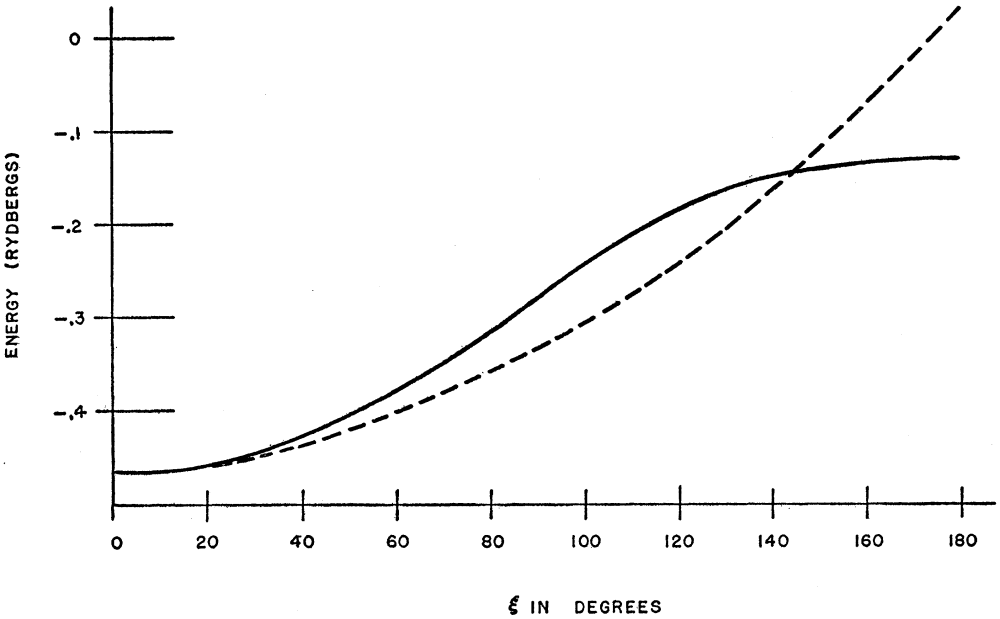

FIG. 3. Lowest energy band along 100 axis in the Brillouin zone as given by Eq. (8) (solid line), and as given by a free-electron approximation for $m/m^*=1.168$ (broken line).

it will be difficult to obtain the proper behavior of $E(\mathbf{k})$ at symmetry points. The Fourier series approach meets this requirement. If we consider the lowest plane waves that are periodic in the reciprocal lattice, we have

$$\begin{aligned} E(\mathbf{k}) = E_0 &+ \alpha \cos\xi \cos\eta \cos\zeta + \beta(\cos2\xi + \cos2\eta + \cos2\zeta) \\ &+ \gamma(\cos2\xi \cos2\eta + \cos2\xi \cos2\zeta + \cos2\eta \cos2\zeta) \\ &+ \delta(\cos3\xi \cos\eta \cos\zeta + \cos3\eta \cos\xi \cos\zeta \\ &\qquad + \cos3\zeta \cos\eta \cos\xi), \qquad (8) \end{aligned}$$

where $\xi = k_x a$, etc. Such an expansion will have the proper zero gradient at symmetry points. This is just the form of expression for a single $S$ band that is obtained from the tight binding interpolation scheme of Slater and Koster.[26]

An attempt was made to fit the lowest band with an expression of this form. A five-parameter scheme was chosen using $E_0$, $\alpha$, $\beta$, $\gamma$ and $\delta$ as in (8). The constants were determined from the energy of the $\Gamma_1$ state [$E(\Gamma_1) = -0.4525$], the effective mass near $k=0$ taken from the calculation of Berman, Callaway, and Woods ($E_2 = m/m^* = 1.168$),[5] and the lowest energies of the states $H_1$, $P_4$, and $N_1$. The constants are given in Table V. The energy bands determined by Eq. (8) are shown in Figs. 3 and 4, for the 100 and 110 axes, where they are compared with the parabolic bands for "free electrons" with an effective-mass ratio $m/m^* = 1.168$.

