If the loss at 22.2 eV is due to collective excitation of the valence-band electrons it is simple to estimate the theoretical plasma frequency ω_p from the expression

$$\omega_p^2=4\pi Ne^2/m. \qquad (11)$$

If only the 6 electrons in the $O^{--}2p$ valence band are included, then $\hbar\omega_p$ is about 21 eV. In view of the simplicity of this model, the agreement with experiment is good. Since interband transitions are also occurring in this region, though weakly, the actual plasma resonance may be shifted from the free-electron plasma energy in any case, as has been pointed out by Wilson.[22]

In considering plasma oscillations in metals, both Wolff[23] and Kanazawa[24] derive an expression governing the half-width for the resonance in the form

$$\hbar\Gamma/\hbar\omega_p=nk. \qquad (12)$$

It is difficult to determine the half-width of the resonance in Fig. 5, because of the proximity of losses due to interband transitions (at 20.3, 23.9 and 24.7 eV, for example). It appears to be about 3 eV, however, and therefore the ratio of half-width to plasma frequency (22.2 eV) is 0.14. This is of the right magnitude since, in practice, $\epsilon_2/2$ is about 0.18 at 22.2 eV.

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Calculation of the Spin-Orbit Parameters for the Valence Bands of the fcc Alkali Chlorides, Alkali Bromides, and Alkali Iodides*

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The spin-orbit parameters for the fcc alkali chlorides, alkali bromides, and alkali iodides have been calculated. Tight-binding wave functions and potentials of a type used in earlier calculations by the author were used. Various overlap corrections were computed; of these the only significant one was found to be the correction to the normalization of the wave functions due to overlap. The theoretical spin-orbit splittings for the point Γ in the first Brillouin zone, obtained by the assumption of *LS* coupling, were found to compare favorably with existing optical data.

I. INTRODUCTION

In the past few years, calculations on the structure of the valence bands of the alkali halides have become very refined. In many cases such corrections as spin-orbit effects have been included.[1–5] There have also been recent attempts by Phillips[6] to relate the results of band-structure calculations to the measured spectra of these substances. The results of these interpretations have proved somewhat controversial,[3,7] and this points out the need for more study of the band structure of the alkali halides. Even for substances such as the alkali chlorides, where the spin-orbit splittings are small, one should include these effects in a band-structure calculation, if one is to attempt to relate the results of the calculation to the existing spectral data. The necessity of including spin-orbit corrections in the alkali iodides is obvious, because their magnitude is of the order of 1 eV. In fact, the size of the splitting in the NaI valence band, which is 1.25 eV at the Γ point, has only recently been satisfactorily explained.[5]

There have been other recent calculations on other chlorides, some of which do not include spin-orbit results but which are complete in other respects.[8–10] It is possible to modify these results to include spin-orbit effects by the use of perturbation theory. To do this, one would obtain band structures in the tight-binding formulation of Slater and Koster[11] by performing a curve fitting for the available bands. In this paper, tight-binding theory is assumed, and spin-orbit parameters have been calculated for the various fcc alkali chlorides, alkali iodides, and alkali bromides.

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II. DETAILS OF THE CALCULATION AND RESULTS

In order to perform this calculation, potentials and wave functions for the ground states of the several alkali and halide ions were obtained.[12] This was done by using essentially the method of Herman and Skillman.[13] The crystal potential is given by

$$V(\mathbf{r})=\sum_{\mu}\left[V_x(\mathbf{r}-\mathbf{R}_\mu)+V_A(\mathbf{r}-\mathbf{R}_\mu-\mathbf{g})\right]. \tag{1}$$

Here $V(\mathbf{r})$ is the crystal potential, $V_x(\mathbf{r}-\mathbf{R}_\mu)$ is the potential due to the halide ion about the lattice site $\mathbf{R}_\mu$, and $V_A(\mathbf{r}-\mathbf{R}_\mu-\mathbf{g})$ is the potential due to the alkali ion about the site $\mathbf{R}_\mu+\mathbf{g}$. The sum is over all the sites in the lattice. $\mathbf{R}_\mu$ is a vector in the direct lattice, and if a is the lattice constant, $\mathbf{g}$ is found to be $(\frac{1}{2}a,0,0)$. The valence orbitals are assumed to be formed primarily from the outermost p states centered on the halide ions. This assumption is certainly not valid for the rubidium halides because of the small negative energy of the outermost electron of the rubidium ion, but it is a good approximation as far as spin-orbit calculations are concerned for other alkali halides. The p states, formed to have x, y, and z symmetry, yield Bloch[14] functions

$$\psi_{nx}(\mathbf{r})=N^{-1}\sum_{\mu}\exp(i\mathbf{k}\cdot\mathbf{R}_\mu)\varphi_{nx}(\mathbf{r}-\mathbf{R}_\mu)\,,\ \text{etc.} \tag{2}$$

