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Band structures and charge densities of KCl, NaF, and LiF obtained by the intersecting-spheres model

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The self-consistent electronic structures of KCl, NaF, and LiF have been calculated by the intersecting-spheres model and the results were compared with band structures calculated by other methods using the approximation of the exchange potential adopted by us. While for KCl close agreement was found between the augmented-plane-wave non-muffin-tin results by De Cicco and the intersecting-spheres-model (ISM) band structure, in the case of LiF differences of even 2.5 eV were found between conduction bands calculated by the ISM and the corresponding levels determined by linear-combination-of-atomic-orbitals (LCAO) methods. This disagreement seems to be imputable to a lack of convergence occurring in the LCAO calculations. The Fourier components of the charge densities (scattering factors) were determined using the Kohn-Sham-Gáspár form of the exchange potential. The agreement of the calculated scattering factors with experiment is not much worse than that obtained by Hartree-Fock calculations.

I. INTRODUCTION

In a previous paper[1] it has been shown that the intersecting-spheres model (ISM) is able to predict the electronic structure of covalent semiconductors such as Si and Ge with rather good accuracy. Since the model is conceptually very simple (and very easy to handle in actual calculations) it seems useful to provide evidence about the accuracy that the model attains when dealing with other forms of bonding. Concerning metals, e.g., it was found that the ISM closely replicates the APW (augmented-plane-wave)[2] and the LCAO (Ref. 3) results for aluminum.[4]

In the present work we intend to study the behavior of the ISM when applied to the alkali halides and compare its findings with results obtained by other methods, in particular, by LCAO methods,[5-7] which are the preferred approach to the electronic structure of these crystals.

II. GENERAL CONSIDERATIONS

In this work the band structures of KCl, NaF, and LiF were calculated paying due attention to convergence problems. As usual for the intersecting-spheres model, the trial Bloch sums were built with atomiclike orbitals obtained by solving the self-consistent atomic problem for each atom in the crystal and imposing that these functions vanish at a given radius. In order to reduce to a minimum the overlaps between functions centered on different atomic sites, the orbitals were then warped according to the criteria reported in Ref. 1.

All the computations were performed using the frozen core approximation, which easily fits into the model without modifications,[8] and gives band structures and charge densities which are in very close agreement with the all-electron results. (Typically, 0.1-eV accuracy for the valence and conduction levels and four-digit accuracy for the scattering factors are obtained.) After careful study it was found that for all the crystals under investigation, well-converged energy levels for the valence bands and for the conduction bands up to about 2 Ry above the top of the valence band could be obtained if atomiclike orbitals with any value of l, lying within 3.5 Ry from the p valence levels of the halogen atoms, were included in the trial function. At this level of variational flexibility the results are rather insensitive to the partition in cells. In any case the optimum partition (the one which gave the lowest valence and conduction levels at the first cycle of the iteration process) was obtained when the atomic cells had equal volumes and the interstitial regions had a thickness of 0.8–0.9 a.u. We have also verified that if the free-ion solutions are used instead of the free-atom ones to build the basis set, the final band structure is not significantly affected (maximum level shift of about 0.2 eV).

The self-consistent charge density was determined for all the crystals investigated by substituting the integration over the irreducible segment of the Brillouin zone with a weighted sum over the usual cubic mesh constituted by the six points Γ, X, L, W, $\Delta(\frac{1}{2},0,0)$, and $\Sigma(\frac{1}{2},\frac{1}{2},0)$. If the mesh size is halved, thus requiring nineteen points in the irreducible segment, the resulting band structure is not significantly modified.

