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Energy Bands and Optical Properties of NaCl[†]

Nuzio O. Lipari and A. Barry Kunz
Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

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The energy bands of NaCl are investigated using the nonrelativistic mixed-basis (MB) method developed by one of us (ABK). Using local orbitals, the self-consistent Hartree-Fock energy bands are first obtained. Correlation effects are then taken into account and they are found to be very important in the reduction of both the energy gap, as proved in previous works, and of the valence bandwidth. Only the points Γ, X, L, and the midpoint of Δ of the first Brillouin zone were actually computed; the final energy bands have been fitted with a pseudopotential, however. The density of states for the upper valence bands and lower conduction bands, together with the imaginary part of the dielectric response function, are obtained. The results are compared with experiment and the agreement is good.

I. INTRODUCTION

In recent years, the energy bands of insulating crystals have been extensively investigated.[1] Efforts for treating the Hartree-Fock exchange correctly have been made by many.[2,3] However, in such cases no self-consistency was obtained.

Very recently, a great amount of investigation has been done toward the computation of energy bands of insulating crystals from a first-principle point of view. The authors have been successful in computing Hartree-Fock energy bands for many rare gases and alkali-halide solids.[4,5] It has been seen that true Hartree-Fock calculations give results which can be very different from the ones obtained when model potentials are used.[6] Furthermore, different model potentials often give different results, so that it seems as if the results obtained strongly depend on the kind of approximations involved in treating the exchange potential.[6]

One of us (ABK) has recently developed a local orbital theory[7] and has been able to obtain accurate wave functions for most of the alkali-halide crystals. These wave functions have been proved to be very useful in the investigation of the energy bands of these solids.

Furthermore, in the previous calculations,[4,5] it has been seen that polarization effects, clearly neglected in the Hartree-Fock approximation, are important and should be included before comparison with experiment is made. These effects can be included in two different ways. One has been proposed by Fowler,[8] and the other is based upon a many-body theory first developed by Hedin[9] and used in semiconductors by Brinkman and Goodman.[10] Both ways have been investigated in previous calculations,[4,5] and it has been seen that they are in qualitative agreement but differences are observable.

The present paper has the purpose of investigating the energy bands and optical properties of NaCl following the same methods previously used. We first compute the bands in the Hartree-Fock energy approximation. Correlation effects are then included. The mixed-basis (MB) method is used in the calculations.[11] This method has been proved to give convergent results for the valence and conduction bands. Actual calculations are performed at few points of the first Brillouin zone, namely, Γ, X, L, and the midpoint of Δ. However, we have used a pseudopotential to get complete bands fitting the computed points. Since useful information can be obtained from the joint density of states, we have calculated it together with the density of the valence and conduction bands using 505 nonequivalent points in 1148 of the first Brillouin zone.

In Sec. II, we briefly review the methods of calculation. In Sec. III, results are presented and compared with available experimental data. In Sec. IV, the main results are summarized and possible further work is suggested.

II. METHOD OF CALCULATION

Since the various techniques used in the present calculations are described elsewhere,[4,5] we will give here only a brief outline of them in order to better appreciate the results obtained. As mentioned before, Kunz[7] has been able to obtain local orbitals correct to first order in the interatomic overlap. These orbitals satisfy the following equation:

$$(F_A + U_A - \epsilon_{Ai})\,\phi_{Ai} = \textstyle\sum_k' \phi_{Ak} \langle \phi_{Ak} | U_A | \phi_{Ai} \rangle \quad , \tag{1}$$

where A denotes nuclear coordinates, i refers to electronic coordinates; the $\sum_k'$ means sum over all electron states except $|Ai\rangle$. F_A is the usual Fock operator (in rydberg units)

$$F_A = -\nabla_1^2 + \sum_B{}' \frac{2Z_B}{|\vec{r}_{B1}|} + 4 \sum_{B,i}{}' \int |\vec{r}_{12}|^{-1} |\phi_{Bi}\rangle \times \langle \phi_{Bi} | d\vec{r}_2 - 2 \sum_{B,i} |\phi_{Bi}\rangle \langle \phi_{Bi} | \, |r_{12}|^{-1} \tag{2}$$

and

$$U_A = -\sum_B{}' \frac{2Z_B}{\vec{r}_{B1}} + 4 \sum_{B,i}{}' \int |\vec{r}_{12}|^{-1} |\phi_{Bi}\rangle \langle \phi_{Bi} | d\vec{r}_2 \; . \tag{3}$$

In all the above summations we include only one member of a spin-up spin-down pair of orbitals.

