

error, and regardless of the reflectivity ratio polarization effect can be neglected. As shown in Fig. 3 the frequency range of interest in the present investigation extends between the maximum and minimum reflectivity. Comparing the two sets of curves, one observes that, except in the narrow range near the minimum reflectivity, the value of the reflectivity ratio at all angles of incidence is fairly high, and for this reason, polarization effects can be neglected. However, this is not the case at high angles of incidence outside the lattice-vibration region.

### ACKNOWLEDGMENTS

The experimental phases of this investigation were carried out while one of the authors (D. E. M.) was with Beckman Instruments, Inc., Fullerton, California. We also wish to thank Dr. E. V. Loewenstein and Dr. A. Engelsrath for a number of stimulating discussions, Miss T. Forni and J. Dolan for preparing the computer program, E. Brown for help in performing the calculations, and Miss O. Denniston for assistance in preparation of the paper.

## 3*p* Energy Band in Lithium Chloride\*

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(Received 13 July 1965; revised manuscript received 11 October 1965)

The tight-binding approach is employed to obtain the structure of the 3*p* Cl<sup>-</sup> valence band in LiCl. This is studied as a function of wave vector in selected directions of high symmetry in the reciprocal lattice. Results are obtained which include spin-orbit effects. The valence band is found to have a width of 1.2 eV when spin-orbit effects are neglected and a width of 1.3 eV when the spin-orbit effects are included.

### I. INTRODUCTION

THE tight-binding method has been used by various workers to investigate the band structure of various solids in which the electrons are thought of as being associated with a given nucleus in the lattice. Solids which are of this type include the ionic crystals and the rare-gas solids. This present work considers the structure of the valence band in LiCl. Previously, other workers have investigated the valence bands in other alkali chlorides. Casella<sup>1</sup> investigated NaCl and Howland<sup>2</sup> investigated KCl. These workers have shown that the valence band in these alkali chlorides are primarily formed from the 3*p* Cl<sup>-</sup> energy states. Howland considered the valence band as being a mixture of the three 3*p* Cl<sup>-</sup> functions, the three 3*p* K<sup>+</sup> functions, the 3*s* Cl<sup>-</sup> functions, and the 3*s* K<sup>+</sup> functions. The results of Howland neglect spin-orbit interactions. Howland found the valence band to be about 1.5 eV wide for KCl. The calculation due to Casella showed the width of the valence band in NaCl to be greater than 1.0 eV.

Parratt and Jossem<sup>3</sup> had found that the valence band in KCl was only about 0.33 eV wide. This result was based upon observations of the x-ray emission spectrum from KCl. The results of Howland<sup>2</sup> and Casella<sup>1</sup> are clearly in disagreement with the measurement of

Parratt and Jossem. Eby, Teegarden, and Dutton<sup>4</sup> have made measurements of the absorption spectra for various alkali halides. They used films which were evaporated onto LiF and then measured the light transmitted by these films as a function of wavelength. These results go to about 10.0 eV in energy. The region from 10.0 to 20.0 eV was investigated for several alkali halides by Philipp and Ehreweich.<sup>5</sup> They used reflections from the crystals. The results of Eby, Teegarden, and Dutton, and of Philipp and Ehreweich were interpreted by J. C. Phillips.<sup>6</sup> J. C. Phillips uses these results to construct hypothetical band structures for the various alkali halides. The predictions of J. C. Phillips tend to agreement with the results of Howland<sup>2</sup> and Casella.<sup>1</sup>

The results of Howland do not include spin-orbit effects and are not directly comparable to the predictions of J. C. Phillips.<sup>6</sup> Furthermore, the complex band obtained by Howland due to the necessity of including 3*p* and 3*s* functions from both the alkali and the halide makes the inclusions of spin-orbit effects difficult. In the present work LiCl is considered. Here in the ground state the lithium ion contains only two 1*s* electrons. These electrons are located near the nucleus and have energy sufficiently below the energy of the 3*p* and 3*s* Cl<sup>-</sup> functions so that they should not appreciably mix

\* Work supported in part by U. S. Atomic Energy Commission.

