

## Calculation of Energy Bands in Alkali Halides\*†

L. J. PAGE‡ AND E. H. HYGH

Department of Physics, University of Utah, Salt Lake City, Utah 84112

(Received 11 August 1969; revised manuscript received 25 November 1969)

The electronic energy bands in LiF, NaCl, and KBr have been calculated using the augmented-plane-wave (APW) method. The usual APW method is improved upon by including nonspherical terms in the potential and by varying the Slater free-electron-exchange approximation in order to match experimental band-gap data. It was found that the nonspherical terms have about an 0.8-eV effect in LiF, a 0.4-eV effect in NaCl, and a 0.1-eV effect in KBr. It was found that if the exchange potential is increased by about 10%, experimental band-gap data can be matched. Transitions calculated from the energy-band calculations were compared with experimental optical-absorption and optical-reflectance data. Agreement is generally good. Using numerical differentiation, the effective mass at the bottom of the conduction band was calculated. The effective masses were found to be approximately  $1.2m_e$  for LiF,  $0.6m_e$  for NaCl, and  $0.5m_e$  for KBr. Experimental values exist only for KBr and are in good agreement.

## I. INTRODUCTION

THE valence- and conduction-band structure of LiF, NaCl, and KBr have been calculated by the augmented-plane-wave (APW) method.<sup>1,2</sup> However, two modifications were made to the usual APW method. The first modification concerns the potential. As originally formulated, the APW method does not take into account any nonspherical potential terms. When the potential for the NaCl structure compound is expanded in spherical harmonics, the first term with less than spherical symmetry is proportional to  $r^4 Y_4^m$ . If point ions are assumed, this term may be written

$$V_4(r) = \frac{2\sqrt{(4\pi)r^4\alpha_m^4}}{(\sqrt{9})a^5} \times \{Y_4^0(\theta, \phi) + 0.5976[Y_4^4(\theta, \phi) + Y_4^{-4}(\theta, \phi)]\}, \quad (1)$$

where  $\alpha_m^4$  is a constant to be determined by summing the contributions from neighboring shells of ions. The constant  $a$  is the nearest-neighbor distance. It is necessary to assume the point-ion approximation in calculating the nonspherical terms in the alkali halides for reasons to be discussed later.

The next term in the expansion is the sixth-order nonspherical potential term. Using point ions, this potential may be written

$$V_6(r) = \frac{2\sqrt{(4\pi)r^6\alpha_m^6}}{(\sqrt{13})a^7} \{Y_6^0(\theta, \phi) - 1.0311 \times 10^{-6}[Y_6^4(\theta, \phi) + Y_6^{-4}(\theta, \phi)]\}. \quad (2)$$

To evaluate the effect of the nonspherical potential,

\* Work supported by the National Science Foundation Grant No. GP-7025.

† This is the essential part of a dissertation submitted to the Physics Department, University of Utah, in partial fulfillment of the requirements of a Doctor of Philosophy Degree.

‡ Present address: Electromagnetic Systems Laboratories, Sunnyvale, Calif. 94086.

<sup>1</sup> J. C. Slater, Phys. Rev. 51, 846 (1937).

<sup>2</sup> T. L. Loucks, *Augmented Plane Wave Method* (W. A. Benjamin, Inc., New York, 1967), Chap. II.

matrix elements of Eqs. (1) and (2) between APW's must be evaluated. To use the actual APW's introduces many calculational difficulties. Because of this fact, the APW's were approximated by plane waves. This is justifiable because the principal contribution from the nonspherical potential occurs for values of  $r$  greater than and approximately equal to the APW sphere radius. For the value of  $r$  equal to or slightly less than the APW sphere radius, the APW is very plane-wave-like; for  $r$  greater than the sphere radius, the APW is a plane wave. For values of  $r$  close to the origin, where the APW's are not very plane-wave-like, Eqs. (1) and (2) are small and the contribution to the matrix element is small, thus introducing little error.

The second rather minor modification to the APW method was to express the Slater free-electron exchange approximation as

$$V_{\text{exch}}(r) = -6\alpha[(3/8\pi)\rho(r)]^{1/3}, \quad (3)$$

where  $\alpha$  is an adjustable parameter which was varied in order to match experimental band-gap data. This is justifiable since free-ion charge densities are used to construct the exchange potential, and they certainly are not free-electron-like.

## II. DETAILS OF CALCULATION

The APW method is discussed at length<sup>1,2</sup> in the literature, therefore, a complete discussion is unnecessary here. Briefly, the method is concerned with solving the Schrödinger equation for a many-centered potential which exhibits the symmetry of the crystal. The actual crystal potential is usually approximated by a potential which is spherically symmetric inside spheres centered at each atomic site and constant in the region between spheres, the so-called "muffin-tin" potential.

The NaCl structure is fcc and has four molecules per unit cell. With two different elements in the cell, there are two APW spheres; some ambiguity exists as to the most appropriate choice of the relative sizes of the spheres centered on the two different atomic sites. In

TABLE I. APW sphere radii in a.u. for LiF, NaCl, and KBr.

Ion	APW sphere radius	Wigner-Seitz radius
Li <sup>+</sup>	1.73	2.22
F <sup>-</sup>	2.01	2.59
Na <sup>+</sup>	2.46	3.00
Cl <sup>-</sup>	2.86	3.49
K <sup>+</sup>	3.00	3.86
Br <sup>-</sup>	3.16	4.05

calculations of the conduction bands of AgCl<sup>3</sup> and KCl,<sup>4</sup> the spheres were taken to be the same size. This seems to be an unsatisfactory choice for the alkali halides considered here, since the halogen ions in them are known to be substantially larger than the alkali ions. Because this is particularly true in our case, the APW sphere radii were chosen to be at the point where the potentials of the two ions meet. Values of the nearest-neighbor distance in atomic units for LiF, NaCl, and KBr are 3.80, 5.33, and 6.25, respectively. Table I shows the APW sphere radii used in the present calculation. Also given in Table I are the radii of the Wigner-Seitz spheres which were used to calculate the spherically averaged muffin-tin potentials and the volume integrals for the plane-wave matrix elements of the nonspherical potentials given by Eqs. (1) and (2).