Solving Eq. (1) self-consistently, we get the local orbitals ϕ_{Ai} and the energies ϵ_{Ai}. These quantities are needed when one uses the MB method.[11] In this method, one writes the one-electron wave functions $\Psi_{n,\vec{k}}^{\alpha,i}(\vec{r})$ as

$$\Psi_{n,\vec{k}}^{\alpha,i}(\vec{r}) = \sum_{j,l} b_{njl}^{\alpha,i} \sum_m C_{l,m}^{\alpha,i}(\vec{k})\, \phi_{jlm\vec{k}}(\vec{r}) + \sum_q d_{n,q}^{\alpha,i} \sum_I A_{q,i}^{\alpha,i}\, e^{i(\vec{k}+\vec{h}_I)q\cdot\vec{r}} \; , \tag{4}$$

where the quantities $C_{l,m}^{\alpha,i}$ and $A_{q,I}^{l,i}$ are chosen so that the Block function $\phi_{jln,\vec{k}}(\vec{r})$ and the plane wave $e^{i(\vec{k}+\vec{h}_I)q\cdot\vec{r}}$, respectively, transform accounting to the ith row of the α'th irreducible representation of the group of the wave vector $\vec{k}$; $\vec{h}_I$ denotes reciprocal lattice vectors, and $b_{njl}^{\alpha,i}$ and $d_{np}^{\alpha,i}$ are variational parameters. In the Hartree-Fock approximation, the functions $\psi_{n,k}^{\alpha,i}$ are solutions of the equations

$$(F - \epsilon_k^{\alpha,i})\; \psi_{n,\vec{k}}^{\alpha,i} = 0 \tag{5a}$$

or

$$(V_c + V_{ex} - \epsilon_k^{\alpha,i})\; \psi_{n,\vec{k}}^{\alpha,i} = 0 \quad . \tag{5b}$$

In (5b) the total Fock operator has been divided into a Coulomb and an exchange part. In order to solve (5a) one has to evaluate the matrix elements of the Fock operator and the overlap matrix. The techniques used for the computation of the matrix elements are extensively described elsewhere,[4,5] so we will not discuss them here.

We have mentioned that no correlation effects, except that coming from the assumption of a total antisymmetric wave function, are included in the Hartree-Fock approximation. The problem of treating these effects is extensively discussed in the literature.[12] It is possible to show[13] that one can write equations, similar to (5b), which include these effects, i.e.,

TABLE I. Atomic parameters for Na⁺. The notation is that of Ref. 7; energy parameters, defined as $\epsilon_{nn'} = \langle \phi_n | F_A + U_A | \phi_{n'} \rangle$ (rydbergs):

$\epsilon_{1s,1s} = -81.05$, $\epsilon_{1s,2s} = 1339 \times 10^{-7}$,
$\epsilon_{2s,2s} = -5.514$, $\epsilon_{2p,2p} = -2.979$.

Basis members A_{lj} and Z_{lj}

	$l=0$		$l=1$	
j	A_0	Z_{0j}	A_{lj}	Z_{lj}
1	0	15.949	0	12.048
2	0	9.439	0	5.703
3	2	11.624	0	3.336
4	1	4.384	0	2.146
5	1	2.811		

Expansion coeffieients C_{nlj}

	$l=0$		$l=1$
j	c_{10j}	c_{20j}	c_{21j}
1	0.213 942	0.014 878	0.012 036
2	0.976 286	0.334 195	0.362 580
3	−0.911 261	0.054 231	0.708 270
4	−0.027 065	−0.600 998	0.605 595
5	0.015 345	−0.723 846	

TABLE II. Atomic parameters for Cl⁻. Energy parameters, defined as $\epsilon_{nn'} = \langle \phi_n | F_A + U_A | \phi_{n'} \rangle$ (rydbergs):

$\epsilon_{1s,1s} = -209.9$ $\epsilon_{1s,2s} = 6\times10^{-7}$, $\epsilon_{2p,2p} = -16.06$,
$\epsilon_{2s,2s} = -21.15$ $\epsilon_{1s,3s} = -43\times10^{-7}$; $\epsilon_{3p,3p} = -0.9689$,
$\epsilon_{3s,3s} = -2.138$ $\epsilon_{2s,3s} = -4\times10^{-7}$, $\epsilon_{2p,3p} = -26\times10^{-7}$.