Concerning the expansion of the self-consistent potential in spherical harmonics, if an accuracy of 0.05 eV for the energy levels is required, it is possible to truncate the series after $l=4$ for all the crystals investigated. A different situation occurs for the scattering factors, defined as

$$F(\vec{q})=\sum_i \int_{\Omega_i} e^{i\vec{q}\cdot\vec{r}}\rho_i(\vec{r}-\vec{R}_i)\,d\vec{r}\,. \qquad (1)$$

In Eq. (1) $\vec{q}$ is a reciprocal-lattice vector, Ω_i is the volume of the ith atomic cell which is centered at $\vec{R}_i$ in the Wigner-Seitz cell, and ρ_i is the charge density associated with it. When the expansion of the charge density in spherical harmonics is inserted in Eq. (1) one finds that

$$F(-\vec{q})=4\pi\sum_{ilm} e^{-i\vec{q}\cdot\vec{R}_i} i^{-l} Y_{lm}(\theta_{\vec{q}},\varphi_{\vec{q}}) \times\int_0^{R_{\max}} j_l(qr)\rho_{ilm}(r)r^2dr\,. \qquad (2)$$

In Eq. (2) the Y_{lm} are spherical harmonics and the j_l are spherical Bessel functions. It is found that in order to obtain three-digit accuracy for the scattering factors the summation of Eq. (2) needs to be extended up to include the terms for $l=8$. This relatively slow convergence is due to the behavior of ρ_i at the boundaries of the cells, where it is abruptly truncated. It is obvious that the expansion in spherical harmonics of the truncated ρ_i cannot converge quickly. The convergence can be significantly improved if a constant term is subtracted from the charge density in order to lower its value as much as possible near to the boundaries. We note further that the slow convergence only affects the even scattering factors, for which the phase factors are such that the errors arising from the individual atomic contributions are added, and not the odd scattering factors, for which a near perfect cancellation of the errors occurs.

III. KCl BAND STRUCTURE

In the case of KCl a basis set which satisfies the above-mentioned general criterion is constituted by three s, three p, two d, one f, and one g atomic-like orbitals both for K and for Cl. We have excluded from our consideration the core states, i.e., two s and one p orbitals for each atom. All these functions were generated by first solving the self-consistent all-electron atomic problem for K and Cl with the outer boundary condition at $R=6.0$ a.u. We assumed the lattice constant of KCl to be[9] $a=11.801$ a.u. The ISM band structure obtained with the Slater approximation of the exchange potential is reported in Fig. 1. In Table I the energy levels at Γ, X, and L are reported and compared with the corresponding levels obtained with the APW non-muffin-tin calculation of Ref. 9, a self-consistent calculation performed with the Slater exchange approximation. As can be seen from Table I and from Fig. 1, when compared with Fig. 1 of Ref. 9, the energy levels obtained by the two calculations closely agree not only for the valence levels but also for the conduction levels over a rather large energy interval; the only few exceptions occur for the highest conduction levels.

We believe that this is a remarkable result for the intersecting-spheres model, since the APW method does not suffer from the convergence problems typical for an energy-independent basis set, like the one adopted by us. We note that the introduction of virtual f and g orbitals was essential to reach such an agreement.

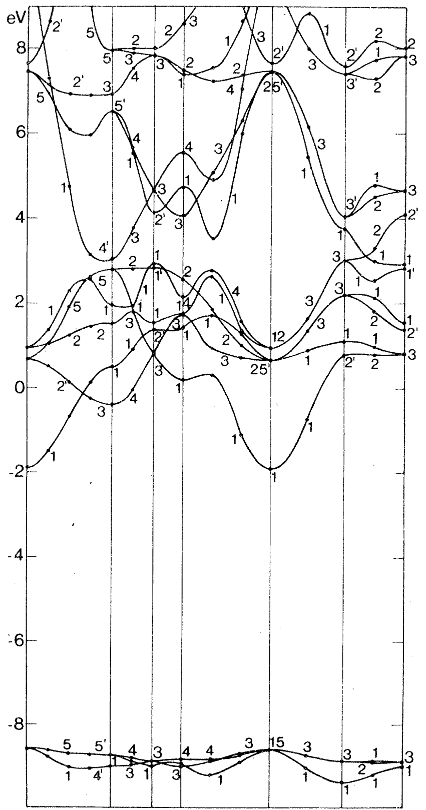

FIG. 1. The conduction bands and the highest valence band for KCl determined by the ISM along symmetry lines of the Brillouin zone using the Slater exchange approximation.

