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Electronic band structure of the alkali halides. II. Critical survey of theoretical calculations

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A review of the results of published energy-band calculations for the alkali halides is presented in which the experimental results of the preceding paper are used as a basis for critical comparison of theory and observation. Band calculations employing Slater exchange are shown to be inadequate, while calculations which take into account correlation effects in a consistent fashion are found to give very good agreement with experiment.

I. INTRODUCTION

In the preceding paper (Paper I) we presented a broad picture of the electronic band structure of the alkali halides as determined experimentally by various techniques. In this paper we review the results of theoretical calculations of the band structure of the alkali halides and compare them with the experimental parameters discussed in Paper I. Some 60 to 70 energy-band calculations have been examined and these all differ in regard to: method, type of potential, scheme, convergence, self-consistency, exchange, correlation, screening, and the degree to which empirical parameters are used. Using the experimental results of Paper I as a basis for comparison, we attempt to highlight the features of band calculations that determine correctly the gross features of the observed energy-band structures. We emphasize that it is the broad picture rather than the finer details at which we are aiming. While the finer details usually dominate the interband excitation processes, they can be determined with confidence only after the over-all features are understood.

In Sec. II we review published band calculations of the alkali halides and discuss briefly the effects of the various physical and computational variables mentioned above. In Sec. III we discuss those calculations which seem most successful.

II. SUMMARY OF BAND-CALCULATION RESULTS

In Tables I–III we list values of band gap E_g, electron affinity χ, and total width of the halide valence band $E_{tw}(H^-)$ for the alkali fluorides, chlorides, and bromides and iodides, respectively, derived from published energy-band calculations of the alkali halides. As is customary, $\chi > 0$ if the bottom of the conduction band is below the vacuum level and $\chi < 0$ if it is above. The values of E_g shown in parentheses are values that have been adjusted in the theoretical work to agree with experimental values, and hence agreement here cannot be claimed as a success of those calculations. In general two methods are used to match the band gap to the experimental value. The first is to adjust the scaling factor α in the Slater exchange approximation. Other effects on band structure as a result of this will be discussed below. The other method is to adjust the magnitude of the potential outside the muffin-tin spheres until agreement is reached. This also has additional effects on the band structure which will be discussed below. In some cases the values listed in Tables I, II, and III are not given explicitly by the authors. In such cases we have measured them as accurately as possible from given energy-band diagrams.

A brief inspection of Tables I, II, and III shows that rarely are values of all three parameters E_g, χ, and $E_{tw}(H^-)$ close to the experimental values listed in Paper I. It is seen that variation in the values for the valence-band width are particularly severe, with the majority of calculations predicting relatively narrow valence bands. However, to generalize directly from the data of the above tables is rather misleading because some values have been corrected for correlation effects whereas others have not.

It was mentioned in Paper I that Fowler has argued that Coulomb-hole self-energies or polarization energies must be included in band calculations before comparison is made with experimental results. In the adiabatic one-electron approximation each electron moves in the effective local potential that is established by the ions and all the other electrons in the crystal. Hence all electron-electron correlation, except that coming from the requirement of antisymmetric total wave functions, is neglected. Since correlation effects are thought to be important,[1,2] provision must be made for their inclusion in a complete energy-band calculation. In the following discussion we consider correlation effects to consist of the exchange potential and the Coulomb-hole or polarization self-energy. In fact Hedin and Lundquist[2] have pointed out that the screening of the Coulomb interaction has a large influence and that a screened exchange term rather than a bare Coulomb interaction exchange should be used.

Painter[3] has performed an excellent comparative study of the effects of scaling the Slater-exchange approximation in band calculations of LiF using the DVM method (see the caption to Table I for this and other abbreviations). Painter finds that the bands are very sensitive to the scale factor α and that varying α from 1.0 to 0.66 results in a narrowing of the band gap by approximately 35% and a broadening of the valence band from about 1.5 to 3.0 eV. It is significant that the valence-band width is so sensitive to α. However, since the theoretical valence-band width is still only approximately half the experimental value for $\alpha = \frac{2}{3}$, it is most unlikely that agreement will be reached by variation of α alone. The results of Painter tend to suggest that the application of the statistical Slater-exchange approximation may be inappropriate for the alkali halides since its progressive removal via a decreasing scaling factor greatly improves the agreement with experiment.