In calculating the spherically symmetric terms in the potential, a superimposed free-ion potential was constructed using the relativistic Dirac self-consistent field atomic calculations due to Liberman *et al.*<sup>5</sup> Once the spherical terms were found and the constant potential adjusted to zero, the nonspherical corrections to the potential were determined.

The spherical term was computed using

$$V(r) = V_c(r) + \sum_i \frac{1}{2a_i r} \times \int_{|a_i - r|}^{|a_i + r|} \left( V_c(r') \pm \frac{2}{r'} \right) dr' \pm \frac{2\alpha_m}{a}, \quad (4)$$

where  $V_c(r)$  is the Coulombic ionic potential,<sup>2</sup>  $\alpha_m$  is the Madelung constant, and the index  $i$  runs over the neighboring ions. This form was used to aid convergence in the sum. It should be pointed out that the Coulombic ionic potential is given by

$$V_c(r) = 2Z/r - U_0(r), \quad (5)$$

where  $U_0(r)$  is the solution to Poisson's equation based on the superposed free-ion atomic charge density

$$\rho_0(r) = \sum_{\text{occ}} |\Psi_{\text{em}}|^2. \quad (6)$$

<sup>3</sup> P. M. Scop, Phys. Rev. **139**, A934 (1965).

<sup>4</sup> P. D. DeCicco, Phys. Rev. **153**, 931 (1967).

<sup>5</sup> D. A. Liberman, J. T. Waber, and D. T. Cromer, Phys. Rev. **137**, A27 (1965).

TABLE II. Potential for alkali-halide ions compared to the potential  $2/r$ . (All values are in a.u.)

Distance	$2/r$	Li <sup>+</sup>	F <sup>-</sup>	Na <sup>+</sup>	Cl <sup>-</sup>	K <sup>+</sup>	Br <sup>-</sup>
1.915	1.0440	-1.0455	0.5550				
2.117	0.9447	-0.9452	0.5887				
2.339	0.8548	-0.8549	0.5976				
2.586	0.7735	-0.7735	0.5893	-0.7763	0.3770		
2.858	0.6999	-0.6998	0.5693	-0.7010	0.4250		
3.158	0.6333	-0.6332	0.5419	-0.6336	0.4455	-0.6433	0.3876
3.490	0.5730	-0.5730	0.5099	-0.5730	0.4464	-0.5770	0.4063
3.857	0.5185	-0.5184	0.4756	-0.5184	0.4345	-0.5199	0.4070
4.263	0.4691	-0.4691	0.4405	-0.4690	0.4144	-0.4695	0.3959
4.711	0.4245	-0.4245	0.4057	-0.4244	0.3897	-0.4245	0.3773
5.206	0.3841	-0.3841	0.3721	-0.3840	0.3624	-0.3840	0.3543
5.754	0.3475	-0.3475	0.3400	-0.3475	0.3340	-0.3475	0.3292
8.854	0.2330	-0.2330	0.2322	-0.2330	0.2317	-0.2329	0.2309
12.807	0.1562		0.1561		0.1562	-0.1562	0.1560
19.106	0.1047		0.1047		0.1047		0.1046
28.503	0.0702		0.0702		0.0702		0.0702

This means  $V_c(r)$  may well be slightly different from the potential for the free ion.

The terms  $V_4(r)$  and  $V_6(r)$  are not as easily evaluated because of the complexity of the currently available expansion techniques such as the Löwdin  $\alpha$ -function technique<sup>2,4,6</sup> used to obtain Eq. (4) above. The method was tried but the accuracy was poor because the equations were expressed in terms of the differences of very large numbers. In contrast, the  $\alpha$ -function expansion terms can be evaluated accurately from the potential  $V = \pm 2/r$  which is the point-ion approximation to the crystal potential. The point approximation was used for two reasons. (a) The calculational difficulties discussed above were too expensive to overcome. (b) The ionic potentials  $V_c(r)$  are "fairly well approximated" by  $2/r$  for distances greater than the APW sphere radii, as can be seen from Table II. For distances greater than the APW sphere radius the metal ions are represented by  $2/r$  to 0.1% or better. The halogens, however, are rather poorly represented by  $2/r$  until distances greater than the lattice constant are reached. However, the table clearly shows that  $2/r$  overestimates the influence the halogen ion has on the conduction-band electron, so that it clearly overemphasizes the effect of the nonspherical potentials on the bands.

The calculations were not carried out self-consistently, since a final set of eigenvalues often times are found<sup>7</sup> to be very close to the values obtained from the first iteration. To check this effect, we compared the results on KCl using our method with the self-consistent APW calculation for KCl by DeCicco.<sup>4</sup> The results agree to within 0.02 Ry for the bottom two bands at  $\Gamma$ ,  $X$ , and  $L$ , except for the  $X_1$  point which differs by 0.05 Ry. The average disagreement within the six lowest bands is  $\sim 0.04$  Ry which is acceptable consider-

<sup>6</sup> P. O. Löwdin, Advan. Phys. **5**, 1 (1956).

<sup>7</sup> J. W. D. Connolly, S. J. Cho, J. B. Conklin, Jr., and J. C. Slater, Solid State and Molecular Theory Group, Massachusetts Institute of Technology, Quarterly Progress Report No. 62, 1966, p. 3 (unpublished).