In Eq. (2), $\psi_{nx}(\mathbf{r})$ is the Bloch function formed from those single-electron halide functions $\varphi_{nx}(\mathbf{r}-\mathbf{R}_\mu)$ which have radial quantum number n and have x-like symmetry. The sum is over all points n in the direct lattice and $\mathbf{k}$ is a vector in the first Brillouin zone.

In order to proceed farther, we need the explicit form for the spin-orbit correction. The procedure is to write a wave function in determinant form using single-particle Dirac spinors[15] and then reduce the problem to a point where we have an equation containing an effective one-electron potential.[16] Having done this, we can isolate the usual spin-orbit Hamiltonian;

$$H_{\text{so}}=(\hbar/4m^2c^2)\boldsymbol{\sigma}\cdot[\nabla V(\mathbf{r})\times\mathbf{p}]. \tag{3}$$

In Eq. (3) m is the mass of an electron, c is the velocity of light in a vacuum, $\boldsymbol{\sigma}$ is the spin operator, and $\mathbf{p}$ is the electron's momentum. H_{so} still has the symmetry of the lattice and hence transforms according to the Γ_1 irreducible representation of the group O_h for a fcc lattice. We keep here the first-order term involving angular dependence, with the familiar result[4,5,17]

$$H_{\text{so}}=\frac{\hbar}{4m^2c^2}\frac{1}{r}\frac{dV(\mathbf{r})}{dr}\boldsymbol{\sigma}\cdot\mathbf{L}\,, \tag{4}$$

where $\mathbf{L}$ is the angular momentum $\mathbf{r}\times\mathbf{p}$. In order to incorporate Eq. (4) into the tight-binding formalism, we form linear combinations of Bloch functions of the type given in Eq. (2) which transform according to the several irreducible representations of the double group appropriate for the point in the Brillouin zone in question.[18,19] In order to use results of band-structure calculations without spin-orbit effects, we shall define a spin-orbit parameter ξ to be

$$\xi=\frac{\hbar^2}{4m^2c^2}\int_{\text{all space}}\frac{1}{r}\frac{dV(r)}{dr}[\psi_{nx}^*(\mathbf{r})\psi_{nx}(\mathbf{r})]d\tau. \tag{5}$$

Equation (5) contains $V(r)$, which is the spherical average of the crystal potential $V(\mathbf{r})$. This is done in order to include terms in the expression for ξ other than the usual one-center terms. We may reduce Eq. (5) further,

$$\xi=\frac{\hbar^2}{4m^2c^2}\int_{\text{all space}}\frac{1}{r}\frac{dV(r)}{dr}\times\varphi_{nx}(\mathbf{r})\sum_{\mu}\exp(i\mathbf{k}\cdot\mathbf{R}_\mu)\varphi_{nx}(\mathbf{r}-\mathbf{R}_\mu)d\tau. \tag{5'}$$

In keeping with usual tight-binding methods, the sum over μ is only over those sites nearest to the one chosen as the origin. Also, in keeping with usual tight binding usage, we may define terms to yield

$$\begin{aligned}\xi_{pp}&=\frac{\hbar^2}{4m^2c^2}\int_{\text{all space}}\frac{1}{r}\frac{dV(r)}{dr}|\varphi_{nx}(\mathbf{r})|^2d\pi\,,\\ \xi_{pp\pi}&=\frac{\hbar^2}{4m^2c^2}\int_{\text{all space}}\frac{1}{r}\frac{dV(r)}{dr}\varphi_{nx}(\mathbf{r})\varphi_{nx}(\mathbf{r}-\mathbf{R}_\mu)d\tau\,, \qquad (6)\\ \xi_{pp\sigma}&=\frac{\hbar^2}{4m^2c^2}\int_{\text{all space}}\frac{1}{r}\frac{dV(r)}{dr}\varphi_{nz}(\mathbf{r})\varphi_{nz}(\mathbf{r}-\mathbf{R}_\mu)d\tau\,.\end{aligned}$$