Other aspects of difficulties associated with the use of Slater exchange have been reported by Brener and Fry[4] and by Drost and Fry.[5] From an LCAO study of NaF Brener and Fry conclude that it is not possible to find an exchange parameter in the range $\frac{2}{3} \leq \alpha \leq 1$ in a non-self-consistent band calculation to match the experimental band gap. Perhaps more importantly, they report that in the case of LiF the fundamental band gap E_g is fitted for $\alpha = 0.87$ but the Li 1s edge is in disagreement with experiment by 5 eV, and this failure may reflect the inadequacy of the local-exchange-potential approximation. Drost and Fry from an LCAO study of LiF report that a superposition of ionic potentials, with α adjustable, yields agreement with optical data, but that a self-consistent potential with the full Slater exchange is required to produce agreement with optical and photoelectron data. Reference to Table I shows that the values for electron affinities obtained in the above studies are about −3.5 and 3.4 eV for LiF and NaF, respectively. The value for LiF has been corrected from a value of about −6.4 eV by the application of a static polarization correction. The NaF value is uncorrected; however, correction would further increase this value. These values are rather different from those expected from the discussion of electron-affinity values given in

TABLE I. Values of band gap E_g, electron affinity χ, and total width of the halide valence band $E_{\mathrm{tw}}(H^-)$ for the alkali fluorides (all in eV), as obtained from published theoretical calculations. The abbreviations listed in the second column refer to the following theoretical procedures: APW, augmented plane wave; OPW, orthogonalized plane wave; MB, mixed basis; EPM, empirical pseudopotential method; LCLBF, linear combination of localized basis functions; LCAO, linear combination of atomic orbitals; CNDO, complete neglect of differential overlap; DVM, discrete variational method; RGF, relativistic Green's function; KKR, Korringa-Kohn-Rostoker.

Material	Method	Ref.	E_g	χ	$E_{\mathrm{tw}}(H^-)$
LiF	MB	29	12.8	positive	2.3
	APW	12	14.5	−6.1	2.03
	LCLBF	10	18.8	−3.5	3.5
	CNDO	15	12.15	8.1	4.0
	APW	30	(13.58)	−7.2	0.88
	LCAO	31	(13.6)	5.4	1.8
	Tight binding	32	10.9	1.4	2.4
	LCAO	5	(13.7)	−3.5	1.3
	APW	33	11.27	3.0	2.3
	Cellular	16	•••	•••	3.9
	LCAO	17	•••	•••	5.4
	DVM	3	14.3	2.2	1.5
NaF	APW	12	12.7	−3.5	0.88
	LCAO	4	(11.4)	3.4	0.7
	Tight binding	18	•••	•••	3.44
	OPW/tight binding	13	9.6	3.66	1.3
KF	APW	12	11.1	−2.3	0.27
	OPW/tight-binding	9	8.9	3.1	0.8
RbF	OPW/tight-binding	13	8.5	2.9	0.6
CsF	MB/tight-binding	13	5.8	5.5	0.2

TABLE II. Values for the alkali chlorides, arranged as in Table I (all values in eV).

Material	Method	Ref.	E_g	χ	E_{tw} (H^-)
LiCl	MB	19	10.81	−3.47	7.84
	Tight-binding	34	···	···	1.3
	OPW	35	8.7	2.5	2.32
	MB	20	11.47	−3.47	7.84
	Tight-binding	21	···	···	4.16
	APW	12	8.5	−4.6	2.64
NaCl	OPW	36	7.4	3.3	···
	Tight-binding	37	···	···	1.7
	Tight-binding	21	···	···	2.31
	APW	30	(8.78)	−2.7	0.57
	APW	38	5.9	···	1.5
	Tight-binding	39	···	···	≥1.0
	APW	12	8.4	−2.4	1.63
	OPW	35	7.4	3.4	1.35
	EPM	40	(8.97)	···	1.5
	EPM	41	(8.97)	···	1.5
	MB	22	9.96	0.0	4.38
	APW	42	(8.6)	2.0	1.2
	Cellular	23	···	···	4.4
KCl	OPW	35	6.5	3.4	0.87
	APW	12	8.6	−1.1	0.53
	EPM	40	(8.69)	···	1.5
	Tight-binding	21	···	···	1.56
	LCAO	43	···	···	1.52
	OPW	44	9.6	0.9	1.52
	APW	45	6.3	−3.7	0.82
	KKR	6	(8.7)	−0.6	0.7
	MB	24	8.7	0.3	2.58
RbCl	Tight-binding	21	···	···	1.22
	OPW	14	6.12	3.4	1.0