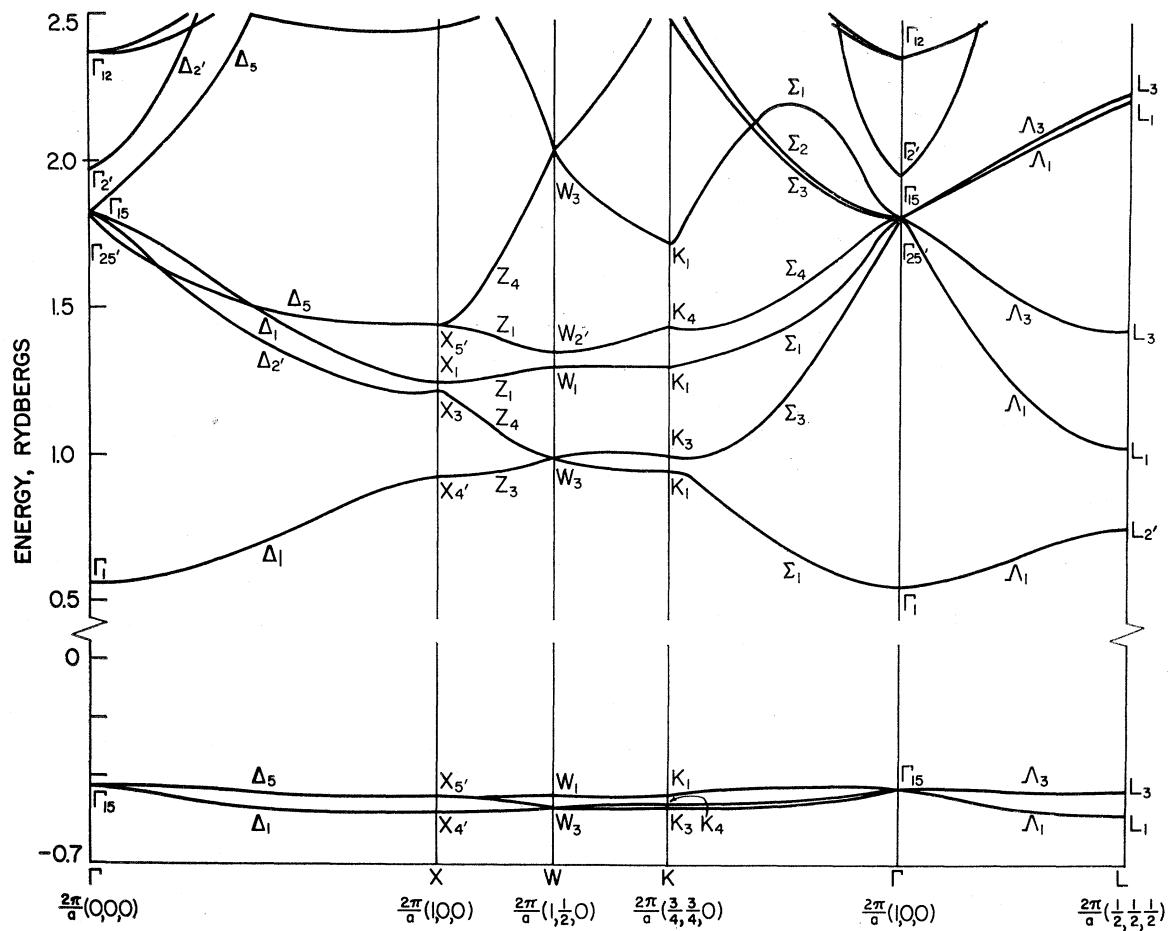


FIG. 1. APW calculation of LiF.

ing the completely different methods of computing the nonspherical corrections.

In all calculations reported here, the expansion in the logarithmic derivatives was carried out to  $l=12$ , and the expansions involving nearest neighbors were carried out to 26th nearest neighbors. The number of APW's used is determined by the number of reciprocal-lattice vectors used in the trial function. The expansion in this calculation involved 27 "recips" in computing the conduction bands and 49 "recips" in computing the valence bands. These numbers provided convergence of the eigenvalues to within 0.005 Ry when the number was increased slightly. The eigenvalues of the valence

and conduction bands were calculated at 15 points along high-symmetry directions and at high-symmetry points for LiF and KBr and at 18 points in NaCl (which included the *LU* symmetry direction and the point *U*).

### III. RESULTS OF CALCULATIONS

#### A. General Features of Bands

The valence and conduction bands of LiF are shown in Fig. 1. The valence band consists of the  $2p^6$  state of F. The band is fairly flat and has a width of 0.88 eV.

TABLE IV. Comparison of theoretical and experimental optical transitions for LiF. (All values are in eV.)

TABLE III. Effective masses at the bottom of the conduction band for LiF. (All values in units of the free-electron mass  $m_e$ .)

Symmetry point	Effective mass
$\Gamma$ (toward <i>X</i> )	1.174
$\Gamma$ (toward <i>L</i> )	1.240
$\Gamma$ (toward <i>K</i> )	1.245
<i>X</i>	-0.394
<i>L</i>	-1.796

<sup>a</sup> See Ref. 5.

<sup>b</sup> See Ref. 6.

<sup>c</sup> See Ref. 7.