TABLE I. Valence and conduction-band levels for KCl at the symmetry points Γ, X, and L according to the ISM. The APW non-muffin-tin results of Ref. 9 are reported for comparison. The valence bandwidths (VBW) are also indicated. The energies, relative to the Γ_{15} valence level, are in eV units.

	ISM	APW[a]		ISM	APW
Γ_1	6.69	6.30	X_5'	15.10	14.87
Γ_{25}'	9.28	9.02	X_3	15.51	15.28
Γ_{12}	9.54	9.43	X_5	16.53	
Γ_{25}'	16.04	15.82	L_1	−0.78	
Γ_2'	16.23	14.60	L_3	−0.28	
Γ_{15}	18.27	19.22	L_2'	9.38	8.75
X_4'	−0.41		L_1	9.70	9.16
X_5'	−0.15		L_3	10.80	10.52
X_3	8.18	7.52	L_3	11.60	11.47
X_1	9.10	9.16	L_1	12.35	12.29
X_2	10.11	10.11	L_3'	12.62	12.42
X_1	10.54	10.65	L_3'	16.01	
X_5	11.38	11.20	L_3'	16.17	
X_4'	11.64	10.79	VBW	0.78	0.82

[a] Reference 9.

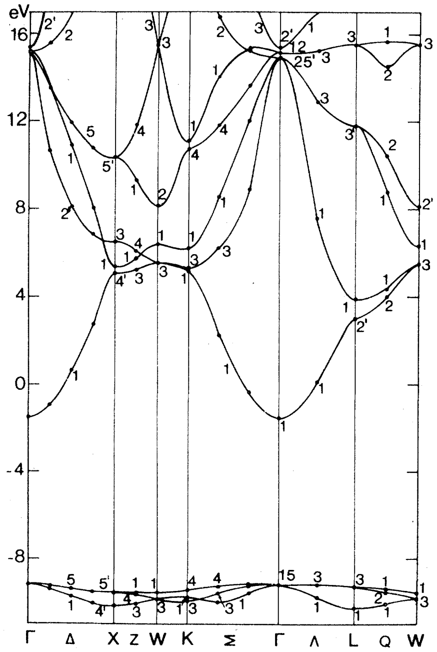

FIG. 2. The conduction bands and the highest valence band for NaF determined by the ISM along symmetry lines of the Brillouin zone using the Slater exchange approximation.

IV. NaF BAND STRUCTURE

For NaF the lattice constant was assumed to be $a = 8.731$ a.u. (Ref. 10) and the atomiclike orbitals were generated with the outer boundary condition at $R = 5.2$ a.u. for both Na and F. According to the previously mentioned criterion we used three s, three p, one d, one f atomiclike orbitals for Na; three s, two p, one d, one f orbitals for F to build the trial Bloch sums. We have not considered the core states, i.e., one s function for each atom. With such a basis set and using the Slater exchange approximation, the self-consistent band structure reported in Fig. 2 was obtained. The energy levels at the symmetry points Γ, X, and L are reported in Table II together with some of the corresponding levels determined by a self-consistent LCAO calculation performed with an exchange scaling parameter $\alpha = 1.06$. These data were taken from Fig. 6 of Ref. 6. Despite the rather small difference in the exchange scaling parameters we note that very large differences exist between the two calculations concerning the position of the lowest conduction band relative to the valence band. We note that a similar discrepancy was found in the case of LiF by Zunger and Freeman between their results[5] and the results of Drost and Fry.[11] In Ref. 5 such a discrepancy was mainly attributed to inappropriate treatment of the exchange potential by the authors of Ref. 11.