Paper I in two aspects. First we expect the values to be much closer to zero, and second we would not expect a change of about 7 eV in the electron affinity in going from one compound to the next in the series. The valence-band widths reported are 1.3 and 0.7 eV for LiF and NaF, respectively, and these are very narrow compared to the corresponding experimental values of 6.1 and 4.9 eV. Hence, the work of Brener, Drost, and Fry[4,5] tends to reaffirm the suspected inadequacies of Slater exchange even when well converged expansions and self-consistent potentials are employed. The narrow bands are consistent with Painter's findings where the scaling factor is large.

Overhof,[6] using the KKR method, has calculated the energy bands of KI using ionic potentials with a Slater exchange and also with a Kohn-Sham exchange ($\alpha = \frac{2}{3}$). In both calculations the potential V_0 is adjusted to match the experimentally determined band gap. In addition to changes in the structure of the conduction band, the Kohn-Sham exchange produces a χ of about 1.2 eV whereas full Slater exchange produces a value of about −1.4 eV. Overhof favors the full Slater calculation; however, the electron affinity should be positive (see Table II, Paper I). In principle this could be corrected by the inclusion of Coulomb-hole self-energy corrections, but this raises a serious difficulty with the sequence of computation. In particular, the self-energy is a correlation effect occurring during excitation of the unperturbed band structure, and it results in narrowing of the band gap. Thus, in fitting the calculation to the experimental band gap, this effect has largely been taken into account. What is required in this type of semiempirical band calculation is to take correlation effects into account in the initial calculations and then to adjust parameters such as V_0 to match the experimental values.

Over all, band calculations of the alkali iodides including Slater exchange produce slightly larger values for the valence-band widths than for the other alkali halides. This is probably a result of the large (~1.0 eV) spin-orbit splitting of the iodide ionic *p* levels. Even so, the calculated values are still only approximately half the experimental values. A result of the failure to take the Coulomb-hole self-energy into account before adjustment of V_0 has been noted by DiStefano[7] in the RGF calculation of CsI by Onodera.[8] DiStefano observes that, in order to obtain a calculated band gap of 6.37 eV, an unusually high inter-muffin-tin potential of 6.94 eV is required, and this may cause an abnormal narrowing of the valence bands.

Kunz and Lipari,[9] using the MB method on LiBr, report that large differences occur between calculations performed using the Slater exchange and those using the Fock exchange. These differences are mainly associated with the widths of the va-

TABLE III. Values for the alkali bromides and iodides, arranged as in Table I (all values in eV).

Material	Method	Ref.	E_g	χ	E_{tw} (H^-)
LiBr	OPW	14	7.6	3.4	2.3
	MB	9	8.4	0.0	7.57
NaBr	OPW	14	6.39	3.4	1.7
	MB	25	7.5	0.96	3.75
KBr	OPW	14	6.02	3.4	1.2
	KKR	6	(7.3)	−1.0	1.0
	APW	30	(7.80)	−2.3	0.31
RbBr	OPW	14	5.88	3.4	1.0
KI	RGF	46	(6.2)	2.0	1.7
	RGF	47	(6.2)	2.0	1.7
	MB/OPW	48	5.5	3.6	1.8
	KKR	6	(6.34)	−1.4	1.6
RbI	OPW	48	5.6	3.1	0.86
CsI	RGF	49	6.45	4.2	1.5
	RGF	7	(6.4)	···	1.5
	RGF	8	(6.4)	1.34	1.8

lence bands and it is the use of the Slater exchange that results in narrow bands. Similarly Mickish and Kunz[10] have studied LiF using the LCLBF method and report that the main differences in the results of band calculations are due to differences between statistical exchange approximations and the Hartree-Fock exchange, and to a lesser extent on the use or otherwise of a muffin-tin type of potential. They also argue that the particular method used in the band calculation is of secondary importance. Lipari[11] points out that the results of energy-band calculations for the alkali halides depend on the particular approximation made to the exchange potential to such an extent that they reflect the particular approximation involved rather than the Hartree-Fock equations which they were originally meant to solve.