Transition	Theory	Experiment <sup>a</sup>	Experiment <sup>b</sup>	Experiment <sup>c</sup>
$\Gamma_{15} \rightarrow \Gamma_1$	13.6	<14.0	13.6	13.5
$L_3 \rightarrow L_2'$	16.4	15.6	14.3	16.0
$X_5' \rightarrow X_4'$	18.5	17.8	17.4	18.0
$L_3 \rightarrow L_1$	20.2	20.75	21.7	21.5
$X_5' \rightarrow X_3$	22.4	22.6	23.0	24.4
$X_5' \rightarrow X_1$	22.9	23.9		

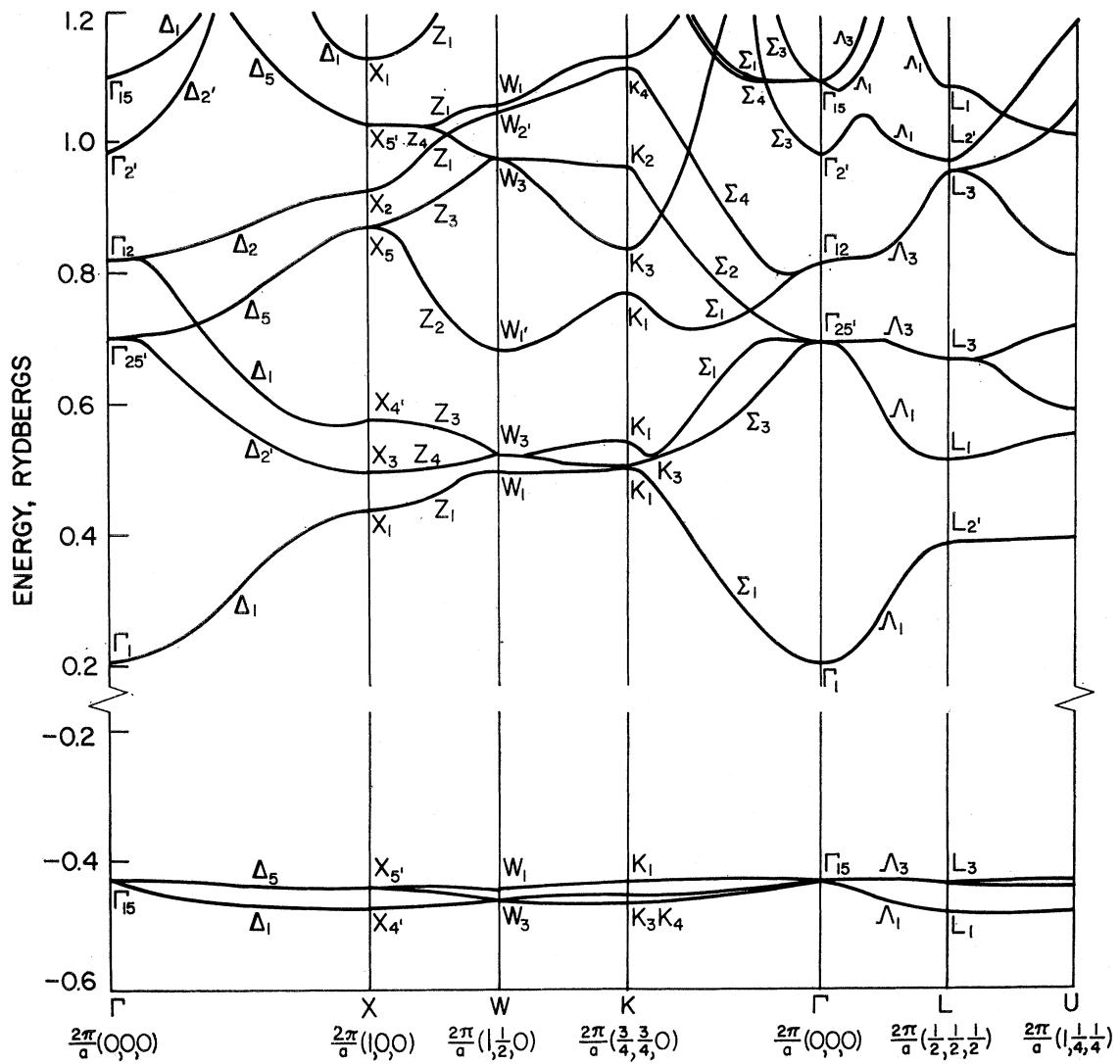


FIG. 2. APW calculation of NaCl.

The conduction band of LiF consists of the 2s state of Li, 2p state of Li and 3d state of F. The bands are quite plane-wave-like as can be seen by the s to p energy gap at  $\Gamma$  of 1.26 Ry versus the plane wave s to p gap of 3.0 Ry; the width of the p band, 0.6 Ry versus the plane-wave width of 1.0 Ry; the 0.38-Ry width of the s band versus 1.0 Ry for the plane-wave case. All of these values are much closer to the plane-wave case than KBr or NaCl. The s-like band never crosses the d-like bands as it does in KBr. (See Fig. 3.) There are a few,  $\Gamma_2'$ , higher f states from the F ion which appear around the  $\Gamma$  point.

The effective mass  $m^*$  was calculated for the bottom of the conduction band at various symmetry points. The equation

$$m^* = h^2 / \frac{d^2 E}{dk^2} \quad (7)$$

was evaluated by taking numerical derivatives. The values of the effective mass at the bottom of the conduction band are given in Table III. In Table III, as well as in Tables VI and VIII, values of the effective mass are given for the three directions around  $\Gamma$  for which the band structure was calculated. Since the effective mass is isotropic at  $\Gamma$ , the three values should

TABLE V. Comparison of the energy-loss function<sup>a</sup> for NaCl and present APW band calculations. (All values are in eV.)

Symmetry point	Theory	Experiment
$\Gamma_{15} \rightarrow \Gamma_1$	8.78	8.97
$L_3 \rightarrow L_2'$	11.30	11.40
$X_5' \rightarrow X_1$	11.90	11.80
$X_5' \rightarrow X_3$	12.80	12.90
$L_3 \rightarrow L_1$	13.10	13.20

<sup>a</sup> See Ref. 9.