In the above Eqs. (6) we assume the z axis to be along the direction $\mathbf{R}_\mu$, and thus may define the spin-orbit contributions in a manner completely analogous to the potential terms in the usual tight-binding approximation. Furthermore, as will be shown, the terms $\xi_{pp\pi}$ and $\xi_{pp\sigma}$ are so many orders of magnitude smaller than the ξ_{pp} that they may be neglected. Thus,

$$\xi\approx\xi_{pp}.$$

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TABLE I. The spin-orbit parameters for the various fcc alkali chlorides, alkali bromides, and alkali iodides. The lattice parameter is a. The N.C. indicates the parameter in question has not been calculated. The quantities ξ_{ion}, ξ_{pp}', $\xi_{pp\sigma}$, and $\xi_{pp\pi}$ are defined by Eqs. (6). Energies in Rydbergs.

Substance	a	ξ_{ion}	ξ_{pp}'	$\xi_{pp\sigma}$	$\xi_{pp\pi}$
LiCl	9.68	0.0027	-6.59×10^{-7}	-1.14×10^{-10}	9.83×10^{-12}
NaCl	10.6	0.0027	-7.07×10^{-7}	N.C.	N.C.
KCl	11.8	0.0027	-6.79×10^{-7}	N.C.	N.C.
RbCl	12.3	0.0027	-6.74×10^{-7}	N.C.	N.C.
LiBr	10.4	0.0111	N.C.	N.C.	N.C.
NaBr	11.4	0.0111	N.C.	N.C.	N.C.
KBr	12.5	0.0111	N.C.	N.C.	N.C.
RbBr	13.0	0.0111	N.C.	N.C.	N.C.
LiI	10.3	0.0232	-5.12×10^{-7}	N.C.	N.C.
NaI	12.3	0.0232	-4.99×10^{-7}	N.C.	N.C.
KI	13.3	0.0232	-5.33×10^{-7}	N.C.	N.C.
RbI	13.8	0.0232	-5.29×10^{-7}	N.C.	N.C.

We may now give expressions for the energy of the various p states in terms of the irreducible representations of the double group of the $\mathbf{k}$ vector in question. We shall consider the point Γ and the lines Δ and Λ. Let us define $E(\Delta_1)$ to be the energy of the p-like states which transform according to the Δ_1 irreducible representation of the group C_{4V} when spin-orbit effects are neglected. In analogous manner we define $E(\Delta_5)$, $E(\Gamma_{15})$, $E(\Lambda_1)$, and $E(\Lambda_3)$. The line Δ is for $(0,0,0)<\mathbf{k}<(2\pi/a,0,0)$, Γ is the point $\mathbf{k}=(0,0,0)$, and the line Λ is for $(0,0,0)<\mathbf{k}<(\pi/a,0,0)$. We define the overlap matrix elements as follows:

$$O(\Delta_1)=\sum_{\mu,\nu}\exp(i\mathbf{k}\cdot\mathbf{R}_\nu)\times\int_{\text{all space}}\varphi(\Delta_1)(\mathbf{r}-\mathbf{R}_\mu)\varphi(\Delta_1)(\mathbf{r}-\mathbf{R}_\nu)d\tau\,,$$

where $\varphi(\Delta_1)$ is the linear combination of the p-type functions which transforms as a basis for Δ_1. In a like manner, we define $O(\Delta_5)$, $O(\Gamma_{15})$, $O(\Lambda_1)$, and $O(\Lambda_3)$. We then write energy expressions for the functions transforming according to the irreducible representations of the $\mathbf{k}$ vector in question in terms of the E's, O's, and ξ.

TABLE II. The overlap integrals for the $5p\mathrm{I}^{-}$-$5p\mathrm{I}^{-}$, $4p\mathrm{Br}^{-}$-$4p\mathrm{Br}^{-}$, and $3p\mathrm{Cl}^{-}$-$3p\mathrm{Cl}^{-}$ wave functions. These are defined in Eqs. (9). See Ref. 20.