Basis members A_{lj} and Z_{lj}

	$l=0$		$l=1$	
j	A_{0j}	Z_{0j}	A_{1j}	Z_{1j}
1	0	18.9832	0	13.7900
2	0	14.7941	0	8.8355
3	1	14.7181	0	5.3987
4	1	9.6220	1	4.0186
5	1	6.7665	1	2.4367
6	2	6.2190	1	1.6382
7	2	3.2450	1	0.8219
8	2	2.1679	1	0.4120
9	2	1.3550		

Expansion coefficients C_{nlj}

	$l=0$			$l=1$	
j	c_{10j}	c_{20j}	c_{30j}	c_{21j}	c_{31j}
1	0.839156	0.273972	0.085814	0.035859	0.015226
2	0.017518	0.002839	−0.000188	0.341278	0.059636
3	0.322597	0.282125	0.098834	0.938990	0.326528
4	−0.313230	−0.249242	−0.126646	−0.002829	−0.125450
5	0.282344	−0.797500	−0.196723	0.020594	−0.591599
6	−0.112521	−0.383622	−0.284218	−0.010095	−0.617191
7	0.026217	−0.002114	0.519177	0.002630	−0.369542
8	−0.015657	−0.005896	0.729958	−0.000774	0.079862
9	0.004179	0.001632	0.212052		

TABLE III. Hartree-Fock valence and conduction energies calculated with two different number of sets of plane waves at Γ.

Irr. reps.	Energies (eV) Plane waves up to ⟨422⟩	 Plane waves up to ⟨440⟩
Γ_1	−30.1550	−30.1612
	1.4464	1.4460
	22.3671	22.3465
Γ_{15}	−10.1322	−10.6293
	15.3024	15.2572
	27.5856	27.1736
$\Gamma_{25'}$	9.4897	9.4697
Γ_{12}	11.9570	11.8407
$\Gamma_{2'}$	11.8501	11.8451

$$(V_c + M - \epsilon_{\vec{k}}^{\alpha,i})\;\psi_{n,k}^{\alpha,i} = 0 \quad , \tag{6}$$

where M is the so-called self-energy operator. All correlation is included in it. It is obviously impossible to treat M exactly; however, one can approximate it. In accord with the previous calculations,[5] we shall treat M in the random-phase approximation. In this case, M can be written as a sum of a screened exchange potential and a self-energy term.[5]

Another way of treating polarization effects has been proposed by Fowler,[8] whose method is an extension of the theories of Haken and Schottky,[14] and Toyozawa.[15] Essentially, Fowler shows that these theories reduce, for most insulators, to a static limit which he evaluates using the Mott and Littleton[16] approach. The effect of electronic correlation, when treated this way, is only a rigid shift of the conduction and valence bands, with a consequent reduction of the energy gap.

Before actually computing the energy bands of NaCl, it is worth saying that, in principle, Eqs. (5) and (6) could be solved for any point in the first Brillouin zone. However, the amount of work involved is, in general, large. The amount of work gets larger and larger as one goes from points of high symmetry to points of low symmetry because, in doing so, group theory gives less and less help. It is therefore economically inconvenient to consider many points and we have computed the energy bands only at Γ, X, L, and the midpoint Δ. However, in order to facilitate comparison between theory and experimental data, we have fitted the valence bands with tight-binding expressions[17] and the conduction bands with a pseudo-Hamiltonian of the following form[18]:

$$H_{ps} = \alpha p^2/2m + \textstyle\sum_k v(\vec{k})\, e^{i\vec{k}\cdot\vec{r}} \quad , \tag{7}$$

where α and $v(\vec{k})$ are adjustable parameters.