TABLE VI. Effective mass at the bottom of the conduction band for NaCl. (All values in units of the free-electron mass  $m_e$ .)

Symmetry point	Effective mass
$\Gamma$ (toward $X$ )	0.573
$\Gamma$ (toward $L$ )	0.712
$\Gamma$ (toward $K$ )	0.676
$X$	-1.461
$L$	-0.512

agree. The differences in the values reflect the difficulty of taking numerical derivatives on a rather coarse grid of points. The values at  $X$  are in the [100] direction and the values at  $L$  are in the [111] direction. Around  $\Gamma$  the effective mass is approximately  $1.2m_e$  which further verifies that the bands are very plane-wave-like for LiF.

The experimental ultraviolet-absorption data for LiF<sup>8-10</sup> has several well-defined peaks. Apparently there has been no previous attempt using an energy-band calculation to identify the transitions responsible for these peaks. In Table IV, the experimental data and the theoretical results for the energies which correspond to the transitions from the valence band to several points in the conduction band are given. Some disagreement exists between the three sets of experimental data. In particular, a peak around 15 eV and a peak around 23 eV both have been resolved into three peaks by Milgram and Givens.<sup>8</sup> There is general agreement that the  $\Gamma_{15} \rightarrow \Gamma_1$  transition occurs at about 13.6 eV. There also seems to be agreement concerning peaks at about 16.0, 18.0, and 21.0 eV. We attribute these peaks to  $L_3 \rightarrow L_2$ ,  $X_5 \rightarrow X_4$ , and  $L_3 \rightarrow L_1$ . In two sets of data there is indication of a transition around 23 eV which probably is  $X_5 \rightarrow X_3$  and  $X_5 \rightarrow X_1$ . Since the calculated band structure of LiF is different in many ways from NaCl or KBr, the fact that agreement with experiment is good is quite encouraging.

The valence band and conduction bands of NaCl are shown in Fig. 2. The valence band consists of the  $3p^6$  state of Cl. The width of this band is 0.57 eV.

The conduction bands of NaCl consist of the  $3s$  band of Na, the  $3d$  band of Cl, and the  $3p$  band of Na. There is also a low-lying  $f$  state which appears around  $\Gamma$ . The bands are not very plane-wave-like, and they resemble the bands of KCl,<sup>4</sup> except that  $X_1$  is lower in energy than  $X_3$ .

Roessler and Walker<sup>11</sup> have experimentally examined the electronic spectra of NaCl. Their experiments consisted of measurements of the reflectance spectrum at near normal incidence. From this data, they calculated the real and imaginary parts of the dielectric constant and then attempted to identify various interband

<sup>8</sup> A. Milgram and M. Givens, Phys. Rev. **125**, 1506 (1962).

<sup>9</sup> D. M. Roessler and W. C. Walker, J. Phys. Chem. Solids **28**, 1507 (1967).

<sup>10</sup> C. Grout and F. Pradal, J. Phys. Chem. Solids **29**, 581 (1968).

<sup>11</sup> D. M. Roessler and W. C. Walker, Phys. Rev. **166**, 599 (1968).

TABLE VII. Comparison of experimental<sup>a</sup> and theoretical absorption for KBr. (All values are in eV.)

Transition	Theory	Experiment
$\Gamma_{15} \rightarrow \Gamma_1$	7.80	7.90
$X_5 \rightarrow X_3$	9.50	9.50
$L_3 \rightarrow L_2$	10.30	10.20
$\Gamma_{15} \rightarrow \Gamma_{25}$	10.40	10.40
$X_5 \rightarrow X_1$	10.80	11.10
$L_3 \rightarrow L_1$	10.60	10.50
$X_5 \rightarrow X_5$	11.50	11.80

<sup>a</sup> See Ref. 15.

transitions, thus obtaining information about the band structure. Such identifications are very speculative. In Table V is shown a comparison of the four highest energy peaks in their data with possible transitions from the present calculations. The possible transitions are not the same as those proposed by Roessler and Walker. When the four smallest magnitude absorptions in their data are left out, the agreement is quite good.

Values of the effective mass for NaCl are shown in Table VI. The values around  $\Gamma$  are in good agreement with a previous calculation of  $0.624m_e$  by Evseev<sup>12</sup> using an entirely different method.

There exist several other calculations<sup>13-15</sup> of the band structure of NaCl. The APW calculation of Clark and Kliewer<sup>15</sup> is in substantial agreement with the present calculation. The orthogonalized-plane-wave (OPW) calculation of Kunz differs from the present calculation mainly in the fact that  $X_1$  is higher in energy than  $X_3$  in the OPW calculation. It has been suggested<sup>16</sup> that the muffin-tin approximation is responsible for this. Since we have improved on the muffin-tin approximation and still find  $X_3$  above  $X_1$  in NaCl, we cannot agree with this. Our nonspherical terms did not affect the gross features of the bands enough to explain the discrepancy. Another difference between the two calculations is that the band gap calculated by Kunz does not match experimental information whereas ours is adjusted so that it does.

The electronic band structure of KBr is shown in Fig. 3. The valence band consists of the  $4p^6$  band of bromine. The width of the valence band is 0.31 eV.

The conduction band of KBr is extremely complicated. It evidently consists of the  $4s$ ,  $4p$ , and  $4d$  bands of K and  $4d$  and  $4f$  bands of Br. In Fig. 4 is shown a sketch of recent experimental optical-absorption data<sup>17</sup> on KBr along with the identifications of the transitions which produce the peaks in this data. Table VII shows a comparison between the exact numerical values of the transitions from the APW calculation in Fig. 3 and

<sup>12</sup> Z. Ya. Evseev, Fiz. Tverd. Tela **5**, 2345 (1963) [English transl.: Soviet Phys.—Solid State **5**, 1705 (1964)].