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<sup>1</sup> R. C. Casella, *Phys. Rev.* **104**, 1260 (1956).

<sup>2</sup> L. P. Howland, *Phys. Rev.* **109**, 1927 (1958).

<sup>3</sup> L. G. Parratt and E. L. Jossem, *Phys. Rev.* **97**, 916 (1955).

<sup>4</sup> J. E. Eby, K. J. Teegarden, and D. B. Dutton, *Phys. Rev.* **116**, 1099 (1959).

<sup>5</sup> J. R. Philipp and H. Ehreweich, *Phys. Rev.* **131**, 2016 (1963).

<sup>6</sup> J. C. Phillips, *Phys. Rev.* **136**, A1705 (1964).

in the formation of the valence band. Thus, this solid is somewhat simpler and it may thus be possible to give a more complete calculation of its valence band. The atomic system of units is used.

## II. ASSUMPTIONS REGARDING THE ONE-ELECTRON WAVE FUNCTIONS AND THE CRYSTAL POTENTIAL

In this work, tight-binding approximations are made. The crystal wave function  $\Psi_{mk}^{\alpha l}(\mathbf{r})$  is given as a linear combination of Bloch functions formed from the 3p Cl<sup>-</sup> orbitals. These orbitals are chosen to have  $x$ ,  $y$ , and  $z$  symmetry, and are designated as  $\varphi_{3pz}$ ,  $\varphi_{3py}$ , and  $\varphi_{3px}$ , respectively. At appropriate points in the Brillouin zone the 3s Cl<sup>-</sup> function is allowed to mix with the various 3p functions. In general the crystal functions are given as:

$$\Psi_{mk}^{\alpha l}(\mathbf{r}) = \sum_{j=1}^4 A_j(\mathbf{k}) \psi_{mj}(\mathbf{r}), \quad (1)$$

where, for example,

$$\psi_{3lk}(\mathbf{r}) = \sum (\mu) \exp(i\mathbf{k} \cdot \mathbf{R}_\mu) \varphi_{3px}(\mathbf{r} - \mathbf{R}_\mu). \quad (2)$$

Here  $\mathbf{R}_\mu$  is the vector from that chlorine nucleus chosen as the origin to the  $\mu$ th chlorine nucleus. The nuclei are assumed to remain fixed. The sum over  $\mu$  runs over all the chlorine nuclei in the lattice. The lattice in question is face-centered cubic. The function  $\varphi_{3px}(\mathbf{r} - \mathbf{R}_\mu)$  is the 3p $x$  function which is the solution to the free-ion Hartree-Fock equation for the chlorine ion centered at  $\mathbf{R}_\mu$ . The constants  $A_j(\mathbf{k})$  in Eq. (1) are chosen so that  $\Psi_{mk}^{\alpha l}(\mathbf{r})$  transforms as a basis vector for the  $l$ th row of the  $\alpha$ th irreducible representation of the group of the wave vector  $\mathbf{k}$ . The values of  $A_j(\mathbf{k})$  may be determined by a projection-operator technique.<sup>7,8</sup> The directions chosen are [100], [110], and [111] directions in reciprocal lattice space. This is initially carried out neglecting spin in the wave functions. One obtains for example in the [100] direction with  $\alpha = \Delta_1$ :

$$\Psi_{3k}^{\Delta_1} = \sum (\mu) \exp(i\mathbf{k} \cdot \mathbf{R}_\mu) \varphi_{3pz}(\mathbf{r} - \mathbf{R}_\mu),$$

or

$$\Psi_{3k}^{\Delta_1} = \sum (\mu) \exp(i\mathbf{k} \cdot \mathbf{R}_\mu) \varphi_{3s}(\mathbf{r} - \mathbf{R}_\mu). \quad (3)$$

The spin-orbit interactions are taken into account by using first-order perturbation theory. The detailed results of this are to be found in the literature in a convenient form and are not included here.<sup>9,10</sup>

The functions used as the radial part of the  $\varphi_{3s}(\mathbf{r})$  and  $\varphi_{3pi}(\mathbf{r})$  wave functions were obtained by Löwdin.<sup>11</sup> These functions were obtained from the argon atom and then scaled to fit the chlorine ion. The potential

<sup>7</sup> R. S. Knox and A. Gold, *Symmetry in the Solid State* (W. A. Benjamin and Company, Inc., New York, 1964).

