ence of the {111} and {311} planes, which have nonzero structure factor and may therefore be expected to affect the momentum distribution, especially in the regions where they are close to the {220} planes. The effect of these planes may show up more strongly in the [111] and [100] orientations; because in these orientations the {220} planes are inclined with respect to p_z so that no one plane plays a dominant role at any point in the distribution.

Each calculated curve in Figs. 8, 9, and 10 was obtained by assuming an energy gap of 5 eV. The energy gap in our calculation is the discontinuity in energy corresponding to a direct transition; this is much larger than the energy difference between the highest valence-band level and lowest conduction-band level. Reflectance experiments[16] yield values of the energy gaps on the order of 3–4 eV for direct transitions. Comparison of Fig. 6 (zero energy gap) with Fig. 10 shows that the fit would not be changed greatly by use of a gap of 3–4 eV rather than 5 eV.

SUMMARY

We have observed marked anisotropies in the angular distribution of annihilation from silicon and germanium single crystals. The simple Jones-zone model predicts distributions which are similar enough to the actual ones, particularly in the widths, to give confidence that this picture has some relevance. It is possible that better agreement could be obtained by a similar calculation which included the effects of the {311} and {111} planes, but such a calculation would be very tedious. It is also possible that the lack of agreement is an indication that the nearly free-electron model cannot be pushed this far.

ACKNOWLEDGMENTS

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[16] H. Ehrenreich, H. R. Phillip, and J. C. Phillips, Phys. Rev. Letters 8, 59 (1962).

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Electronic Band Structure in the Sodium Iodide Crystal*†

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The electronic band structure of sodium iodide has been calculated by using the tight-binding method for the valence bands and an empirical method for the lowest conduction bands. Functions for the I^- and Na^+ ions have been obtained by solving the Hartree-Fock-Slater modified equation. The $5p$ and $5s$ I^- functions are allowed to mix at appropriate points in the Brillouin zone. The lattice parameter is varied and yields results for shifts in energy which agree with those observed when the lattice temperature is changed. Spin-orbit interactions are included and yield results for the $5p$ bands which are in agreement with experiment. Effective masses for electrons and holes are calculated at the points Γ, L, and X in the valence and conduction bands.

I. INTRODUCTION

THE band structure of the alkali halides has been considered in various degrees of detail and success by use of the tight-binding method. This method also seems to be useful for calculations on other ionic crystals and the rare gases. In the present work, the structure of NaI is considered. Previously, most of the work has been on the alkali chlorides. Casella[1] investigated the structure of NaCl, Howland[2] investigated KCl, and Kunz and Van Sciver[3] investigated LiCl. Calculations of interest other than those for alkali halides are for solid krypton by Fowler[4] and AgCl by Bassani, Knox, and Fowler.[5] The result of Casella, Howland, and Bassani, Knox, and Fowler ignore spin-orbit interaction insofar as giving band structures with spin-orbit interactions included. In presenting his results, Casella did not consider the possibility of mixing of other states with the $3p$ Cl^- states. Both Fowler and Kunz and Van Sciver consider such mixing but since the effect is small, it is not included in their results. Howland and Bassani, Knox, and Fowler include this mixing, and find it to have significant effects in the structure of KCl and

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‡ National Aeronautics and Space Administration fellow in physics.

[1] R. C. Casella, Phys. Rev. 104, 1260 (1956).

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[3] A. B. Kunz and W. J. Van Sciver, Phys. Rev. 142, 462 (1966).

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AgCl, respectively. In the present work the mixing of the $5s\mathrm{I}^-$ state with the $5p\mathrm{I}^-$ state is considered in obtaining the valence structures as is spin-orbit interaction. Ionic wavefunctions and potential for the free I^- and Na^+ ions are obtained by the method of Herman and Skillman.[6] Here, in applying a tight-binding calculation, one has the advantage that in a first approximation the wave functions are eigenfunctions of the potential used to construct the crystal potential.

There is a certain amount of experimental evidence available about NaI which one might hope to explain. Eby, Teegarden, and Dutton[7] examined the absorption spectrum of a thin film of NaI in the range of energies from 5 to 11 eV. Measurements were made at 77°K and about 300°K. The spectrum of NaI, along with that of other face-centered-cubic alkali-halide crystals, was subjected to detailed analysis by Phillips.[8] By analysis of the density of states for the valence bands, Phillips was able to identify certain peaks in the absorption spectrum with definite electronic transitions. These include both exciton and band-to-band transitions. Phillips observed in the case of NaI that the spin-orbit splitting at the Γ point was 1.25 eV and that for the free ion the splitting should be only 0.9 eV for the $5p$ I^- level. Being unable to explain the magnitude of the spin-orbit effect, Phillips considered NaI as some sort of anomaly and did not draw band shapes for NaI as he did for the other alkali halides.

Eby, Teegarden, and Dutton[7] obtained shifts in the spectrum of NaI with temperature which are not explained by thermal broadening. Recently, Meincke and Graham[9] measured the thermal expansion of NaI in the temperature range of 4 to 300°K. Using the data of Meincke and Graham, this paper will show that the shift in the band edge with temperature may be explained by the thermal expansion of the lattice. The enhanced spin-orbit splittings noted by Phillips[8] are also accounted for. The atomic system of units is used. The lattice constant a is defined as the distance separating a given I^- ion from its nearest-neighbor Na^+ ion.