Substance	$S_{pp\pi}$	$S_{pp\sigma}$
LiCl	0.0296	−0.101
NaCl	0.0196	−0.0744
KCl	0.0111	−0.0502
RbCl	0.00916	−0.0416
LiBr	0.0319	−0.111
NaBr	0.0221	−0.0847
KBr	0.0132	−0.0579
RbBr	0.0105	−0.0494
LiI	0.0365	−0.119
NaI	0.0261	−0.0970
KI	0.0161	−0.0714
RbI	0.0133	−0.0615

TABLE III. The energy difference $E(\Gamma_8^-)-E(\Gamma_6^-)$ is given for the various fcc alkali chlorides, alkali bromides, and alkali iodides. The theoretical values are obtained from the expression $E(\Gamma_8^-)-E(\Gamma_6^-)=3\xi O(\Gamma_{15})^{-1}$. The experimental values are from Ref. 21.

Substance	Expt. (eV) $E(\Gamma_8^-)-E(\Gamma_6^-)$	Theoret. (eV) $E(\Gamma_8^-)-E(\Gamma_6^-)$	$3\xi_{\text{ion}}$ (eV)
LiCl	Uncertain	0.131	0.11
NaCl	0.13	0.128	0.11
KCl	0.11	0.123	0.11
RbCl	0.13	0.115	0.11
LiBr	0.52	0.55	0.46
NaBr	0.52	0.53	0.46
KBr	0.49	0.51	0.46
RbBr	0.48	0.50	0.46
LiI	Uncertain	1.23	0.95
NaI	1.17	1.15	0.95
KI	0.90	1.12	0.95
RbI	0.77	1.10	0.95

These are found to be[17]:

for the point Γ:

$$E(\Gamma_6^-)=E(\Gamma_{15})-2\xi/O(\Gamma_{15})$$

and

$$E(\Gamma_8^-)=E(\Gamma_{15})+\xi/O(\Gamma_{15})\,; \tag{7}$$

for the line Δ:

$$E(\Delta_6)=\tfrac{1}{2}[E(\Delta_1)+E(\Delta_5)]-\xi/O(\Delta_5)\pm\tfrac{1}{2}\{[E(\Delta_1)-E(\Delta_5)+\xi/O(\Delta_5)]^2+8\xi^2/O(\Delta_1)O(\Delta_5)\}^{1/2}$$

and

$$E(\Delta_7)=E(\Delta_5)+\xi/O(\Delta_5)\,;$$

for the line Λ:

$$E(\Lambda_6)=\tfrac{1}{2}[E(\Lambda_1)+E(\Lambda_3)-\xi/O(\Lambda_3)]\pm\tfrac{1}{2}\{[E(\Lambda_1)-E(\Lambda_3)+\xi/O(\Lambda_3)]^2+8\xi^2/O(\Lambda_1)O(\Lambda_3)]^{1/2}$$

and

$$E(\Lambda_{4,5})=E(\Lambda_3)+\xi/O(\Lambda_3)\,.$$

The ionic potentials for the alkali and halide ions in question have been used to form the crystal potential. Using a given halide ion as the origin, the potential has been averaged spherically. The spin-orbit parameters have been evaluated using Eqs. (6). In order to present the results, the contribution to ξ_{pp} from the ion at the origin has been removed as this term is just the spin-orbit parameter calculated for the free ion before it is put in the crystal. We find

$$\xi_{pp}=\xi_{\text{ion}}+\xi_{pp}'\,. \tag{8}$$

In Eq. (8), ξ_{ion} is the spin-orbit parameter for the free ion and is evaluated by using the wave function for the valence state of the free halide ion, the potential for that ion, and Eq. (5), and ξ_{pp}' is the term due to the remainder of the lattice and is evaluated using the free-halide-ion valence states for the halide at the origin and the spherical average of the potential given by Eq. (1) minus the potential of the halide ion at the origin. The values of the various spin-orbit parameters are given in Table I. The values of the overlap integrals are taken from Hafemeister and Flygare[20] and are given in Table II.