<sup>8</sup> J. C. Slater, *Rev. Mod. Phys.* **37**, 68 (1965).

<sup>9</sup> W. Beall Fowler, thesis, University of Rochester, 1963 (unpublished); *Phys. Rev.* **132**, 1591 (1963).

<sup>10</sup> J. C. Slater and G. F. Koster, *Phys. Rev.* **94**, 1498 (1954).

<sup>11</sup> P. O. Löwdin and K. Appel, *Phys. Rev.* **103**, 1746 (1956).

TABLE I. A comparison between the analytic Hartree-Fock functions used as the radial parts for the wave functions and the Hartree-Fock-Slater functions which would be solutions for the potential used in this calculation.  $r$  is the radial coordinate,  $3p(r)$  signifies the radial part of the 3p wave functions. Atomic units are used.

$r$	$3p(r)$ Hartree-Fock	$3p(r)$ Slater
0.0043	0.1495	0.1822
0.0172	0.5416	0.6534
0.0301	0.8584	1.0262
0.0516	1.2476	1.4713
0.0774	1.5350	1.7850
0.1033	1.6782	1.9264
0.1549	1.6883	1.9038
0.2066	1.4991	1.6660
0.2755	1.1358	1.2377
0.3788	0.5924	0.6137
0.4820	0.1623	0.1299
0.6542	-0.2898	-0.3596
0.8607	-0.5295	-0.5949
1.0674	-0.5869	-0.6332
1.4806	-0.4945	-0.5087
1.8938	-0.3565	-0.3630
2.4447	-0.2189	-0.2072
3.2710	-0.1052	-0.0963
4.0973	-0.0525	-0.0491
5.4747	-0.0181	-0.0183
7.1270	-0.0054	-0.0076
8.7801	-0.0015	-0.0023
12.0855	-0.0001	-0.0003
15.3910	-0.0000	-0.0000
19.7983	-0.0000	-0.0000

used for the Cl<sup>-</sup> potential is that given by Casella<sup>1</sup> for the argon atom which is then scaled to fit the Cl<sup>-</sup> potential. In effect this potential is similar to that seen by an electron when the modified Hartree-Fock-Slater equation described by Herman and Skillman<sup>12</sup> is solved. The potential is

$$V_{\text{Cl}}(\mathbf{r}) = 2r^{-1} - r^{-1} [27.2 \exp(-2.91r) + 8.8 \exp(-12.4r)]. \quad (4)$$

The analytic wave function is compared to a numerical Hartree-Fock-Slater wave function in Table I.

The lithium potential is obtained by applying the variational principle to a hydrogen-like wave function using the free lithium ion Hamiltonian. The wave functions obtained are then used to construct a Hartree-Fock potential for the lithium ion. The potential is

$$V_{\text{Li}}(\mathbf{r}) = -2r^{-1} - (4r^{-1} + 10.75) \exp(-5.375r). \quad (5)$$

The crystal potential is constructed as a sum of the lithium and chlorine free-ion potential located at their respective places in the lattice. The crystal potential is

$$V(\mathbf{r}) = \sum (\mu) [V_{\text{Cl}}(\mathbf{r} - \mathbf{R}_\mu) + V_{\text{Li}}(\mathbf{r} - \mathbf{R}_\mu - \mathbf{g})]. \quad (6)$$

The lattice parameter is  $a$  and  $g$  is  $(a00)$ .  $V_{\text{Cl}}(\mathbf{r} - \mathbf{R}_\mu)$  is the chlorine ion potential due to the chlorine ion situated at  $\mathbf{R}_\mu$ , and  $V_{\text{Li}}(\mathbf{r} - \mathbf{R}_\mu - \mathbf{g})$  is the lithium ion potential about the point  $(\mathbf{R}_\mu + \mathbf{g})$ .