II. CONSTRUCTION OF THE CRYSTAL POTENTIAL AND THE VALENCE BANDS

Using the tight-binding method, one may construct the single-particle crystal wave function as a sum of Bloch functions[10] formed from the various orbitals on the free I^- and Na^+ ions. Thus one obtains

$$\Psi_{m\mathbf{k}}{}^{\alpha l}(\mathbf{r})=\sum_{j,n} A_{jn}{}^{\alpha l}(\mathbf{k})\psi_{nj}(\mathbf{r}). \qquad (1)$$

TABLE I. The values of $rV(r)$ and $r\varphi(r)$ are given as a function of r for Na^+ and I^-. The states considered are the I^- $5s$ and $5p$ states. Atomic units are used throughout.

For Na^+		For I^-			
r	$-rV(r)$	r	$-rV(r)$	$r\varphi(r)_{5s}$	$r\varphi(r)_{5p}$
0.0099	21.55	0.0058	103.1	8.002×10^{-2}	6.729×10^{-3}
0.0199	21.08	0.0117	100.1	1.110×10^{-1}	2.297×10^{-2}
0.0298	20.60	0.0170	97.33	1.089×10^{-1}	4.403×10^{-2}
0.0398	20.13	0.0235	95.99	8.585×10^{-2}	6.655×10^{-2}
0.0597	19.22	0.0353	92.19	9.577×10^{-3}	1.073×10^{-1}
0.0796	18.36	0.0471	87.59	-7.196×10^{-2}	1.346×10^{-1}
0.0995	17.56	0.0589	83.47	-1.364×10^{-1}	1.451×10^{-1}
0.1094	16.81	0.0707	79.73	-1.754×10^{-1}	1.396×10^{-1}
0.1394	15.45	0.0942	74.64	-1.767×10^{-1}	9.111×10^{-2}
0.1792	14.25	0.1178	68.66	-1.042×10^{-1}	1.522×10^{-2}
0.2189	13.19	0.1414	63.44	1.042×10^{-3}	-6.487×10^{-2}
0.2587	12.28	0.1649	58.85	1.078×10^{-1}	-1.336×10^{-1}
0.3184	10.70	0.2121	52.99	2.516×10^{-1}	-2.093×10^{-1}
0.3980	9.497	0.2592	46.68	2.712×10^{-1}	-1.997×10^{-1}
0.4777	8.447	0.3064	41.40	1.908×10^{-1}	-1.286×10^{-1}
0.5573	7.990	0.3535	37.09	5.601×10^{-2}	-2.659×10^{-2}
0.6767	7.573	0.4478	31.75	-2.254×10^{-1}	1.773×10^{-1}
0.8359	6.254	0.5421	26.31	-3.922×10^{-1}	3.035×10^{-1}
0.9952	5.355	0.6363	22.17	-4.118×10^{-1}	3.301×10^{-1}
1.154	4.728	0.7306	18.84	-3.179×10^{-1}	2.800×10^{-1}
1.234	4.272	0.9192	14.91	2.685×10^{-2}	5.371×10^{-2}
>1.234	4.00	1.107	11.18	3.743×10^{-1}	-2.038×10^{-1}
	4.00	1.29	8.582	6.228×10^{-1}	-4.144×10^{-1}
	4.00	1.484	6.732	7.626×10^{-1}	-5.610×10^{-1}
	4.00	1.861	4.861	8.081×10^{-1}	-6.900×10^{-1}
	4.00	2.239	3.249	6.973×10^{-1}	-6.810×10^{-1}
	4.00	2.616	2.151	4.740×10^{-1}	-6.110×10^{-1}
	4.00	2.993	1.367	2.945×10^{-1}	-5.214×10^{-1}
	4.00	3.747	0.5571	1.485×10^{-1}	-3.577×10^{-1}
	4.00	4.501	0.0	7.448×10^{-2}	-2.441×10^{-1}
	4.00	5.256	0.0	3.733×10^{-2}	-1.693×10^{-1}
	4.00	6.010	0.0	1.325×10^{-2}	-1.187×10^{-1}
	4.00	7.518	0.0	3.329×10^{-3}	-5.965×10^{-2}
	4.00	9.027	0.0	8.366×10^{-4}	-3.050×10^{-2}
	4.00	10.53	0.0	2.103×10^{-4}	-1.576×10^{-2}
	4.00	12.04	0.0	2.64×10^{-5}	-8.20×10^{-3}
	4.00	15.06	0.0	1.67×10^{-6}	-2.25×10^{-3}
	4.00	18.07	0.0	1.05×10^{-7}	-6.24×10^{-4}
	4.00	21.09	0.0	6.66×10^{-9}	-1.74×10^{-4}

In Eq. (1) the vector $\mathbf{k}$ refers to a point in the first Brillouin zone for the solid, m or n refers to the orbital quantum number associated with the state, j refers to the angular quantum numbers of the Bloch function, α refers to a specific irreducible representation of the group of the wave vector $\mathbf{k}$, and l refers to the row of the irreducible representation α for which $\Psi_{m\mathbf{k}}{}^{\alpha l}(\mathbf{r})$ is an eigenvector. That is, $\Psi_{m\mathbf{k}}{}^{\alpha l}(\mathbf{r})$ is formed to be an eigenvector of the lth row of the αth irreducible representation of the wave vector $\mathbf{k}$. One defines $\psi_{nj}(\mathbf{r})$ to be

$$\psi_{nj}(\mathbf{r})=\sum(\mu)\,\exp(i\mathbf{k}\cdot\mathbf{R}_\mu)\,\varphi_{nj}(\mathbf{r}-\mathbf{R}_\mu). \qquad (2)$$