<sup>13</sup> A. B. Kunz, Phys. Rev. **175**, 1147 (1968).

<sup>14</sup> C. Y. Fong and M. L. Cohen, Phys. Rev. Letters **21**, 22 (1968).

<sup>15</sup> T. D. Clark and K. L. Kliewer, Phys. Letters **27A**, 167 (1968).

<sup>16</sup> A. B. Kunz, W. B. Fowler, and P. M. Schneider, Phys. Letters **28A**, 553 (1969).

<sup>17</sup> K. Teegearden and G. Baldini, Phys. Rev. **155**, 896 (1967).

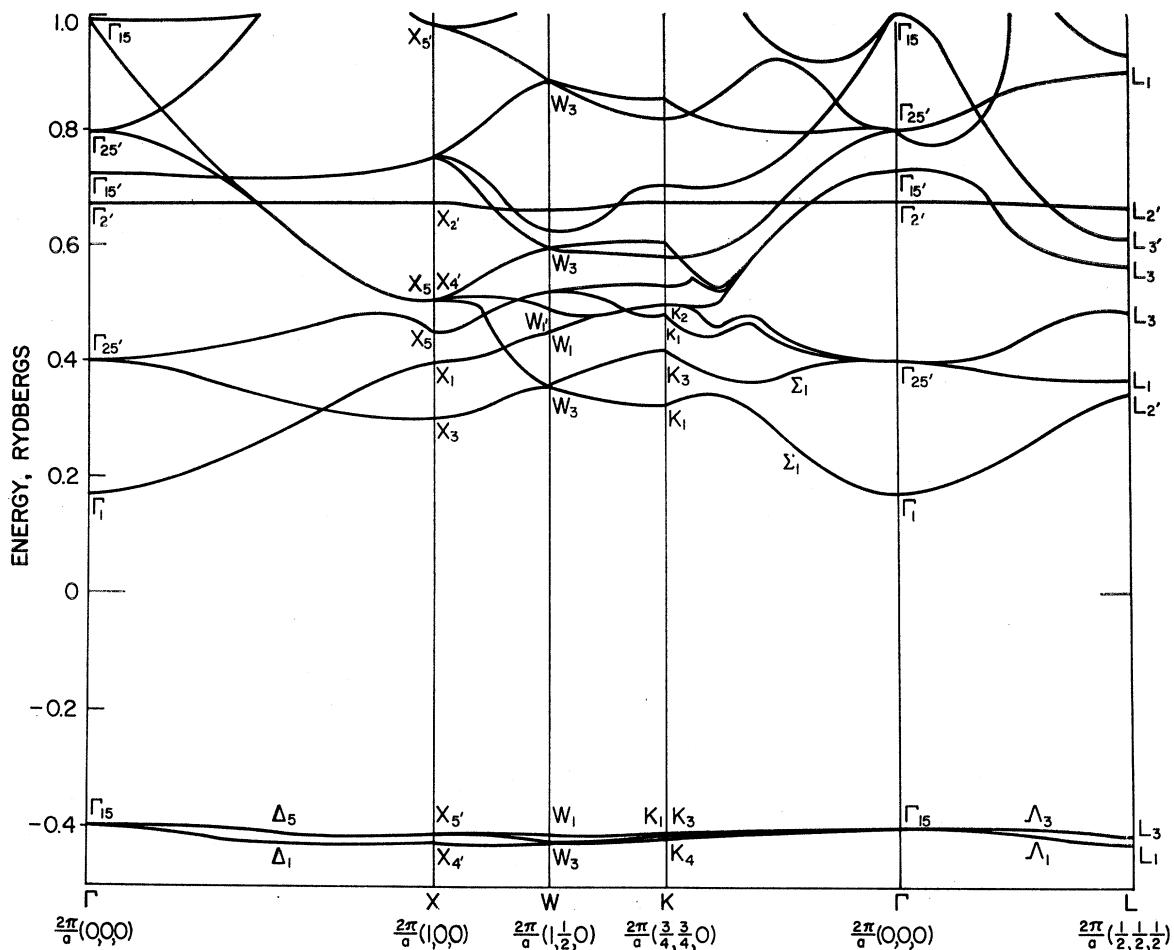


FIG. 3. APW calculation of KBr.

values taken from the data in the paper. The agreement is good and lends confidence to the present APW method of band calculations.

In Table VIII, values of the effective mass at the bottom of the conduction band for KBr are given. The calculations are from the band-structure calculation shown in Fig. 3. Several experimental values of the effective mass for KBr are available. Hall mobility experiments<sup>18</sup> have given values from  $0.34m_e$  to  $0.62m_e$  which are in good agreement with the calculated values at  $\Gamma$  given in Table VIII. Cyclotron resonance experiments<sup>19,20</sup> have given values for the effective mass in KBr of  $0.5m_e$  and  $0.428m_e$ . Both of these values are in good agreement with the calculated values at the  $\Gamma$  point.

Fowler<sup>21</sup> has suggested that there may be strong

<sup>18</sup> R. K. Ahrenkril and F. C. Brown, Phys. Rev. 136, A223 (1964).

<sup>19</sup> M. Mikkor, K. Kanazawa, and F. Brown, Phys. Rev. Letters 15, 489 (1965).

<sup>20</sup> J. W. Hodby, J. A. Borders, and F. C. Brown, Phys. Rev. Letters **19**, 952 (1967).  
<sup>21</sup> W. E. Farley, Phys. Rev. **174**, 922 (1968).