<sup>12</sup> F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

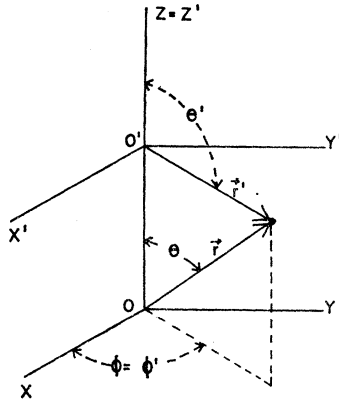


FIG. 1. A diagram of the coordinate system used to evaluate the two center integrals which arise in this problem. The two origins are called  $O$  and  $O'$ .

In considering the spin-orbit interaction, the effective spin-orbit Hamiltonian is taken to be

$$H_{so} = (4c^2r)^{-1} [dV_{Cl}(\mathbf{r})/dr] \boldsymbol{\sigma} \cdot \mathbf{L}. \quad (7)$$

In obtaining this one realizes that  $V_{Cl}(\mathbf{r})$  has its largest value and gradient near the point  $\mathbf{r}=0$ , and one thus considers only a single center term in evaluating the matrix element for  $H_{so}$ . Thus, here the spin-orbit parameter will be the same as that for the free-ion Hartree-Fock case. This question is discussed in some detail by Fowler.<sup>9</sup> The relevant group theory is discussed by Koster and Statz.<sup>13</sup>

### III. DETAILS OF THE CALCULATIONS AND RESULTS

The one-electron Hamiltonian for the crystal is given by

$$H = -\nabla^2 + V(\mathbf{r}) + H_{so}. \quad (8)$$

In this calculation, only nearest-neighbor chlorine and lithium ions will be considered in full detail. Here however, the three center terms will be neglected. The contribution to the crystal potential due to the other ions will be included by using the Madelung energy  $V_M$ . First one considers

$$H' = -\nabla^2 + V(\mathbf{r}) \quad (9)$$

and the  $jl$  matrix element of  $H^1$  is defined as<sup>9</sup>

$$H_{jl}' = \epsilon_{\alpha j} \delta_{jl} + [V_{\alpha j} \delta_{jl} + \sum (\mu) \exp(i\mathbf{k} \cdot \mathbf{R}_\mu) V_{\alpha \mu j l}] \times [1 + \sum (\mu) \exp(i\mathbf{k} \cdot \mathbf{R}_\mu) \delta_{\alpha \mu j l}]^{-1}, \quad (10)$$

where  $\epsilon_{\alpha j}$  is the energy of an electron in the  $j$ th state of the free ion.  $V_{\alpha j}$  is the term obtained by integrating the square of the atomic function about the origin and the potential due to the nearest-neighbor chlorine and lithium ions plus the Madelung potential due to the

TABLE II. The band parameters for the  $3p$   $Cl^-$  valence band of  $LiCl$ . The parameters are defined in the text. The atomic system of units is used.

$a$	$\epsilon_{3p}$	$V_{\alpha m}$	$V_{pp\sigma}$	$V_{pp\pi}$	$S_{pp\sigma}$	$S_{pp\pi}$
4.89	-0.297	-0.820	0.0909	-0.0225	-0.0986	0.0285

rest of the lattice. In Eq. (10)  $V_{\alpha \mu j l}$  and  $S_{\alpha \mu j l}$  are given as

$$V_{\alpha \mu j l} = \int_{\text{All space}} \varphi_{3pj}(\mathbf{r}) \varphi_{3pl}(\mathbf{r} - \mathbf{R}_\mu) [V_{cl}(\mathbf{r} - \mathbf{R}_\mu) - 2(\mathbf{r} - \mathbf{R}_\mu)^{-1} + V_M] d\tau, \quad (11)$$

and

$$S_{\alpha \mu j l} = \int_{\text{All space}} \varphi_{3pj}(\mathbf{r}) \varphi_{3pl}(\mathbf{r} - \mathbf{R}_\mu) d\tau. \quad (12)$$

The summation is over those 12 chlorine ions which are nearest to that one chosen as the origin. In evaluation of these elements, one finds that only two  $V_{\alpha \mu j l}$  and two  $S_{\alpha \mu j l}$  are needed for this case. The evaluation is carried out using the coordinate system shown in Fig. 1.