Here one choses a given I^- ion to serve as the origin of the coordinate system and then $\mathbf{R}_\mu$ is the vector separating the μth I^- ion from the origin. The sum is over all the I^- ions in the lattice. The function $\varphi_{nj}(\mathbf{r})$ is the solution to the free-ion Hartree-Fock-Slater modified equation for the n, j state in the free I^- ion. One may write a similar expression if wave functions for the Na^+ ions are used. One choses the $\varphi_{nj}(\mathbf{r})$ such that the functions have simple symmetry, that is, they transform as a scalar or the functions x, y, or z if one considers only

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[6] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

[7] J. E. Eby, K. J. Teegarden, and D. B. Dutton, Phys. Rev. **116**, 1099 (1959).

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[9] P. P. M. Meincke and G. M. Graham, Can. J. Phys. 43, 1853 (1965).

[10] F. Bloch, Z. Physik **52**, 555 (1928).

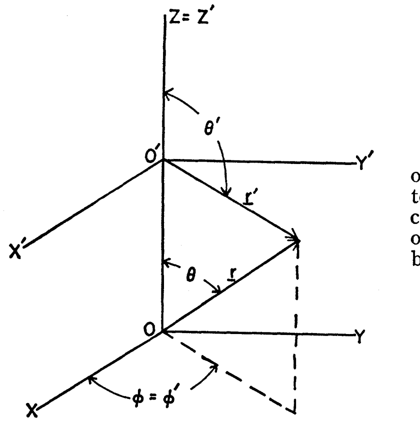

FIG. 1. The coordinate system used to evaluate the two-center integrals which occur in the tight-binding theory.

s or p states. For these states one identifies $j=1$ for a scalar $j=2$ for x-like, $j=3$ for y-like, $j=4$ for z-like states. One might they have

$$\psi_{n2}(\mathbf{r})=\psi_{nx}(\mathbf{r})=\sum (\mu)\exp(i\mathbf{k}\cdot\mathbf{R}_\mu)\varphi_{n2}(\mathbf{r}-\mathbf{R}_\mu).$$

The constant $A_{jn}{}^{\alpha l}(\mathbf{k})$ in Eq. (1) is chosen such that one has the vector for the αth irreducible representation of the group of $\mathbf{k}$. This constant is chosen using a projection-operator technique.[11,12] In doing this one eliminates much labor in obtaining energies in that the matrix elements between vectors which correspond to different rows of a given irreducible representation or to different irreducible representations are identically zero. Thus if one uses the notation of Bouckaert, Smoluchowski, and Wigner,[13] one finds that

$$\Psi_{3\Delta}{}^{\Delta_1}=\sum (\mu)[A_{15}{}^{\Delta_1}(\Delta)\exp(i\mathbf{k}\cdot\mathbf{R}_\mu)\varphi_{51}(\mathbf{r}-\mathbf{R}_\mu)+A_{25}{}^{\Delta_1}(\Delta)\exp(i\mathbf{k}\cdot\mathbf{R}_\mu)\varphi_{52}(\mathbf{r}-\mathbf{R}_\mu)]. \quad (3)$$

Here the projector is unable to obtain a unique value for $A_{jn}{}^{\alpha l}(\mathbf{k})$ in that both the s-like function and the x-like function are bases for the same row of the same irreducible representations. Here it is necessary to form matrix elements for the s-like function and the x-like function and solve a two-by-two secular determinant for the energies. It is assumed that Δ is in the (100) direction.

TABLE II. The band parameters for NaI. The atomic system of units is used throughout. $\epsilon_{5s}=-0.8384$ and $\epsilon_{5p}=-0.1742$.

Parameter	$a=6.22$	$a=6.15$	$a=6.08$	$a=5.98$
V_s	−0.5700	−0.5774	−0.5849	−0.5965
V_p	−0.6130	−0.6243	−0.6360	−0.6546
V_{ss}	−0.00249	−0.00277	−0.00302	−0.00354
$V_{sp\sigma}$	−0.0366	−0.04612	−0.0489	−0.0532
$V_{pp\sigma}$	0.06253	0.06581	0.06920	0.07479
$V_{pp\pi}$	−0.01658	−0.01766	−0.01878	−0.02066
S_{ss}	0.00285	0.00312	0.00337	0.00391
$S_{sp\sigma}$	0.0284	0.0326	0.0342	0.0370
$S_{pp\sigma}$	−0.08274	−0.08609	−0.08930	−0.09454
$S_{pp\pi}$	0.02366	0.02495	0.02621	0.02830

Using the Hartree-Fock-Slater modified method,[6] the crystal potential is found to be given as a sum over the potentials for the free ions centered about their respective lattice sites, and one finds that

$$V(\mathbf{r})=\sum (\mu)[V_I(\mathbf{r}-\mathbf{R}_\mu)+V_{\mathrm{Na}}(\mathbf{r}-\mathbf{R}_\mu-\mathbf{g})]. \quad (4)$$