<sup>21</sup> W. B. Fowler, Phys. Rev. **174**, 988 (1968).

couplings with the conduction band at points other than  $\Gamma$  if there is a minimum in the band structure at these points. Since  $X_3$  is lower than  $X_1$  in KBr, there is a band minimum at  $X$  and thus there may be a coupling of this sort.

There exists one other calculation of KBr. Kunz has performed OPW calculations<sup>22</sup> on all the alkali bromides. His calculation for KBr is similar to ours in that  $X_1$  is higher in energy than  $X_3$ . The main difference between the two calculations are: (a) In the present calculation

TABLE VIII. Effective masses for KBr at the bottom of the conduction band. (All values in units of the free-electron mass  $m_e$ .)

Symmetry point	Effective mass
$\Gamma$ (toward $X$ )	0.481
$\Gamma$ (toward $L$ )	0.558
$\Gamma$ (toward $K$ )	0.687
$X$	0.982
$L$	-0.276

<sup>22</sup> A. B. Kunz, Phys. Status Solidi **29**, 115 (1968).

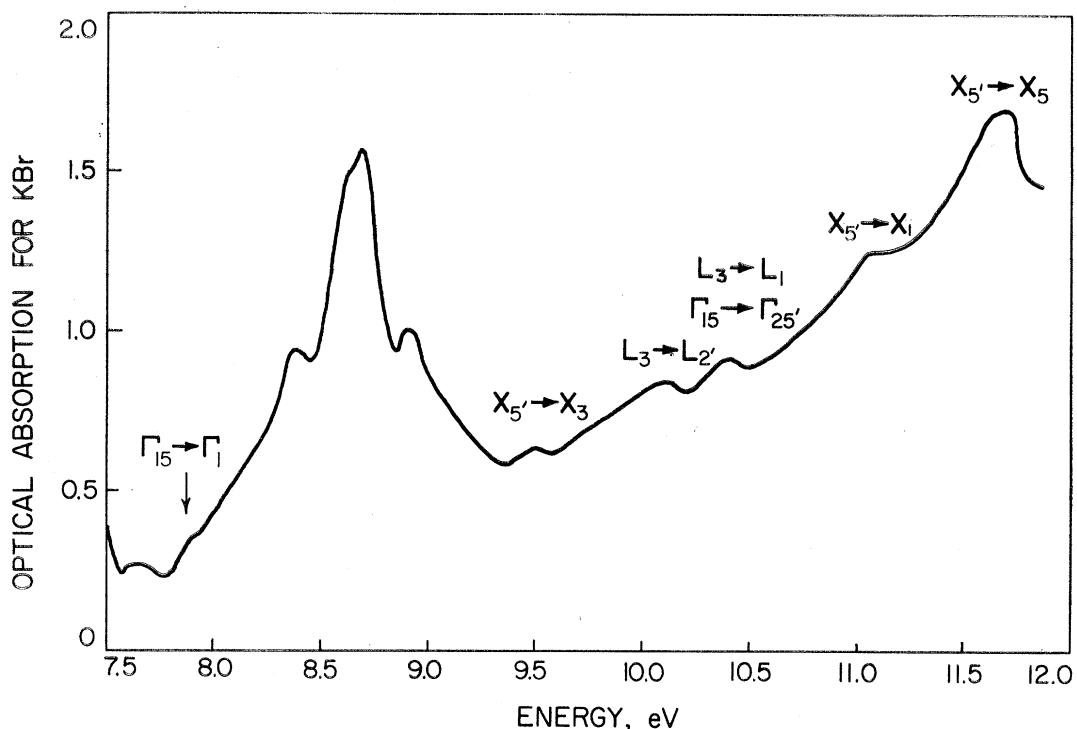


FIG. 4. Optical absorption for KBr with transitions from the present calculation.

$\Gamma_{12}$  is considerably higher in energy than  $\Gamma_{25}$  and (b) the present band gap of 7.80 eV versus the OPW value of 6.02 eV. In matching the experimental band gap, we forced the  $\Gamma_{12}$  state higher in energy. It appears at about 1.3 Ry.

### B. Band Gaps

Large amounts of experimental optical-absorption and optical-reflectance data are available which supposedly determine the band gap in the alkali halides. The usual interpretation is that a "shoulder" in these data marks the onset of band-to-band transitions. Band calculations for alkali halides and related substances usually give values of the band gap which are too small. To overcome this difficulty, the parameter  $\alpha$  in Eq. (3) was varied until the experimental values were matched. The effect on the bands of varying  $\alpha$  was to move the valence band down rigidly with respect to the conduction band. The structure of the conduction band remained mostly unchanged except for the  $\Gamma_{12}$  state which becomes more separated from the  $\Gamma_{25'}$  state as  $\alpha$  increased.

A value of 1.12 and 1.132 for  $\alpha$  gave band gaps of 7.80 and 8.78 eV for KBr and NaCl, respectively. The experimental values are 8.0 eV<sup>23</sup> and 8.75 eV<sup>24</sup> for KBr and NaCl from single-photon absorption experiments. Two-photon spectroscopy experiments of

Fröhlich and Staginnus<sup>25</sup> suggest that the optical band gap is 7.3 eV for KBr. The 7.80-eV value for KBr is thus about midway between these two experimental values. The band gap of NaCl was chosen to match the single-photon absorption data. Ultraviolet absorption data (Refs. 8–10) put the band gap of LiF between 12.9 and 14 eV. The value of 13.58 eV, which was obtained with  $\alpha$  equal to 1.0, is thus acceptable.