III. RESULTS AND COMPARISON WITH EXPERIMENT

All the calculations presented here have been performed using the IBM 360-75 of the University of Illinois. In Tables I and II, we show the local orbitals and energies as obtained from Eq. (1). The core states included in the MB calculation were the Na⁺ 1s, 2s, 2p, and Cl⁻ 1s, 2s, 2p. The lattice constant used has been 10.66 Bohr radii. Through all the paper we use the notation of Bouckaert, Smoluchowski, and Wigner.[19] In Table III, the band energies at Γ calculated with two different number of sets of plane waves are shown. The first calculation was done using 137 plane waves (up to ⟨422⟩) and the second using 181 plane waves (up to ⟨440⟩). These calculations were performed in order to test

TABLE IV. Hartree-Fock valence and conduction energies at X and L.

Point	Irr. reps.	Energies (eV) 1st	 2nd	 3rd
X	X_1	−28.7349	4.4140	16.0742
	$X_{4'}$	−15.5340	9.1234	
	$X_{5'}$	−12.1852	13.0355	
	X_3	4.7743		
	X_2	14.8095		
	X_5	18.5412		
L	L_1	−29.0941	3.8069	16.5631
	$L_{2'}$	−16.5138	8.5178	12.6152
	$L_{3'}$	−11.2505	15.2427	
	L_3	8.5254	15.5254	

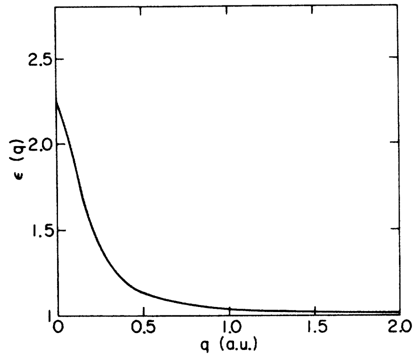

FIG. 1. NaCl dielectric function $\epsilon(q)$ using Fowler's parameters, Ref. 8 in text.

TABLE V. Calculation with correlation. Valence and conduction energies calculated with two different number of sets of plane waves at Γ.

Irr. reps.	Energies (eV) Plane waves up to ⟨422⟩	 Plane waves up to ⟨440⟩
Γ_1	−27.9320	−27.9379
	0.0254	0.0217
	20.7469	20.6681
Γ_{15}	−9.4858	−9.9410
	13.6508	13.5941
	25.7629	25.3438
$\Gamma_{25'}$	7.6470	7.6271
Γ_{12}	10.1279	10.0381
$\Gamma_{2'}$	9.9171	9.8945

the convergence of the results. As one can see, the convergences appear to be quite good for all irreducible representations. Table IV shows the energies calculated at X and L using plane waves up to $p^2 = 32$. The probable Hartree-Fock energy bands are shown in Fig. 1. We summarize the main results as follows: The computed band gap is 12.08 eV, the width for the 3s-like valence bands is 1.43 eV, the width of the 3p-like valence bands is 5.88 eV. The calculated electron affinity is −1.45 eV and the photoemission threshold is 10.63 eV.

The experimental band gap is 8.97 eV.[20] As we can see, the computed Hartree-Fock band gap is considerably larger than the experimental one, in perfect agreement with previous calculations.[4,5] Also, the valence bandwidths are very large. It is therefore evident the importance of the inclusion of correlation effects.

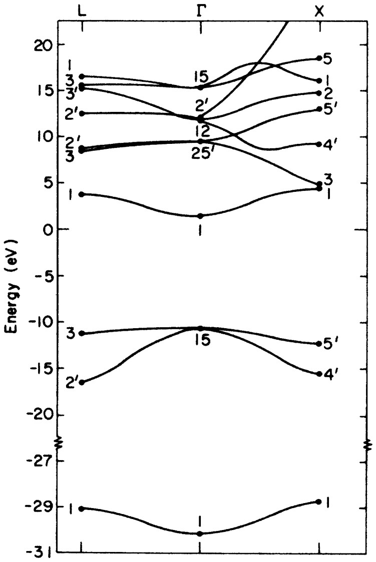

FIG. 2. Hartree-Fock energy bands for NaCl. Only the points Γ, X, L, and the midpoint of Δ were actually computed. The numbers on the figure refer to the irreducible representations corresponding to particular $\vec{k}$ values.