TABLE V. Parameters in Eq. (8).

| | |
|---|---|
| $E_0 = -0.2410$ | $\gamma = +0.0106$ |
| $\alpha = -0.1937$ | $\delta = +0.0112$ |
| $\beta = -0.0277$ | |

The bands shown in Figs. 3 and 4 deviate in important respects from the free-electron approximation. It is likely that these deviations are too large, since if $E_4$ is calculated from (8), it turns out to be considerably larger, though of the same sign, than that found from the cellular method. It is not easy to fit a spherical free-electron band accurately in this way. However, the qualitative features may be correct. The bands first rise somewhat faster than the free-electron approximation indicates and then level off so as to have zero slope coming into $H$ and $N$.

It was believed that the accuracy of Eq. (8) with the five parameters given was not sufficient to justify a detailed and accurate calculation of the density of states. The numerical calculation of a density of states from (8) would have to be done very carefully since we are looking for deviation from the $[E - E(\Gamma_1)]^{\frac{1}{2}}$ behavior of a free-electron band. In order to get some insight into the qualitative features of the density-of-states curve, it is probably sufficiently accurate to use the method of Houston[27] in which the density-of-states curve is computed along certain symmetry lines in the Brillouin zone, and the over-all density of states is found by interpolation. Houston's method is known to give use to spurious singularities resulting from exaggerated contributions from symmetry points such as $N$, $H$, and $P$ where the energy surfaces have zero gradient. But the occupied portion of the band, with which we are primarily concerned, does not extend up to $N$, which is the critical point closest to the origin. Consequently, Houston's method will give no spurious

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[26] J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1948 (1954).

[27] W. V. Houston, Revs. Modern Phys. **20**, 161 (1948).

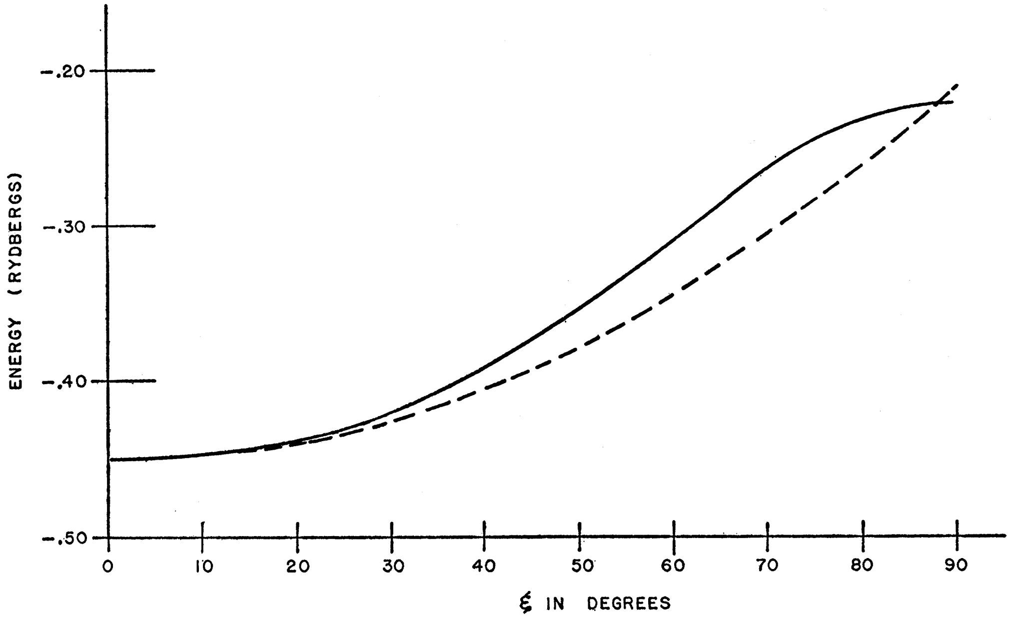

FIG. 4. Lowest energy band along 110 axis in the Brillouin zone as given by Eq. (8) (solid line), and as given by a free-electron approximation for $m/m^*=1.168$ (broken line).

singularities in the occupied portion of the density of state curve.

A qualitative density of states curve is shown in Fig. 5 where it is compared with that for a parabolic band. For energies only slightly above the bottom of the band, the density of states curve must coincide with that for a free-electron band, since one of the conditions on Eq. (8) was that it yield the correct effective mass. As the energy increases, the physical curve rises more slowly than the free electron curve due to the effect of the positive $k^4$ terms. But as the energy rises still further, the band flattens, and the density-of-states curve crosses the free-electron curve. This crossover has probably occurred before the Fermi surface is reached, so that the density of states on the Fermi surface should be higher than for a free-electron gas. One would also expect deviations from spherical symmetry.