With the above comments in mind we are now in a position to assess critically the results of the various calculations listed in Tables I–III. Since the values of χ are largely dependent on whether or not polarization-energy corrections have been made, and whether E_g in a large number of calculations has been adjusted to agree with experiment, in the first instance we will concentrate on the valence-band width, which is largely independent of these considerations, returning to E_g and χ later.

Several systematic studies of valence-band widths have been made through part of an alkali-halide series. Perrot[12] has reported values of 2.03, 0.88, and 0.27 eV for LiF, NaF, and KF, respectively, and 2.64, 1.63, and 0.53 eV for LiCl, NaCl, and KCl, respectively. Kunz *et al.*[13] have reported values of 1.3, 0.8, 0.6 and 0.2 eV for NaF, KF, RbF, and CsF, respectively. Approximate valence-band widths for the alkali bromides as reported by Kunz[14] are 2.3, 1.7, 1.2, and 1.0 eV for LiBr, NaBr, KBr, and RbBr, respectively. All of these studies show a progressive narrowing of the valence band through the series from the lithium halide due to electron wave-function overlap. Since it was shown in Paper I that the experimentally determined valence-band broadening of the F^- $2p$ band was well correlated with the lattice constant, to a first approximation it should be relatively insensitive to details of the potential used to approximate the crystal potential.

The valence-band widths shown in Tables I–III may be divided into two groups. The first group consists of those calculations in which a statistical exchange approximation of the Slater type has been used. This group is characterized by very narrow bands relative to the second group in which exchange approximations other than the Slater type have been employed. The second group consists of Refs. 10 and 15–18 for the alkali fluorides, Refs. 19–24 for the alkali chlorides and Refs. 4 and 25 for the alkali bromides, with no alkali iodides qualifying for this group.

The calculations of the second group can be further categorized on a chronological basis. In the early pioneering work of Ewing and Seitz,[16] Grimley,[17] Shockley,[23] and Kucher and Tolpygo[21] much of the emphasis was on developing the methods (since these did not exist at that time) as well as producing results. At this time there was also a lack of computational power which only became available later with the widespread deployment of large high-speed electronic computers. This restriction is reflected in the fact that only the valence bands are reported in these works, and consequently they inadequately describe the band structure as defined in the present work. Although these calculations are considered to be successful within the framework of their time they will not be considered further.

The second group contains three calculations which warrant further consideration. The calculation of Gout *et al.*[18] would appear incomplete on two counts. First, as mentioned above, only the valence band is calculated, and second, the reported bandwidth of 3.44 eV is substantially below the experimental value of 4.9 eV. The CNDO calculation of Hayns[15] on LiF is means to be a feasibility study rather than a detailed band calculation. The results reported in regard to valence-band width and E_g compare favorably to the experimental values; however, the electron affinity is very large (~8 eV) and it appears that the F^- $2s$ band is abnormally broad (~35 eV). The LCLBF-method calculation of LiF by Mickish and Kunz[10] also produces results for E_g, χ, and $E_{tw}(F^-\ 2p)$ that do not compare favorably with experiment. This calculation contains, however, some interesting features that will be explored briefly after the more successful calculations have been discussed.

III. SUCCESSFUL BAND CALCULATIONS

The number of calculations remaining in the second group has been reduced to six. Since Refs. 19 and 20 are essentially similar calculations this number further reduces to five separate calculations (Refs. 9, 19, 22, 24, 25). Since all these calculations have been performed by the same authors, Kunz and Lipari, using essentially the same theoretical methods, we take a brief look at the methods employed before proceeding to compare the results of their calculations with experiment.

Initially Lipari and Fowler[26,27] made a comparative study of the correlation effects in the energy bands of insulating crystals using the OPW method on solid argon as an example. They found that the Hartree-Fock calculation gives an energy gap which is too large, but that the inclusion of correlation yields a band gap in good agreement with experiment and that the valence band is broad. They also found that the Slater-exchange approximation yields a much smaller value for the band gap, suggesting that it behaves as though it includes correlation effects (but too grossly).

The main feature of the procedures of Lipari, Kunz, and Fowler is the treatment of the nonlocal Hartree-Fock exchange potential in a consistent fashion. Correlation effects are treated using the random-phase approximation for the self-energy operator M, which requires a knowledge of the wave-vector-dependent dielectric function. In this approximation the matrix elements of the self-energy operator M are written as the sum of two terms. The first term is the exchange potential with the valence part screened and the second term is the Coulomb-hole self-energy. Lipari[11] shows that the differences between the Hartree-Fock exchange and the screened exchange are quite large. He emphasizes that the valence-band widths are large in the Hartree-Fock-approximation calculation and that when correlation effects, as described above, are taken into account the valence-band widths narrow considerably. However, even with correlation effects taken into account they are still much larger than those obtained using a local approximation to the exchange potential.