In Eq. (4) one has $V_I(\mathbf{r}-\mathbf{R}_\mu)$ as the potential of the I$^-$ ion centered at the point $\mathbf{r}-\mathbf{R}_\mu$; $\mathbf{g}$ is given as (a00), and $V_{\mathrm{Na}}(\mathbf{r}-\mathbf{R}_\mu-\mathbf{g})$ is the potential of the Na$^+$ ion centered at the point $\mathbf{r}-\mathbf{R}_\mu-\mathbf{g}$. The sum is over all lattice points. Using the program of Herman and Skillman,[6] the author obtained solutions for the free Na$^+$ and I$^-$ in their ground state using the Hartree-Fock-Slater modified option. The solutions included the radial parts of the single-particle wave functions and the potentials for the ions. These are used in Eqs. (1) and (4). The values for $V(r)$ for the Na$^+$ and I$^-$ ions and $\varphi(r)$ for the $5p$ and $5s$ levels of I$^-$ are given in Table I.

The one-electron Hamiltonian is given as

$$H=-\nabla^2+V(\mathbf{r}). \quad (5)$$

In this calculation only nearest-neighbor I$^-$ ions are considered in full detail. However, certain three-center terms are neglected here. The potential $V(\mathbf{r})$ is divided into two parts; these are $V_s(\mathbf{r})$, which is the short-range part of the potential, and $V_M(\mathbf{r})$ which is the long-range ionic or Madelung potential.[5] Thus one has

$$V(\mathbf{r})=V_s(\mathbf{r})+V_M(\mathbf{r}). \quad (6)$$

In this calculation $V_M(\mathbf{r})$ is formed from the entire lattice; however, one only consideres $V_s(\mathbf{r})$ to the nearest-neighbor extent and that only in two-center terms. It is found that $V_M(\mathbf{r})$ has a much larger effect on the results than $V_s(\mathbf{r})$.

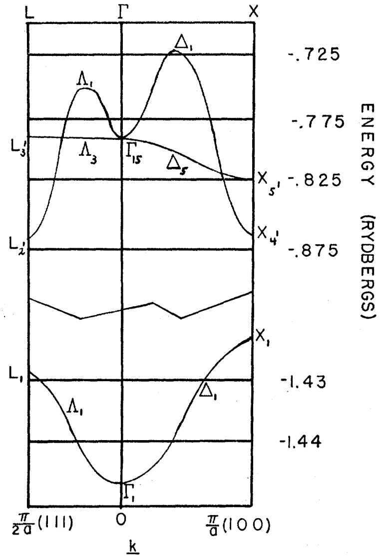

FIG. 2. The $5s$ and $5p$ valence bands for NaI are shown as a function of $\mathbf{k}$ for the lines Δ and Λ in the first Brillouin zone. Spin-orbit effects are not included here. The mixing of states is only shown for the $5p$ bands. Note changes of scale. $a=5.98$ Bohr units.

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[11] J. C. Slater, Rev. Mod. Phys. **37**, 68 (1965).

[12] R. S. Knox and A. Gold, *Symmetry in the Solid State* (W. A. Benjamin, Inc., New York, 1964).

[13] L. P. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. **50**, 58 (1936).

The jl matrix element of the Hamiltonian is given as

$$H_{jl}=\epsilon_{jl}\delta_{jl}+[V_{\alpha j}\delta_{jl}+\sum(\mu)\exp(i\mathbf{k}\cdot\mathbf{R}_\mu) V_{\alpha\mu jl}][1+\sum(\mu)\exp(i\mathbf{k}\cdot\mathbf{R}_\mu)S_{\alpha\mu jj}]^{-1/2} \times[1+\sum(\mu)\exp(i\mathbf{k}\cdot\mathbf{R}_\mu)S_{\alpha\mu ll}]^{-1/2}. \quad (7)$$

In Eq. (7) $\epsilon_{\alpha j}$ is the energy of the electron in the jth state of the free ion. $V_{\alpha j}$ is the term obtained by integrating the square of the atomic function centered at the origin and the potential due to the short-range part of the nearest-neighbor Na$^+$ and I$^-$ ions and the Madelung potential. The terms $V_{\alpha\mu jl}$ and $S_{\alpha\mu jj}$ are given as

$$V_{\alpha\mu jl}=\int_{\text{all space}}\varphi_{5j}(\mathbf{r})\varphi_{5l}(\mathbf{r}-\mathbf{R}_\mu)\times[V_{SI}(\mathbf{r}-\mathbf{R}_\mu)+V_\mu(\mathbf{r})]d\tau,$$

and $\qquad (8)$

$$S_{\alpha\mu jj}=\int_{\text{all space}}\varphi_{5j}(\mathbf{r})\varphi_{5j}(\mathbf{r}-\mathbf{R}_\mu)d\tau.$$

The summation in Eq. (7) is over those 12 I$^-$ ions nearest to that one chosen as origin. In the above, one limits oneself to consideration of mixing only of the 5p and 5s states in the I$^-$ ion. This is found to be sufficient to obtain accurate results for NaI. It is also found that the use of only nearest-neighbor terms yields sufficient accuracy. Numerically, the results are accurate to about ±2 in the third significant figure. The integrations are performed using the coordinate system shown in Fig. 1. Using this system one can use a few different $V_{\alpha\mu jl}$ and $S_{\alpha\mu jj}$ to specify the energy. This notation is defined by several authors and no further definition is given here.[4,5,14] To illustrate this system one may use the example

$$\alpha=\Delta_1 j\mathbf{k}_x=(\pi/a)f;\ f=0\rightarrow a;\ k_y=k_z=0,$$

$$H_{xx}=\epsilon_{5p}+[V_{5p}+4V_{pp\pi}+4(V_{pp\pi}+V_{pp\sigma})\times\cos ka][1+4S_{pp\pi}+4(S_{pp\pi}+S_{pp\sigma})\times\cos ka]^{-1}. \quad (9)$$