Beyond the Fermi level, the density of states should rise rapidly to a peak at an energy in the neighborhood of the $N_1$ level. The density of states will then fall. At an energy 0.46 ev above the $N_1$ level, the second Brillouin zone begins with the $P$-like level $N_{1'}$. The proximity of $N_{1'}$ to $N_1$ will cause the lowest band to curve sharply coming into $N_1$. This curvature is not reproduced by Eq. (8). $N_{1'}$ is still $\frac{3}{4}$ ev below the top of the first zone at $H_{12}$, so that there is considerable overlapping of the bands. The total band width from $\Gamma_1$ to $H_{12}$ is 4.36 ev, approximately two volts less than would be expected on the basis of the effective mass approximation alone. The occupied portion of the band has a width of about 3.1 volts using $E(\Gamma_1)$, $E_2$, and $E_4$. Equation (8) would not give a significantly different result.

The structure of the x-ray $K$-absorption edge in potassium has been examined by Platt.[28] Deviations from free-electron absorption in the direction of less absorption are noticed in a region beginning a little more than 1 ev above the Fermi level. One would expect $D$ states to be important in this region, and these might serve to reduce the transition probability to the $1s$ core level.

It is interesting to compare the energy bands of potassium with those of the other alkali metals. Since reliable band calculations have not yet been performed for rubidium and cesium, the principal comparison will be with sodium. The band structure of sodium has been studied by many workers, the most recent calculation being those of Ham[11] and Howarth and Jones.[29] Both calculations utilize the cellular method, but Ham's work is based on the Quantum Defect Method and does not utilize an explicit potential.

According to Howarth and Jones, the lowest level at the zone corner $H$ is $H_{15}$, which is a $P$-like state. Next comes $H_{12}$ and then $H_1$. (This ordering was also found by Ham.) $H_{12}$ appears to be the lowest state at this point in potassium. At $P$, the lowest state in sodium is $P_1$, which is $S$-like. It lies 1.76 ev below $P_4$ which mixes $P$ and $D$ states. In potassium, this order is reversed. At $N$ the lowest level according to Howarth and Jones is $N_1$, but Ham has found $N_{1'}$, which contains $P$ functions to lie lower than $N_1$. $N_1$ appears to be lower in potassium.

It is likely that the principal differences in band forms between sodium and potassium can be explained in terms of increased importance $D$ bands in the latter element. In potassium, the lowest states which contain

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[28] J. B. Platt, Phys. Rev. **69**, 377 (1946).