### C. Effect of Nonspherical Terms

One of the main reasons for undertaking this study was to assess the effect of nonspherical terms in the APW method. Several questions must be answered. Is the effect of  $V_4$  significant? If the effect of  $V_4$  is large, is the effect of  $V_6$  large?

In Table IX is shown the difference in eigenvalues with and without the term  $V_4$ . Where identifications are difficult, especially in KBr, the values have been left out of the table. For degenerate points such as  $\Gamma_{12}$ ,  $X_5$ , etc., it is difficult to obtain the eigenvalue with three figure accuracy. These values are indicated by the  $\sim$  sign. Comparisons were only made at  $\Gamma$ ,  $X$ ,  $K$ ,  $W$ , and  $L$  to cut down on the amount of computer time used.

No reference is made to the valence-band states in Table IV. The effect of  $V_4$  on the valence bands was less than 0.01 eV in all three compounds. This is due to the fact that the valence-band wave functions are confined to a region of space close to the ions where the

<sup>23</sup> G. R. Huggett and K. Teegarden, Phys. Rev. **141**, 797 (1966).

<sup>24</sup> J. E. Edy, K. J. Teegarden, and D. R. Dutton, Phys. Rev. **116**, 1099 (1960).

<sup>25</sup> D. Fröhlich and B. Staginnus, Phys. Rev. Letters **19**, 496 (1967).

TABLE IX. Effect of the nonspherical potential  $V_4$  on the conduction-band states. All values are in eV. Listed is the value with no  $V_4$  minus the value with  $V_4$  included.

Symmetry point	LiF	NaCl	KBr
$\Gamma_1$	0.839	0.487	0.170
$\Gamma_{25'}$	0.680	0.336	-0.024
$\Gamma_{12}$	~1.020	~0.340	...
$\Gamma_{2'}$	0.544	0.282	-0.051
$\Gamma_{15}$	0.680	0.674	...
$X_1$	1.215	0.614	0.135
$X_3$	0.673	0.260	0.096
$X_4'$	0.713	0.675	...
$X_5'$	...	0.544	...
$X_2$	...	0.263	...
$X_5'$	~0.600	~0.447	...
$W_1$	0.360	0.837	0.084
$W_3$	~0.600	~0.500	~0.130
$W_1'$	...	0.457	0.105
$W_3'$	~1.000	~0.200	~0.100
$W_2'$	1.263	...	...
$K_1$	0.737	0.408	0.065
$K_3$	0.776	0.295	-0.004
$K_1'$	1.192	0.418	-0.283
$K_1$	0.895	0.410	...
$K_3$	...	0.128	...
$K_2$	...	0.472	...
$K_4$	1.302	0.281	...
$L_2'$	0.828	0.370	0.017
$L_1$	0.818	0.479	0.118
$L_3'$	~1.000	~0.480	~0
$L_3$	~1.000	~0.360	~1.200
$L_2'$	...	0.768	0.087
$L_1$	1.316	0.280	0.001

nonspherical potential is small. Consequently, they are affected little by the nonspherical potential.

The  $s$  states in the conduction band are affected the most by the nonspherical potential. The largest change is at the  $X$  point. The  $p$  and  $d$  states are about equally affected.

The next question to be discussed is that of convergence of the expansion of the potential. One way to answer this question is to look at the relative size of the matrix elements of  $V_4$  and  $V_6$ . In numerically evaluating the matrix elements for the effect of  $V_4$  and  $V_6$ , it is found that the matrix element containing  $V_4$  is at least a factor of 10 larger than the matrix element containing  $V_6$ . This certainly shows convergence of the series. To check the convergence further, the effect of  $V_6$  on the eigenvalues at  $\Gamma$  for LiF was evaluated. The biggest change was 0.03 eV for the  $s$  state at the bottom of the conduction band. Since this is much smaller than the average effect of  $V_4$  in LiF, this again indicates convergence of the expansion of the potential.

#### IV. CONCLUSIONS

Several conclusions may be drawn from the data which have been presented. First, the method presented above is adequate to calculate the band structure of alkali halides. This conclusion is supported by the good agreement with optical-absorption data, although the interpretations given to this data are always speculative. The fact that the effective masses calculated from the energy bands are in good agreement with previous calculations and some experimental data is also encouraging. There does not appear to be any clear-cut experimental value of the width of the valence band in the alkali halides. However, for KCl Parratt and Jossem<sup>26</sup> suggest that from  $K\beta$  x-ray emission data the width at half-maximum of the  $Cl^- 3p$  band is 0.33 eV. With a valence-band width of 0.57 eV, NaCl appears to have a width at half-maximum of about 0.3 eV, although it is difficult to be sure without an accurate density-of-states calculation. Also, the width of the valence bands of LiF and KBr are comparable to that of NaCl and thus appear to be correct.

Second, it appears that the  $X_3$  point is lower in energy than the  $X_1$  point in all potassium halides. This possibly makes  $X$ -point excitons important in the absorption spectrum of such compounds.

Third, the inclusion of nonspherical terms, at least with the approximations made herein, produces no gross changes in the over-all band structure other than to shift the bands more or less rigidly.

Finally, the fact that the nonspherical corrections do not solve the band-gap problem means that attention must be focused elsewhere. We have seen that the free-electron-exchange potential can be used to scale the band gap without essentially altering the shape of the bands. This suggests that it is possibly more important to concentrate effort toward improving the approximations to the exchange potential, rather than attempting to assess the adequacy of or even greatly improving the muffin-tin approximation.

#### ACKNOWLEDGMENTS

A special note of thanks is given to Dr. David Liberman for providing the results of his hfs self-consistent field calculations for the halogen and alkali ions in a form amenable to the APW method.

<sup>26</sup> L. G. Parratt and E. L. Jossem, Phys. Rev. **97**, 916 (1955).