When  $\varphi_{3pj}(\mathbf{r}) = \varphi_{3pl}(\mathbf{r}) = \varphi_{3pz}(\mathbf{r})$ , one defines  $V_{\alpha \mu zz} = V_{pp\sigma}$  and  $S_{\alpha \mu zz} = S_{pp\sigma}$ . When  $\varphi_{3pj}(\mathbf{r}) = \varphi_{3pl}(\mathbf{r}) = \varphi_{3px}(\mathbf{r}) = \varphi_{3py}(\mathbf{r})$ , then one defines  $V_{\alpha \mu xx} = V_{\alpha \mu yy} = V_{pp\pi}$  and  $S_{\alpha \mu xx} = S_{\alpha \mu yy} = S_{pp\pi}$ . To illustrate this we give a sample result. In the  $[100]$  direction, for  $\alpha = \Delta_1$ ;  $k_x = (\pi/a)f$ ;  $f=0 \rightarrow 1$  and  $k_y = k_z = 0$  one has

$$H_{xx}' = \epsilon_{3p} + [V_{3p} + 4V_{pp\pi} + 4(V_{pp\pi} + V_{pp\sigma}) \cos(ka)] \times [1 + 4S_{pp\pi} + 4(S_{pp\pi} + S_{pp\sigma}) \cos(ka)]^{-1}.$$

The integration indicated in Eqs. (10)–(12) are carried out using the method of Keil<sup>14</sup> and results are in Table II. This method uses analytic functions and evaluates the integrals by the  $\alpha$ -function method of Löwdin.<sup>15</sup> As a check, some of the integrals were evaluated by a direct application of Simpson's rule. The results of these calculations are given in Table II. The

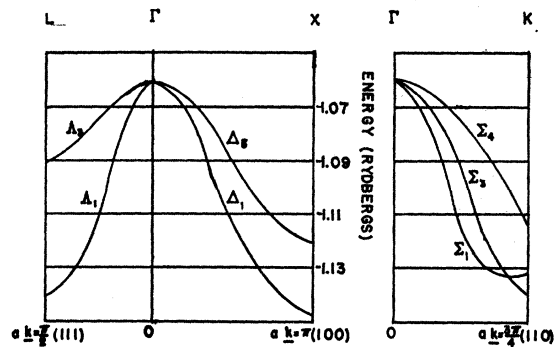


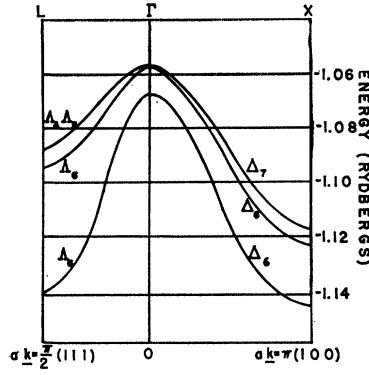
Fig. 2. The  $3p$  valence band for  $LiCl$ . Energy is given as a function of wave vector  $\mathbf{k}$  for values of  $\mathbf{k}$  in the  $[100]$ ,  $[110]$ , and  $[111]$  directions. The notation used is standard group-theoretical notation of Bouckaert, Smoluchowski, and Wigner. Spin-orbit effects are neglected.

<sup>13</sup> G. F. Koster and H. Statz, Quarterly Progress Report No. 39, 1961, Solid State and Molecular Theory Group, MIT, Cambridge, Massachusetts (unpublished).

<sup>14</sup> T. H. Keil, University of Rochester (unpublished).

<sup>15</sup> P. O. Löwdin, Advan. Phys. **5**, 1 (1956).