Since the band structure of NaF reported in Ref. 6 was calculated using the treatment of the ex-

TABLE II. Valence and conduction-band levels for NaF at the symmetry points Γ, X, and L according to the ISM. The results of Ref. 6 are reported for comparison. The energies, relative to the Γ_{15} valence level, are in eV units.

	ISM	LCAO[a]		ISM	LCAO
Γ_1	7.65	11.43	X_3	15.69	
Γ_{25}'	24.13		X_5'	19.54	
Γ_{12}	24.36		L_1	−1.07	
Γ_2'	24.49		L_3	−0.08	
X_4'	−0.96		L_2'	12.25	
X_5'	−0.39		L_1	13.13	16.83
X_4'	14.27	17.95	L_3'	21.03	
X_1	14.55		L_3	24.70	
			VBW	1.07	0.7

[a] Figure 6 of Ref. 6.

change potential adopted in Ref. 11, the considerations of Zunger and Freeman should apply also in this case. We note also that for NaF the contribution of the d and f levels to the low-lying conduction bands is surely not negligible.

V. LiF BAND STRUCTURE

For LiF the lattice constant was assumed to be $a = 7.594$ a.u. (Ref. 5) and the atomiclike orbitals were constrained within spheres of radius $R = 4.5$ a.u. both for Li and for F. According to the general criterion, the basis set was generated using three s, two p, one d, one f functions for Li and two s, two p, one d, one f valence functions for F. The shallow Li 1s core state was included in the trial function. The self-consistent band structure calculated using the Slater approximation of the exchange potential is reported in Fig. 3. In Table III the valence and conduction levels at Γ, X, and L are reported together with results obtained by the LCAO method using either a Gaussian expansion of the trial function[12] or a numerical basis set.[5] It can be noted that rather good agreement exists between the results obtained by the ISM and by the LCAO methods concerning the p valence bands. This agreement occurs also for the low-lying F 2s band, as can be seen by inspection of Fig. 3 and comparison with Fig. 2 of Ref. 5. (Incidentally, we remember that the labeling of the representations at L and W depends on which atomic site in the unit cell is taken as origin. In this paper we have adopted the convention of Ref. 9. If we want to express the results with the other convention it is sufficient to perform at W and L the interchanges $2' \rightleftarrows 1$ and $2 \rightleftarrows 1'$. At L also the interchange $3 \rightleftarrows 3'$ must be done.)

For the conduction bands, the situation is somewhat different. Although the behavior of the bands calculated by the ISM is qualitatively very similar to that reported in Fig. 3 of Ref. 5 (when improper labels and connections appearing in that figure are corrected), there are quantitative differences up to 2.5 eV for the highest conduction bands. These differences are always in the same direction, the ISM results lying lower than the results of Ref. 5, which are, instead, in good agreement with the Gaussian LCAO calculation.[12] It seems, therefore, that the energy levels obtained by the ISM may be incorrect by the previously cited

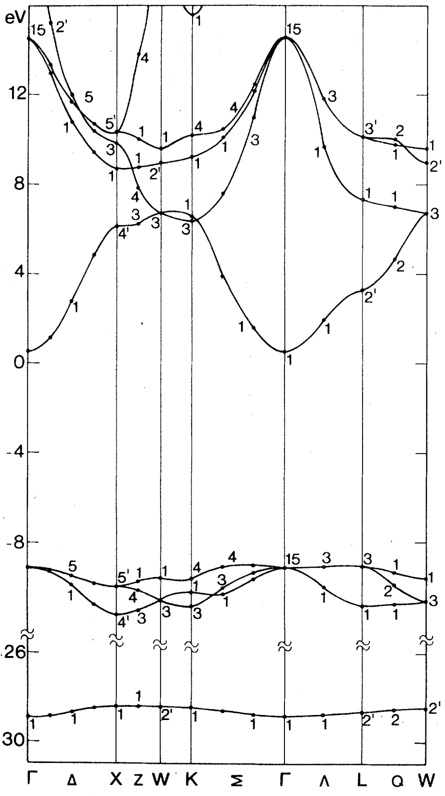

FIG. 3. The conduction bands and the valence bands for LiF determined by the ISM along symmetry lines of the Brillouin zone using the Slater exchange approximation. The low-lying F 2s band is also shown.