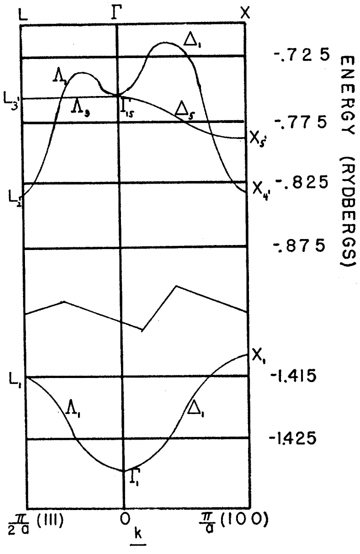

FIG. 4. The 5s and 5p valence bands for NaI are shown as a function of **k** for the lines Δ and Λ in the first Brillouin zone. Spin-orbit effects are not included here. The mixing of states is only shown for the 5p bands. Note changes of scale. $a=6.15$ Bohr units.

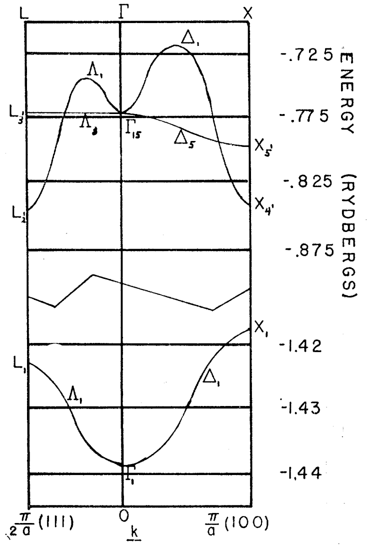

FIG. 3. The 5s and 5p valence bands for NaI are shown as a function of **k** for the lines Δ and Λ in the first Brillouin zone. Spin-orbit effects are not included here. The mixing of states is only shown for the 5p bands. Note changes of scale. $a=6.08$ Bohr units.

The integrations are performed using a double Simpson's rule.[15] The lattice parameter is given as equal to 5.98, 6.08, 6.15, 6.22 a in Bohr units, where 6.15 is the normal lattice parameter. The various band parameters are given in Table II.

Using Eq. (7), the values of the 5p and 5s bands are evaluated along the Δ and Λ direction in the reciprocal lattice. The mixing of 5s and 5p levels are included in

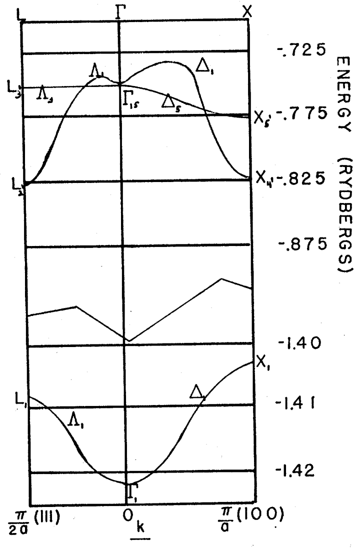

FIG. 5. The 5s and 5p valence bands for NaI are shown as a function of **k** for the lines Δ and Λ in the first Brillouin zone. Spin-orbit effects are not included here. The mixing of states is only shown for the 5p bands. Note changes of scale. $a=6.22$ Bohr units.

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[15] J. B. Scarborough, *Numerical Mathematical Analysis* (The Johns Hopkins Press, Baltimore, Maryland, 1962), 5th ed., Chap. 8.

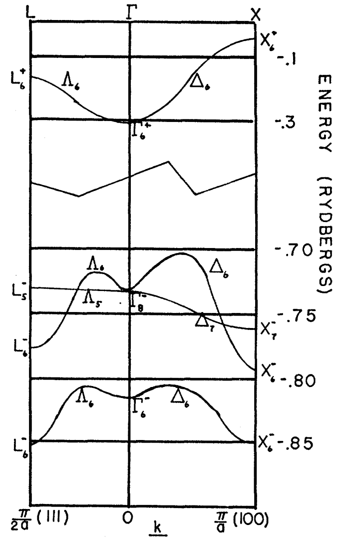

FIG. 6. The $5p$ valence bands and the lowest conduction band for NaI are shown as a function of **k** for the lines Δ and Λ in the first Brillouin zone. Spin-orbit effects are included. Note changes of scale. $a=5.98$ Bohr units.

the drawings of the $5p$ levels. These bands are shown in Figs. 2 through 5. The author notes that the upward banding of the $5p\Delta_1$ and $5p\Lambda_1$ levels is entirely due to the interaction with the $5s$ level. The interaction, and hence the bending, is seen to be strongly dependent upon the value of the lattice parameter. The previous indications of this upward bending in an ionic crystal were seen by Howland[2] and Bassoni *et al.*[5] Because of the bending, the band width is also strongly dependent upon the lattice parameter. Most of the interaction is due to the presence of the Madelung term in the potential, and thus in a rare gas one might expect this effect to be small or nonexistent.