FIG. 3. The 3p valence band for LiCl. Energy is given as a function of wave vector  $k$  for values of  $k$  in the [100], and [111] directions. Spin-orbit effects are included here.



energy bands are graphed using Eq. (10) in Fig. 2.  $V_{pp\sigma}$  and  $S_{pp\sigma}$  were evaluated for next-nearest-neighbor chlorine ions. These were found to be two orders of magnitude smaller than the contributions due to the similar term in  $V_{pp\sigma}$  and  $S_{pp\sigma}$  for the nearest-neighbor chlorine ions. Three center effects are included only indirectly by the Madelung term. In the elements calculated, it is observed that the contributions due to the electronic structure were smaller than those due to the ionic tails on the potentials. It is assumed that this is true for the three-center integrals also.

When the effects of the spin-orbit Hamiltonian  $H_{so}$  are included, one may then define a spin-orbit parameter  $\xi$  as

$$\xi = \langle 3pi | H_{so} | 3pi \rangle. \quad (13)$$

The value of  $\xi$  is 0.0027 Ry. This is included in the band calculation and the results are obtained in the same convenient form as given by Fowler.<sup>9</sup> As an example of this we use the [100] direction, for  $\alpha = \Delta_6$ . Let

$$O(\Delta_6) = 1 + 2[S_{pp\pi} + S_{pp\sigma}] + 2[3S_{pp\pi} + S_{pp\sigma}] \cos(ka),$$

$$O(\Delta_1) = 1 + 4S_{pp\pi} + 4[S_{pp\pi} + S_{pp\sigma}] \cos(ka),$$

$$E(\Delta_6) = H_{zz'},$$

$$E(\Delta_1) = H_{xx'},$$

then

$$E(\Delta_6) = \frac{1}{2}[E(\Delta_1) + E(\Delta_6) - \xi O(\Delta_6)^{-1}] \pm \frac{1}{2}\{[E(\Delta_1) - E(\Delta_6) + \xi O(\Delta_6)^{-1}]^2 + 8\xi^2[O(\Delta_1)O(\Delta_6)]^{-1}\}^{1/2}.$$

The results obtained with the inclusion of spin-orbit interaction are given in Fig. 3. The notation used is that of Bouckaert, Smoluchowski, and Wigner<sup>16</sup> for the results without spin-orbit effects, for the results with spin-orbit effects notation similar to that of Fowler<sup>9</sup> is used. When the 3s  $Cl^-$  function was allowed to mix with the 3p  $Cl^-$  functions at appropriate points in the reciprocal lattice, it is found that the value of the energy for the 3p  $Cl^-$  function is changed by about 1% or less. This result is not included in the results given.

#### IV. CONCLUSIONS

The width of the 3p  $Cl^-$  band of LiCl is found to be 1.2 eV if spin-orbit interactions are neglected. When spin-orbit interactions are included, it is seen that the 3p bands still overlap considerably. With this effect included, one finds the band width to be 1.3 eV. The inclusion of the spin-orbit term introduces a splitting in the 3p  $Cl^-$  band of 0.13 eV at the point  $\Gamma$ . The results of the analysis due to J. C. Phillips<sup>6</sup> on the spectrum of Eby, Teggarden, and Dutton<sup>4</sup> yields a split of about 0.1 eV at this point. Insufficient information is available for J. C. Phillips to obtain the shape of the 3p  $Cl^-$  band of LiCl and, therefore one cannot make any comparison. Finally, we observe that our bands are much wider than those one might expect from the results of Parratt and Jossem.<sup>3</sup> We did not perform a complete calculation for NaCl or KCl, however, those parameters which were obtained, show results which would be in agreement with the predictions of Casella.<sup>1</sup> The authors believe that this approach has yielded a reasonable result for the valence band in LiCl.

#### V. ACKNOWLEDGMENTS

The authors wish to express their appreciation to Donald Beck for his discussions and help on several computer programs. They also thank Dr. Henry Mullish of the Courant Institute for his aid and hospitality. Finally they wish to thank Dr. W. Beall Fowler and Professor R. S. Knox for reading the manuscript and suggesting improvements in it.

<sup>16</sup> L. P. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. **50**, 58 (1936).