Using Fowler's theory of electronic polarization,[8] we should shift the valence bands up by a quantity of 1.53 eV and the conduction bands down by 2.43 eV. As a result, the energy gap would become 8.12 eV, which is in much better agreement with the experimental value. However, since the shift would be a rigid one, the valence bandwidth would still be the same as those calculated in the Hartree-Fock approximation, which are indeed quite large.

In order to investigate this aspect more closely, we shall treat correlation effects using the second approach as outlined in the previous section and extensively described previously.[5,21] In order to treat the screened exchange potential, a knowledge of the dielectric function is required. Different models have been proposed for the calculation of this function,[22] and the agreement between the various models is, for some aspects, often satisfactory. However, it has been seen[5] that the value of the self-energy depends, quite sensibly, on the particu-

TABLE VI. Calculation with correlation. Valence and conduction energies at X and L.

Point	Irr. reps.	Energies (eV) 1st	 2nd	 3rd
X	X_1	−26.9182	2.9182	14.3749
	$X_{4'}$	−13.7771	7.3909	
	$X_{5'}$	−11.2295	11.3266	
	X_3	3.0106		
	X_2	12.9747		
	X_5	16.6345		
L	L_1	−27.1732	2.2179	14.8575
	$L_{2'}$	−14.3233	6.8178	10.8017
	$L_{3'}$	−10.5030	13.3331	
	L_3	6.8393	13.7408	

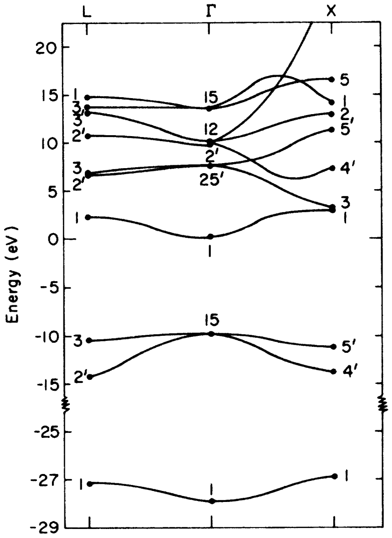

FIG. 3. Energy bands with correlation effects. Only the points Γ, X, L, and the midpoint of Δ were actually computed. The numbers on the figure refer to the irreducible representation corresponding to particular $\vec{k}$ values.

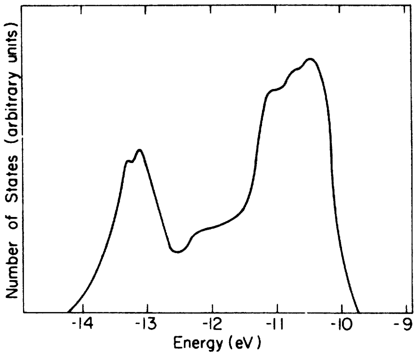

FIG. 5. Density of states for the $3p$ valence bands.

lar dielectric function used. Here we will use the dielectric function, $\epsilon(q)$, which can be obtained from Fowler's paper as described in Ref. 22. Figure 2 shows $\epsilon(q)$. We have repeated the calculations at Γ for two different number of sets of plane waves, as in the Hartree-Fock case, to test the convergence, and the results are shown in Table IV. The convergence is as good as the Hartree-Fock case. Tables V and VI show the energies calculated at X and L (see Fig. 3), using plane waves up to $p^2 = 32$. The value of the energy gap now obtained is 9.96 eV, which is in much better agreement with the experimental value 8.97 eV.[20] It is to be said that the agreement could be improved if a better dielectric function would be used. In effect, the dielectric constant used in the present calculation is not the best. However, no better expressions were available. The valence bandwidths are now 1.02 and 4.38 eV for the $3s$- and the $3p$-like bands, respectively. This is in complete agreement with what one would expect. In effect, when one makes the Slater approximation[23] to the exchange potential one obtains much narrower valence bandwidths. The explanation for this is the following: In the Hartree-Fock approximation, the exchange potential has a strong $\vec{p}$ dependence which is completely canceled by the Slater approximation. When one screens the exchange potential, as we have done in checking correlation, this $\vec{p}$ dependence is smoothened so that one expects the valence bandwidth obtained, including correlation, to be somewhat between the ones obtained in the Hartree-Fock and the Slater approximations, as indeed it is.