III. SPIN-ORBIT INTERACTION

Owing to the high atomic number of iodine it is expected that spin-orbit interactions should have an important effect in the band structure of an alkali iodide. This will be seen to be the case for NaI. To include this effect, **L**·**S** coupling will be assumed. As the spin-orbit interaction in NaI is large, according to Phillips,[8] it is possible that **L**·**S** coupling is not the best assumption. It is noted that the energy separation of the valence band in NaI from the lower bands and from the conduction band is larger than the spin-orbit interaction and thus j-j coupling would not be a good assumption. It is possible that an intermediate coupling scheme might be best; however, the results of using **L**·**S** coupling will be shown to agree with experiment. The spin-orbit Hamiltonian is given as

$$H_{\mathrm{so}}=(4_c{}^2r)^{-1}[dV(r)/dr]\boldsymbol{\sigma}\cdot\mathbf{L}. \qquad (10)$$

Here the gradient of the potential is reduced to the derivative with respect to r since the H_{so} is largest in the vicinity of the nuclei when the Hartree-Fock-Slater modified potential is used. In the vicinity of a nucleus the potential is spherically symmetric. For NaI, the level of interest is the $5p$ level. One defines a spin-orbit parameter ξ to be

$$\xi=\langle 5p|H_{\mathrm{so}}|5p\rangle. \qquad (11)$$

The value of ξ is found to be 0.0232 Ry. To include spin-orbit effects in the valence-band calculation, one uses linear combinations of the valence eigenfunctions before spin-orbit interaction to form the correct linear combination of functions which transform as bases for the irreducible representations of the double group of the wavevector **k**.[16]

The notation used here is an extension of that used for the valence bands without spin-orbit interaction.[4] To illustrate the notation and the results we consider the line Δ and the Δ_σ representation. If one lets

$$O(\Delta_5)=1+2[S_{pp\pi}+S_{pp\sigma}]+2[3S_{pp\pi}+S_{pp\sigma}]\cos ka,$$
$$O(\Delta_1)=1+4S_{pp\pi}+4[S_{pp\pi}+S_{pp\sigma}]\cos ka,$$
$$E(\Delta_5)=H_{zz},$$
$$E(\Delta_1)=H_{xx},$$

then

$$E(\Delta_5)=\tfrac{1}{2}[E(\Delta_1)+E(\Delta_5)-\xi O(\Delta_5)^{-1}] \pm\tfrac{1}{2}\{[E(\Delta_1)-E(\Delta_5)+\xi O(\Delta_5)^{-1}]^2 +8\xi^2[O(\Delta_1)O(\Delta_5)]^{-1}\}^{1/2}. \qquad (12)$$

The results for the lines Δ and Λ are given in Figs. 6 through 9. One notes that the inclusion of spin-orbit interaction has split the $5p$ band into two separate non-overlapping bands. The energy of selected symmetry points is given in Table III. The spin-orbit splitting between $\Gamma_6{}^{\Delta}$ and $\Gamma_8{}^-$ is found to be 1.25 eV, between $X_6{}^-$, and $X_7{}^-$ it is found to be 0.4 eV, and between $L_5{}^-$ and $L_6{}^-$ it is 0.65 eV. One will see in the conclusions that these results are in agreement with experiment. In

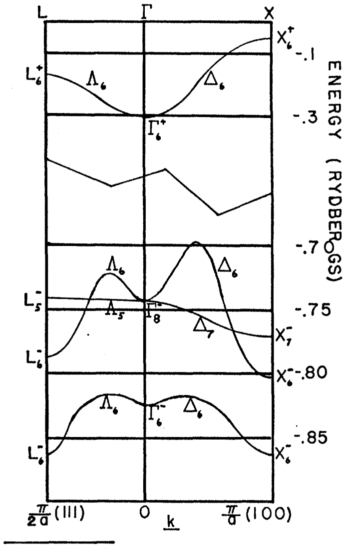

FIG. 7. The $5p$ valence bands and the lowest conduction band for NaI are shown as a function of **k** for the lines Δ and Λ in the first Brillouin zone. Spin-orbit effects are included. Note changes of scale. $a=6.08$ Bohr units.

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[16] G. F. Koster *et al.*, *Properties of the Thirty Two Point Groups* (The MIT Press, Cambridge, Massachusetts, 1963).

TABLE III. Energy of selected symmetry points in the first brillouin zone for the various lattice constants. Spin-orbit effects are included (atomic units).

Point	$a=6.22$	$a=6.15$	$a=6.08$	$a=5.98$
Γ_8^-	−0.7245	−0.7348	−0.7448	−0.7609
X_6^- upper	−0.7817	−0.7928	−0.8053	−0.8241
X_7^-	−0.7523	−0.7632	−0.7748	−0.7928
L_4^-, L_5^-	−0.7223	−0.7322	−0.7423	−0.7580
L_6^- upper	−0.7654	−0.7761	−0.7873	−0.8046
Γ_6^-	−0.8054	−0.8160	−0.8263	−0.8428
X_6^- lower	−0.8444	−0.8558	−0.8680	−0.8871
L_6^- lower	−0.8419	−0.8532	−0.8652	−0.8840
Γ_6^+	−0.303	−0.303	−0.303	−0.303
X_6^+	−0.051	−0.051	−0.051	−0.051
L_6^+	−0.176	−0.176	−0.176	−0.176

Fig. 10 the graph of energy with lattice parameter is given.