III. COMPARISON WITH EXPERIMENT AND CONCLUSIONS

From Eq. (7) one sees that the energy difference between the states Γ_8^- and Γ_6^- is given as

$$E(\Gamma_8^-)-E(\Gamma_6^-)=O(\Gamma_{15})^{-1}3\xi\,, \tag{9}$$

where

$$O(\Gamma_{15})^{-1}=[1+4S_{pp\sigma}+8S_{pp\pi}]^{-1},$$

$$S_{pp\sigma}=\int_{\text{all space}}\varphi_z(\mathbf{r})\varphi_z(\mathbf{r}-\mathbf{R}_\mu)d\tau\,,$$

$$S_{pp\pi}=\int_{\text{all space}}\varphi_x(\mathbf{r})\varphi_x(\mathbf{\Gamma}-\mathbf{R}_\mu)d\tau\,.$$

Using the results of Eby, Teegarden, and Dutton,[21] we make an experimental determination of the energy difference at Γ. These values, along with the results theoretically obtained using Eq. (9), are given in Table III. We note that in the case of sodium chloride and sodium iodide, the agreement of theory and experiment is extremely good, as is the agreement for all the bromides. The agreement for KCl and RbCl is fair. However, the trends are different for both substances. Theoretically the splitting decreases as the size of the alkali increases; however, this is seen to be true up to potassium chloride and then the splitting increases for rubidium chloride. This factor is probably due to a rather large amount of intereaction between the valence electrons of the chloride ions with the valence electrons of the rubidium ions. This was neglected theoretically. In the case of potassium iodide and of rubidium iodide, the agreement with experiment is poor. However, in a recent measurement of the absorption spectrum of rubidium iodide, Baldini and Teegarden[22] reanalyzed the identification of points in the low-energy region of the absorption spectrum. From these new measurements, Baldini and Teegarden find the energy difference in rubidium iodide to be 1.15 eV. This value is in good agreement with the theoretical results. It is possible that a more careful analysis of the spectrum of potassium iodide in the region of the fundamental absorptions might produce values which are in better agreement with theory. In fact, Onodera, Okazaki, and Inui,[3] using the experimental spectrum of Ramamurti and Teegarden,[23] have identified a peak at somewhat higher energy as the transition $\Gamma_6^- - \Gamma_6^+$. With this identification the splitting is found to be 1.35 eV. This result is larger than the predicted splitting of 1.12 eV. This difference could be due to the neglect of configuration interaction in the present calculation. We also note that there is a peak intermediate between the one at 6.7 eV which Eby, Teegarden, and Dutton[21] identify as the transition $\Gamma_6^- - \Gamma_6^+$ and the one at 7.2 eV which Onodera, Okazaki, and Inui identify as the $\Gamma_6^- - \Gamma_6^+$ transition. This is at 6.9 eV. If this were the transition $\Gamma_6^- - \Gamma_6^+$, then the splitting $\Gamma_6^- - \Gamma_8^-$ would be 1.05 eV, which would be in best agreement with this calculation.

Several other conclusions may be drawn from this calculation. Corrections to the spin-orbit parameter ξ, due to more than one center in a crystal, are in general negligible except in cases such as rubidium chloride, where considerable mixing of the valence states of the chlorine and rubidium ions exists. It is seen that the corrections for the chlorides or iodides are at least four orders of magnitude smaller than the splitting in the free ion. This is consistent with the results which Fowler obtained for krypton.[17] Also, the corrections to the ionic splittings ξ_{pp}' due to the crystal are negative. That is, there is an inverted order except for the presence of the ionic splitting. This sign of the splittings is consistent with the results of Smith for the *F* center.[24] However, the splitting due to ξ_{pp}' is about two orders of magnitude smaller than for the corresponding term in the *F*-center calculation of Smith. This is probably due to the fact that the *F*-center wave functions are much more diffuse than the ionic wave functions and hence sample more of the gradient of the lattice potential.

Using Eq. (7), it should be possible to modify previous calculations without spin-orbit effects to include these effects. It is essential to consider corrections to the wave-function normalization due to two center overlaps in order to obtain values of for the spin-orbit splittings (as seen here for the point Γ) in order to obtain results which are in reasonable agreement with experiment. Using the curve-fitting technique described by Slater and Koster[11] and the data of Hofemeister and Flygare,[20] it should be possible to add spin-orbit effects to any alkali halide calculation without spin-orbit. One should use that spin-orbit parameter computed for the valence state of the free-halide ion in question.

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