In order to facilitate comparison with experiment, we have fitted the valence bands with tight-binding expressions using Slater and Koster's theory.[17] For the $3s$ band, we obtained $V_s = -27.14$ eV, $V_{ss\sigma} = -0.06$ eV; for the $3p$-like band, we obtained $V_p = -11.56$ eV, $V_{pp\pi} = -0.08$ eV, and $V_{pp\sigma} = 0.55$ eV. The conduction bands were fitted using expression (7). The parameters used were $\alpha = 1.52$, $v(100) = -10.64$,

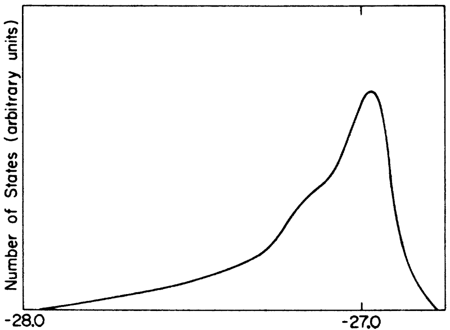

FIG. 4. Density of states for the $3s$ valence band.

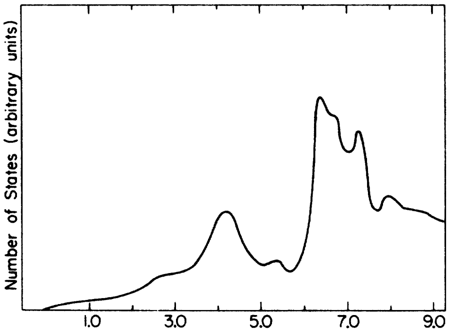

FIG. 6. Density of states for the conduction bands of NaCl.

$v(111) = 7.73$, $v(200) = 1.72$, $v(222) = 0.550$, $v(311) = 0.495$ eV. The density of states for the $3s$, $3p$, and conduction bands are in Figs. 4–6.

In comparing the present results to experiment we shall concentrate on two measurements. These are the near ultraviolet reflectivity measurements of Roessler and Walker[20] and the soft x-ray measurements at about 200 eV of Brown *et al.*[24] In this discussion, the soft x-ray results in the 30-eV region are ignored.[25] This is because the Cl^- $3s$ band lies only a little above the Na^+ $2p$ shell and we felt that an unambiguous interpretation of this region is not currently possible. In Fig. 7, the imaginary part of the dielectric constant is shown as computed using a constant transition matrix element for excitation of the $3p$ Cl^- band. Also shown is that value of the imaginary part of the dielectric constant measured by Roessler and Walker.[20] We have adjusted the theoretical band gap so that it agrees with experiment. As is seen, there is a reasonable correspondence between the experimental and theoretical value of ϵ_2 except for the first peak, an exciton which is ignored in the calculation.

In Fig. 8, the joint density of states for excitation of the Cl^- $2p$ shell is shown along with the absorption data for this level of Brown *et al.*[24] In computing the theoretical joint density a value of 1.6 eV is used for the spin-orbit splitting of the Cl^- $2p$ shell. Since in this calculation the position of the $2p$ shell is not well determined, the joint density of states is shifted so that the first peak in the theoretical spectrum corresponds to the first peak in the experimental spectrum. It is seen that the theory does indeed reproduce the observed spectrum quite well for the first 8 V beyond the edge. Beyond this point the measured spectrum is dominated by a $p \rightarrow d$ transition-matrix-element resonance.[26] It is not necessary in this calculation to postulate the existence of any separate exciton lines in order to explain the observed spectrum, not is it necessary to ask that any theoretical peaks be ignored in such a comparison. This is in great contrast to the work of Fong and Cohen[27] for NaCl. In their pseudopotential calculation of the conduction density of states, it was necessary, when comparing to the $L_{23}Na^+$ absorption, to postulate the existance of $n = 1$ and $n = 2$ excitons, and also to postulate that two peaks in the density of states would disappear due to transition-matrix-element effects in order to bring their results into agreement with experiment. We note that somewhat similar assumptions are necessary if the results of Fong and Cohen are applied to the 200-eV spectrum. Thus our results seem to provide a simpler and less hypothetical explanation of the soft x-ray experiments.