IV. THE LOWEST CONDUCTION BAND

The lowest conduction band is obtained using the results of Phillips.[8] The results of Sec. III for $a=6.15$ Bohr units are used as a determination of the valence bands. The transitions between the state Γ_6^- and Γ_6^+ and between Γ_8^- and Γ_6^+ are identified by Phillips. The transition of Γ_8^- to Γ_6^+ is at 5.75 eV and the one between Γ_6^- and Γ_6^+ at 7.00 eV. Phillips also identifies the transitions between L_6^- and L_6^+ and L_5^- and L_6^+. The L_6^- to L_6^+ transition is at 9.0 eV, and that of L_5^- to L_6^+ is at 8.2 eV. The author identifies the hump in the absorption spectrum of NaI at 9.6 eV as the transition X_7^- to X_6^+, and the hump at 10.1 eV as the transition X_6^- to X_6^+. One notes that the transitions at both L and X are rather broad and subject to error. To obtain the points Γ_6^+, X_6^+, and L_6^+ in the valence bands one simply adds the energies of the transition at Γ, X, and L to the valence energies at these points and thus has located three conduction-band points. This locates the lowest conduction band.

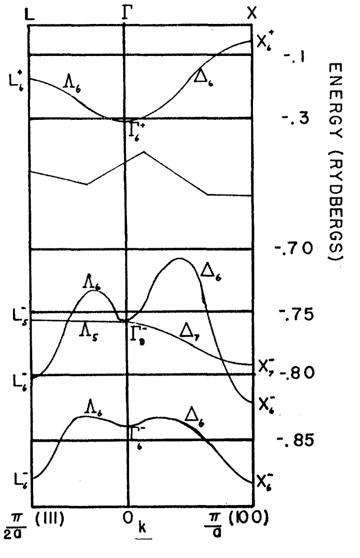

FIG. 8. The $5p$ valence bands and the lowest conduction band for NaI are shown as a function of **k** for the lines Δ and Λ in the first Brillouin zone. Spin-orbit effects are included. Note changes of scale. $a=6.15$ Bohr units.

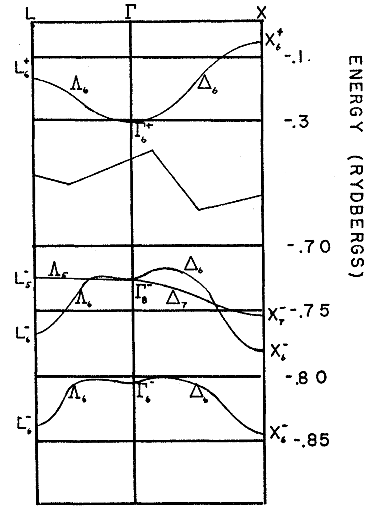

FIG. 9. The $5p$ valence bands and the lowest conduction band for NaI are shown as a function of **k** for the lines Δ and Λ in the first Brillouin zone. Spin-orbit effects are included. Note changes of scale. $a=6.22$ Bohr units.

Bassani and Giuliano[17] using an orthogonalized-plane-wave (OPW) method have shown that the lowest conduction band in the alkali halides is primarily an s band about the point Γ. They also found that the conduction band is insensitive to changes of lattice parameter. Thus the band obtained for $a=6.15$ Bohr units is good for the other lattice parameter used. The three points obtained are fitted using an s band as recommended by Slater and Koster.[14] Here one uses two-center elements and the band parameters are found to be: $\epsilon_5=-0.142$ Ry, $V_{ss1}=0.0158$ Ry, and $V_{ss2}=0.0054$ Ry. The band is drawn from these data and shown in Figs. 6 through 9.

V. EFFECTIVE-MASS THEORY

It is known that for points in **k** space for which $\nabla_{\mathbf{k}}E(\mathbf{k})=0$, the one-electron energy is approximately

TABLE IV. Table of effective masses for electrons in the lowest conduction bands and the valence bands (atomic units).

	Point and direction	m^*/m $a=6.22$	m^*/m $a=6.15$	m^*/m $a=6.08$	m^*/m $a=5.98$
Conduction	Γ_6^+ (isotropic)	0.309	0.319	0.325	0.337
	X_6^+ along Δ_6	−0.152	−0.157	−0.160	−0.166
	L_6^+ along Λ_6	−0.152	−0.157	−0.160	−0.166
Valence	Γ_8^- along Δ_7	−1.71	−1.70	−1.64	−1.63
	Γ_8^- along Δ_6	1.23	0.448	0.384	0.310
	Γ_8^- along Λ_4, Λ_5	26.1	22.4	29.1	21.4
	Γ_8^- along Λ_6	4.53	0.615	0.504	0.386
	Γ_6^- along Δ_6	2.64	0.923	0.797	0.640
	Γ_6^- along Λ_6	2.72	0.934	0.805	0.646
	X_7^- along Δ_7	1.91	1.89	1.82	1.78
	X_6^- along Δ_6^- up	0.554	0.423	0.397	0.367
	X_6^- along Δ_6^- low	0.387	0.272	0.250	0.221
	$L_{4,5}$ along $\Lambda_{4,5}$	−22.2	−18.6	−23.9	−17.1
	L_6^- along Λ_6^- up	0.933	0.718	0.679	0.645
	L_6^- along Λ_6^- low	0.302	0.213	0.196	0.173

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[17] F. Bassani and S. Giuliano in Proceedings of the International Symposium on Color Centers in Alkali Halides, Urbana, Illinois, 1965 (unpublished).