TABLE III. Valence and conduction-band levels for LiF at the symmetry points Γ, X, and L according to the ISM. The LCAO results of Refs. 12 and 5 are reported for comparison. The energies, relative to the Γ_{15} valence level, are in eV units.

	ISM	Gaussian[a] LCAO	Numerical[b] LCAO
Γ_1	9.66	10.58	10.50
Γ_{15}	23.68	25.28	25.93
X_4'	−2.10	−2.45	−2.31
X_5'	−0.86	−0.82	−0.79
X_4'	15.26	15.97	16.11
X_1	17.83	19.07	19.32
X_3	18.98		
X_5'	19.46	22.66	22.09
L_1	−1.72	−2.09	−2.04
L_3	0.04	−0.19	−0.19
L_2'	12.43	12.68	12.79
L_1	16.44	17.90	18.12
L_3'	19.25	22.09	21.79
VBW	2.25	2.45	2.31

[a] Reference 12.
[b] Reference 5.

amount. We note, however, that both the calculations of Refs. 5 and 12 did not include in the basis set, functions of *f* symmetry which, according to our results, were important for the convergence of the high-lying conduction levels. We note by inspection of the eigenvectors of the Γ_{15}, X_5', L_3', and L_1 high-lying levels that the discrepancy between ISM and LCAO results is roughly proportional to the amount of *f* orbitals contained in the Bloch states. It is also interesting to remember that such discrepancies were not present in the case of KCl between our results and those obtained by the APW non-muffin-tin calculation.

VI. SCATTERING FACTORS

The Fourier coefficients of the charge density for KCl, NaF, and LiF were calculated as previously discussed and the results are shown in Table IV. The Kohn-Sham-Gâspâr approximation for the exchange potential was adopted instead of the Slater exchange which was previously used for the band structures in order to allow the comparison with other calculations. For KCl no experimental scattering factors are still available, to our knowledge. For NaF the comparison is possible with the experimental data of Merisalo and Inkinen[13] reported also in Ref. 14. In Table IV the theoretical scattering factors calculated by the ISM are presented together with the model Hartree-Fock results[14] and with the experimental data, reduced to 0°K using the Debye Waller coefficients reported in Ref. 14. The use of the theoretical form factors to perform the reduction could lead to some ambiguity. In the case of NaF we have, however, verified that the use of the model Hartree-Fock form factors[14] instead of the form factors calculated by the ISM leads only to fourth-digit variations in the reduced scattering factors, a negligible change with respect to the experimental uncertainty. We see that the agreement of the ISM results with the experimental data is not particularly good (it is much worse when the Slater exchange is used) and somewhat inferior to that achieved by the model Hartree-Fock results. We believe that this disagreement is to be attributed essentially to the exchange approximation that we are using and not to the intersecting-spheres model itself. In fact in the case of Al, for which the Kohn-Sham-Gâspâr approximation should work better than in the case of the alkali halides, we have obtained agreement with experimental data within the experimental uncertainty.[4]

In Table IV we present also the ISM scattering factors of LiF together with the reduced experimental data.[13,5] We note that in the case of LiF the reduction is more sensitive to the choice of the form factors than in the case of NaF. In Table IV the theoretical results of Refs. 5, 15,

TABLE IV. Scattering factors of KCl, NaF, and LiF calculated by the ISM using the Kohn-Sham-Gâspâr approximation for the exchange potential. For KCl only the theoretical ISM results are presented. For NaF the reduced experimental data and the model Hartree-Fock (HF) results are also shown. For LiF the reduced experimental data together with the theoretical results of Refs. 5, 15, and 16 are also reported.