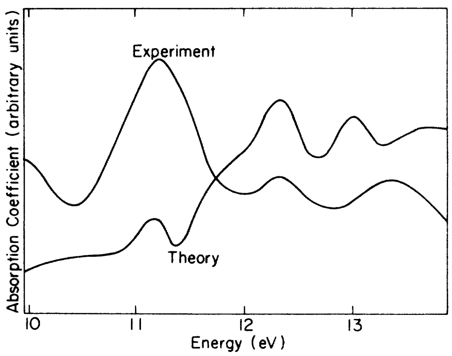

FIG. 7. Shown is the computed imaginary part of the dielectric response function ϵ_2. Comparison is made with the experimental ϵ_2 after Roessler and Walker (Ref. 20).

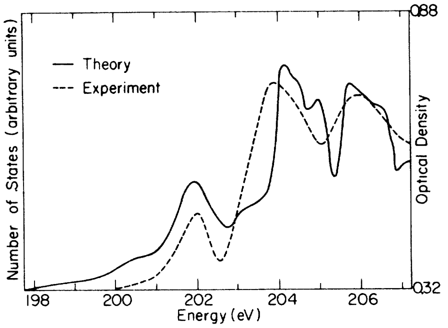

FIG. 8. The joint density of states for the Cl^- $L_{2,3}$ edge is shown and compared with the experimental results of Brown *et al.* (Ref. 24). The theoretical results have been shifted so that the first peaks coincide.

IV. CONCLUSIONS

A first-principle investigation of the energy bands and optical properties of NaCl has been done. We have shown how self-consistent Hartree-Fock calculations can be performed. Correlation effects have been treated and they have been shown to be very important.

It is suggested that more calculations of this type should be done, with particular attention to the treatment of correlation effects. From the experimental point of view, it would be useful to measure emission spectra from the valence bands and also to perform soft x-ray absorption in the range between 60 and 300 eV.

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Absorption, Reflectance, and Luminescence of GaN Single Crystals

R. Dingle, D. D. Sell, S. E. Stokowski, P. J. Dean, and R. B. Zetterstrom
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

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Analysis of the low-temperature absorption, reflectance, and emission spectra of oriented single crystals of hexagonal GaN demonstrates that the features found at 3.62 eV $(E\perp C)$ and 3.72 eV$(E\parallel C)$ are due to the formation of free excitons associated with a direct energy gap. A close analogy exists between these results and similar data from ZnO, consistent with the relative position of Zn and Ga, and O and N atoms in the Periodic Table. Luminescence spectra present good, although not conclusive, evidence for the hypothesis that this direct gap is also the fundamental energy gap in GaN.

Gallium nitride is a hexagonal III-V semiconductor of contemporary interest. Recent experimental attempts to determine the magnitude and nature of the fundamental energy gap have been made with epitaxial films (< 7000 Å)[1] and layers (≤ 150 μ).[2] The conclusions reached in these investigations are in conflict. Kosicki, Powell, and Burgiel[1] suggest $E_g \sim 3.8$ eV at room temperature, whereas Maruska and Tietjen[2] report $E_g = 3.39$ eV. Both groups believe their absorption measurements indicate a direct fundamental energy gap. The only recently published theoretical estimate of the band structure[3] places the direct gap $\Gamma \rightarrow \Gamma$ at 4.80 eV with an indirect gap $\Gamma - X$ at 6.39 eV.

In this paper we report absorption, reflection, and luminescence data taken on *single*-crystal samples between 300 and 2 °K. These data supplement, and in some cases correct earlier estimates, and we believe they allow the best available analysis of the band edge in GaN.