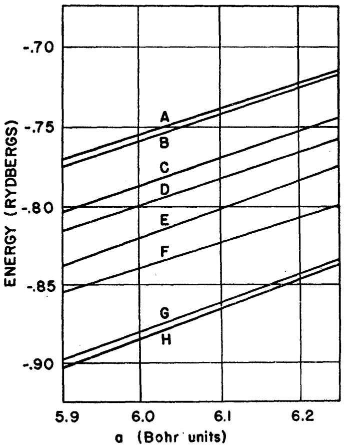

FIG. 10. The energy of selected points in the first Brillouin zone of NaI is shown as a function of lattice parameter. A=L_5^-, B=Γ_8^-, C=X_7^-, D=L_6^- upper, E=X_6^- upper, F=Γ_6^-, G=L_6^- lower, and H=X_6^- lower.

given by

$$E_{\mathbf{k}\downarrow}{}^{n}=E_{\mathbf{k}}{}^{n}+\tfrac{1}{2}\mathbf{k}''^{2}+\sum{}'(\nu)\frac{|\langle\nu,\mathbf{k}|\mathbf{k}\cdot\nabla|n,\mathbf{k}\rangle|^{2}}{E_{\mathbf{k}}{}^{\nu}-E_{\mathbf{k}}{}^{n}},\tag{13}$$

where

$$\mathbf{k}''=\mathbf{k}'-\mathbf{k}.\tag{14}$$

In this region about **k** one sees that the energy is quadratic in **k**. However, the coefficient of this is not $\hbar^2/2m$ but an explicit function of the state in question. In the free-electron picture the coefficient would be $\hbar^2/2m$. However, one may by analogy define a quantity m^* to be the effective mass of an electron and hence obtain an expression similar to that for free electrons. In this, one has an effective-mass tensor, which is

$$(1/m^*)_{ij}=\pm\partial^2E_{\mathbf{k}}/\partial k_i\partial k_j.\tag{15}$$

In Eq. (15) the plus sign corresponds to an electron and the minus sign to a hole.

The points for which $\nabla_{\mathbf{k}}E(\mathbf{k})=0$ are Γ, L, and X for a face-centered-cubic lattice. At these points in the valence band and the conduction band the expression for $E(\mathbf{k})$ was twice differentiated and the values of elements in the effective-mass tensor obtained. These results are given in Table IV. These have been included because they seem useful in the theory of excitons and in studies of electrical conductivity.[18,19]

VI. CONCLUSIONS AND COMPARISON WITH EXPERIMENT

It has been seen that the valence bands in NaI may be determined by use of only nearest-neighbor terms, the use of terms from ions farther out being of negligible importance. The inclusion of spin-orbit effects is seen to be of considerable importance, as in the mixing of the $5p$ and $5s$ states. The uppermost valence band is still mostly $5p$ in character and hence is called the $5p$ band. The bandwidth with spin-orbit interaction is 1.75 eV for $a=6.22$ Bohr units and 2.45 eV when $a=5.98$ Bohr units.

The splitting between Γ_6^- and Γ_8^- is computed to be 1.25 eV, between X_6^- and X_7^- it is 0.4 eV, and it is 0.35 eV between L_5^- and L_6^-. By the analysis of Phillips[8] one sees that the splitting between Γ_6^- and Γ_8^- is 1.25±0.05 eV, between X_6^- and X_7^- it is 0.5±0.1 eV, and between L_5^- and L_6^- it is 0.8±0.2 eV. It is seen that the present theory is able to explain the spin-orbit effect as observed in the absorption spectrum of NaI. Thus the result which disturbed Phillips is seen to have a satisfactory explanation.

Using the results of Meinche and Graham,[9] one finds that the lattice constant for NaI at 300°K is 6.20 Bohr units if the lattice constant is 6.15 Bohr units at 77°K. If one interpolates from Fig. 10, the energy of absorption between Γ_8^- and Γ_8^+ is seen to increase by 0.1 eV when temperature decreases from 300 to 77°K. Using the peak of the Γ exciton absorption as a measure, it is seen that the absorption energy increases by (0.1±0.02) eV when the temperature decreases from 300 to 77°K according to the measurements of Eby, Teegarden, and Dutton.[7] One expects that the shift in the Γ exciton peak should correspond to the shift in the Γ-band edge because both arise from the same initial state. The exciton peak is useful because it is sharp at both 300 and 77°K.

In conclusion then, the author believes that this model is capable of explaining the gross properties of the NaI absorption spectrum. The method converges rapidly since the two-center terms fall off rapidly with distance and since the effect of mixing of several bands is small except for those bands which lie close to the band of interest. The author believes that spin-orbit effects are important and should be included. This is certainly true for a substance of large atomic number. The author believes that by the inclusion of even more terms, the tight-binding method should prove useful in the analysis of the experimental results for NaI which should become available in the future.

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[18] R. J. Elliot, Phys. Rev. **108**, 1384 (1957).

[19] W. Kohn and J. M. Luttinger, Phys. Rev. **98**, 915 (1955).