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

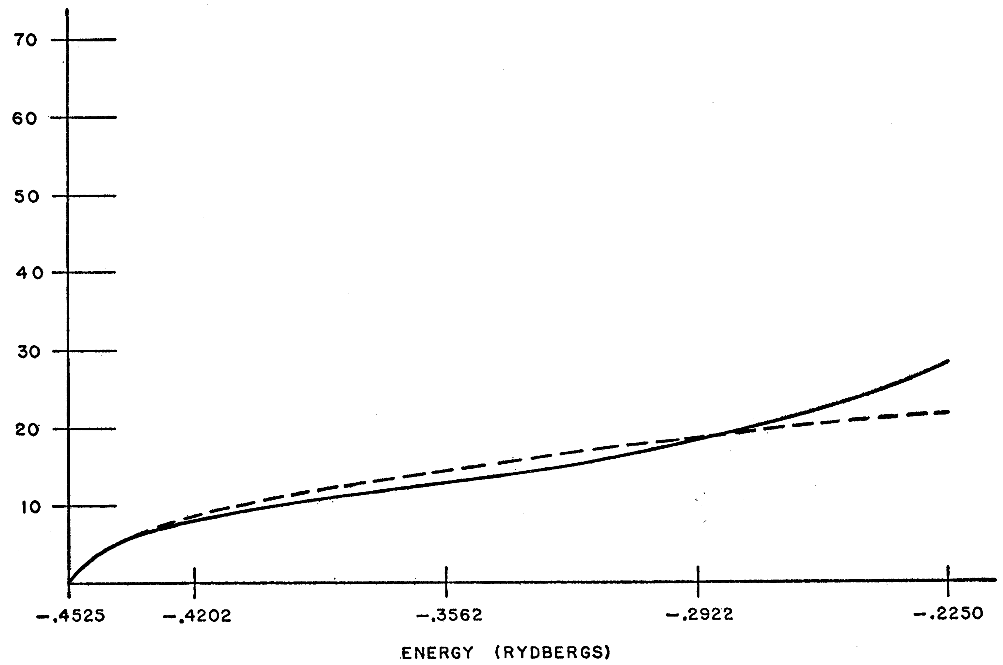

FIG. 5. Density of states in arbitrary units as a function of energy. The solid curve was obtained from Eq. (8) and the broken line from the free-electron approximation.

$D$ functions tend consistently to lie lower than states containing only $S$ or $P$ functions (except of course, for the basic $4S$ level $\Gamma_1$). The increased importance of $D$-like levels seems also to lead to greater deviations from free-electron behavior in this case. That $D$ states should be important in potassium would naturally be expected from observation of the periodic table of the elements since as soon as the $4s$ level has filled in calcium, the $D$ levels begin to be occupied in scandium. For this reason, one would also expect $k^4$ terms in the $E(\mathbf{k})$ expansion to be more important in potassium than in lithium or sodium.

## VI. HIGHER BANDS

It is interesting to discuss not only the lowest band but also higher levels, in particular $P$ and $D$ levels, to see to what extent the bands are similar to those of other elements which have the body centered cubic lattice. We will be concerned here primarily with the order of levels within a given band, rather than relative order of the bands. Wigner has given an interesting analysis of the structure of $P$ and $D$ bands in the body-centered lattice,[30,31] based on possibilities of satisfying the boundary conditions within the cellular method. His work is in general agreement with this calculation.

Wigner predicts for the $P$ band that the $\mathbf{k}=0$ state $\Gamma_{15}$ should be highest, that the state $N_{1'}$ should be lowest with a large separation of states at this point, and that the state $H_{15}$ should be reasonably close to the bottom of the band. The calculation confirms these predictions. However, Wigner also predicts that $P_4$ should lie near the middle of the band whereas here it has been found to be considerably lower than $H_{15}$. However, some of this lowering may be due to the $D$-like functions present in $P_4$.

For the $D$ band we find $N_2$ below $\Gamma_{25'}$ as predicted. States of $\mathbf{k}$ perpendicular to the 111 directions, i.e., at $N$, are predicted to lie lowest. Since $N_1$ may be considered to belong to the $D$ band as well as to the $S$ band, this statement is correct. The state $P_4$ lies below $N_2$. Note that $H_{12}$ is also low. Wigner's diagrams of the relations between $P$ and $D$ bands would seem to be applicable only in lighter elements and are incorrect in this case.

The general shape of the $D$ band found here is in agreement with a recent calculation for body-centered iron[17] by the OPW method, and in also with that found for iron by a modified tight-binding method.[32] We observe that here also, the separation of the triply and doubly degenerate $D$ states is much less at the center of the zone than at the corner $H$, and that the maximum separation of the $D$ band is at the point $N$. Except for the fact that the OPW iron calculation has $N_4$ above $N_3$, the relative order of the $D$ levels at a given symmetry point is much the same in iron and potassium. We note that in all three cases, the triply degenerate $D$-band state is lowest at $k=0$, but the doubly degenerate state is lowest at $H$. The order of $D$ levels in potassium is also in agreement with a calculation for body-centered titanium,[33] except in that case, a more

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[30] E. Wigner, *Proceedings of the International Conference on Theoretical Physics*, Kyoto and Tokyo, September, 1953 (Science Council of Japan, Tokyo, 1954), p. 650.

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

[32] F. Stern, Ph.D. thesis, Princeton University, 1955 (unpublished).

[33] B. Schiff, Proc. Phys. Soc. (London) A68, 686 (1955).

extensive calculation would be desirable in order to make a more detailed comparison.