	KCl		NaF				LiF		
	$\alpha=\frac{2}{3}$		$\alpha=\frac{2}{3}$	atomic[a]		$\alpha=\frac{2}{3}$	$\alpha=\frac{2}{3}$[b]	atomic[c]	crystal[d]
hkl	ISM	Expt.	ISM	HF	Expt.	ISM	LCAO	HF	HF
200	28.39	14.81	14.71	14.82	7.72	7.72	7.79	7.72	7.70
220	24.12	11.77	11.74	11.86	5.70	5.74	5.69	5.78	5.72
222	21.44	9.89	9.80	9.90	4.60	4.61	4.66	4.67	4.60
400	19.67	8.48	8.46	8.50	3.99	3.95	4.03	3.94	3.90
420	18.32	7.50	7.41	7.47	3.45	3.40	3.48	3.44	3.40
422	17.44	6.76	6.69	6.68	3.07	3.09	3.11	3.08	3.04
440	16.05	5.55	5.60	5.57	2.57	2.61	2.57	2.60	2.57
600	15.48		5.22	5.18		2.42	2.40	2.43	2.41
442	15.50		5.18	5.18	2.40	2.41	2.40	2.43	2.41
111	1.42	1.33	1.36	1.34	4.84	4.87	4.88	4.96	4.98
311	1.61	1.77	1.73	1.81	2.36	2.47	2.39	2.38	2.36
331	1.16	1.59	1.48	1.54	1.65	1.71	1.71	1.65	1.63
333	0.83	1.21	1.19	1.24	1.37	1.43	1.43	1.37	1.36
511	0.83	1.21	1.16	1.24	1.37	1.46	1.42	1.37	1.37

[a] Reference 14.

[b] Reference 5.

[c] Reference 15.

[d] Reference 16.

and 16 are also shown. We note again that the agreement of the ISM results with experiment is worse than in the case of the model[15] or crystal[16] Hartree-Fock results; the same thing occurred for NaF. We note also that the differences between the ISM scattering factors and those presented in Ref. 5 are rather large despite the close similarity of the valence-band structure obtained by the two different methods with the Slater exchange approximation. Since we have verified that the correlation corrections of Ref. 5 modify the scattering factors with respect to the Kohn-Sham-Gáspár result in a negligible way, the discrepancy seems to be another indication of the difficulty to obtain really accurate charge densities with a variational calculation.

VII. COMPARISON WITH PHOTOEMISSION AND OPTICAL SPECTRA

Since the calculated band structures refer to a ground-state situation there is no sound theoretical reason[17] to expect that the calculated bandwidths and band gaps agree with the experimental photoemission and optical data. In fact we find that while the calculated valence bandwidth of KCl is $W = 0.78$ eV, the experimental full width at half maximum[18,19] ranges between 1.3 and 2.0 eV. For NaF the calculated bandwidth is $W = 1.07$ eV, while the experimental full width at half maximum[20,21] is between 2.0 and 2.8 eV. For LiF the situation is slightly better, since the calculated bandwidth is $W = 2.25$ eV while the experimental full width at half maximum lies[20,21] roughly between 2.7 and 3.7 eV. A somewhat better agreement with experiment seems to be possible when the Hartree-Fock approximation is used and correlation corrections[22,23] are included.

A similar situation occurs for the calculated fundamental gaps, which result in being considerably smaller than the observed ones[24] both with the Slater and with the Kohn-Sham-Gáspár approximation of the exchange potential. (The experimental values are 8.7 eV for KCl, 11.5 eV for NaF, and 13.6 eV for LiF, respectively.) Also for the gaps the Hartree-Fock plus correlation approach[23] seems able to provide rather accurate results.

VIII. CONCLUSIONS

The calculations reported in this paper show that it is possible to compute by the ISM rather accurate band structures for the alkali halides. This accuracy can be obtained not only for the valence levels but also for the high-lying conduction levels, provided that virtual orbitals of appropriate l behavior are taken into account. These orbitals can be included in the ISM with only a minor increase of computational effort, thanks to the cellular partition of space.

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