There is a simple device which seems to reproduce the calculated level order within a given band very well in this case. Let $\psi_{\mathbf{k}}{}^{i}$ represent the wave function for the $i$th irreducible representation of the wave vector **k**. $\psi_{\mathbf{k}}{}^{i}$ is expanded in orthogonalized plane waves

$$\psi_{\mathbf{k}}{}^{i}=\sum_{\mathbf{h}}\beta^{i}{}_{\mathbf{k},\,\mathbf{h}}\mathrm{M}_{\mathbf{k}+\mathbf{h}}, \tag{9}$$

where $X_{\mathbf{k}+\mathbf{h}}$ is given by (3). The vector **h** runs over all reciprocal lattice vectors. The levels at symmetry points may be ordered accordingly to the quantity $(\mathbf{k}+\mathbf{h}')^2$ where $(\mathbf{k}+\mathbf{h}')$ characterizes the OPW of lowest energy belonging to $\psi_{\mathbf{k}}{}^{i}$. Since this is an ordering according to kinetic energy, there is a vague resemblance to the principle of maximum smoothness.[32]

This prescription says in essence, that the order of levels at symmetry points in a given band is what would be expected for free-electron bands. It is not surprising that it gives the correct results for potassium. It is more interesting that it seems to work reasonably well in iron. Even in potassium, however, one must not suppose that the numerical energy values of the levels will be in good agreement with a free-electron model. Inspection of Fig. 2 will reveal that some levels will connect by bands which must depart severely from the free electron form.

The successful comparison of these results with other calculations for the various bands suggests that at least the relative order of levels within a given band is not very sensitive to details of the potential. It is possible, then, that the general forms of individual $S$, $P$, and $D$ bands are now well understood for the body-centered cubic lattice. It is important to note, however, that the situation in regard to overlap of these bands is much less clear because the overlap is much more sensitive to the potential.[17] It is interesting to note that there is apparently a very considerable degree of overlap in potassium.

Since there is evidence that the general form of a band is reasonably independent of potential, it is interesting to consider the form of the $F$ band. It is a little difficult precisely to define the $F$ band since some representations ($\Gamma_{15}$, $H_{15}$, $P_4$, $N_{1'}$, $N_{3'}$, and $N_{4'}$) also contain $P$ functions. At $k=0$, the states $\Gamma_{25}$, $\Gamma_{2'}$, and $\Gamma_{15}$ contain $F$ functions. At $P$ we have $P_4$, $P_5$, and $P_1$, and at $N$ we have $N_{2'}$, $N_{1'}$, $N_{4'}$, $N_{3'}$. The lowest predominantly $F$-like state is $\Gamma_{25}$, and the top of the band also appears to occur at $\Gamma$ with $\Gamma_{2'}$. This order is reversed at $H$: $H_{2'}$ lies below $H_{25}$. We find $\Gamma_{15}$ intermediate between $\Gamma_{25}$ and $\Gamma_{2'}$ and $H_{15}$ intermediate between $H_{2'}$ and $H_{25}$. At $P$, the order is apparently $P_5$, $P_4$, and $P_1$.

## ACKNOWLEDGMENTS

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# Absorption Spectra, Zeeman Effects, and Magnetic Properties of Neodymium Salts*†

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The absorption spectra of nine neodymium salts were obtained in single crystals at liquid helium temperature and high dispersion. The Zeeman effect of the lines was observed in a field of about 37 000 gauss with different orientations of the crystals, so that the magnetic splitting of the ground and excited states could be measured. This provides valuable clues for the interpretation of the spectra and quantitative data for the dirivation of the crystal field. The results are related to those obtained in paramagnetic resonance measurements.

## 1. INTRODUCTION

It is well known that the salts of the rare earths may give sharp absorption lines particularly at low temperatures and that often these lines are split in a magnetic field. It is also known since the work of Bethe[1] and Kramers[2] that the crystal field splits the

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† In order to conserve journal space, this paper has been considerably condensed. More details can be found in a technical report [U. S. Atomic Energy Commission Report NYO-3977 (unpublished)] of which a limited number of copies are available to interested persons. This report contains in particular the complete wavelength measurements of the field-free absorption spectra of most of the salts and the Zeeman effects of all lines which show resolved patterns. This supplementary material has also been deposited as Document No. 4886 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $13.75 for photoprints or $4.50 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to Chief, Photoduplication Service, Library of Congress.

[1] H. Bethe, Ann. Physik **3**, 133 (1929); Z. Physik **60**, 218 (1930).

[2] H. A. Kramers, Proc. Acad. Sci. Amsterdam **32**, 1176 (1929); **33**, 960 (1930).