We now return to the comparison of the results of the five remaining calculations with the experimental values. In Table IV we have compared the calculated and experimental energy-band parameters $E_{tw}(H^-)$, E_g, and χ. In evaluating the results listed in Table IV it is necessary to distinguish between three groups. The first group consists of[25] NaBr and[24] KCl and the results of the calculations compare excellently with the experimental results. The second group consists of NaCl.[22] The agreement is excellent in regard to valence-band width and electron affinity but is unsatisfactory in regard to the energy-band gap E_g. We note, however, that Kunz and Lipari[25] have recalculated the band structure of NaCl using the Fry model for the dielectric function and obtain a band gap of 8.61 eV. The result of this reduction in band gap would also be to increase χ slightly, that is, to lower the bottom of the conduction band below E_{vac} and hence further improve the agreement in regard to electron affinity. As a result there is good over-all agreement in regard to NaCl.

The third group consists of[9] LiBr and[19] LiCl. Very large differences between the calculated and experimental values are apparent. However, these differences are easily explained, and indeed are expected, when the details of the calculations are considered. The valence-band widths in both calculations are considerably greater than the experimental ones. The reason for this is that both calculations have been performed with the Hartree-Fock approximation but without the inclusion of the self-energy operator M, and hence correlation effects have not been included in a consistent fashion. It has been noted above that Lipari has shown that the effect of the inclusion of correlation effects via the self-energy operator is to substantially narrow the valence-band widths. We can obtain an approximate estimate of this effect by reducing the valence-band width in proportion to that reported for other alkali halides. Kunz and Lipari[25] report a reduction in the valence-band width of NaBr by a factor of 0.67 as a result of the inclusion of correlation effects as described above. If we apply this factor to the valence-band widths of LiBr and LiCl we obtain 5.1 and 5.2 eV, respectively, which compare much more favorably with the experimental values of 4.8 and 4.5 eV, respectively. The band gaps and electron affinities are seen to compare reasonably well in the case of LiBr and badly in the case of LiCl. The reason for this is that static Coulomb-hole self-energy corrections along the lines suggested by Fowler[28] have been included in the LiBr results but not in the LiCl results. It is apparent that Coulomb-hole self-energy corrections must be applied to LiCl before comparison with experimental results is made. It is suggested that these corrections should be made in the same manner as those for NaBr,[25] KCl,[24] and NaCl,[25] that is, in a consistent fashion as part of the self-energy operator using the Fry model for the dielectric function.

We can summarize the results of Table IV by saying that excellent agreement between calculation and experiment occurs for NaBr, KCl, and NaCl and that we expect that similar agreement

TABLE IV. Comparison between calculated and experimental values of the parameters $E_{tw}(H^-)$, E_g, and χ in those cases where excellent agreement has been obtained. All values are in eV.

	Calculated			Experimental			
Material	$E_{tw}(H^-)$	E_g	χ	$E_{tw}(H^-)$	E_g	χ	Ref.
NaBr	3.76	7.5	0.96	3.8	7.5	0.4	25
KCl	2.58	8.7	0.3	2.7	8.4	0.5	24
NaCl	4.38	9.96	0.0	4.1	8.5	0.5	22
		8.61					25
LiBr	7.57	8.4	0.0	4.8	7.6	0.2	9
LiCl	7.84	10.81	−3.47	4.5	9.4	⋯	19

will result from a full calculation of LiBr and LiCl as suggested above.

Finally, the valence-band widths of the alkali fluorides are experimentally determined to be the largest of the alkali halides, and there appears to be no energy-band calculation that produces such results. The nearest is probably the LCLBF calculation of Mickish and Kunz[10] on LiF. However, as noted earlier, the valence-band width of 3.5 eV compares unfavorably to the experimental value of 6.1 eV (Table IV, Paper I). It may be that a calculation on LiF using the successful method developed by Kunz, Lipari, and Fowler will be fruitful.

IV. CONCLUSIONS

A review of the results of published energy-band calculations of the alkali halides has been given using the experimental results of Paper I as a basis for comparison. The criterion used for comparison was that an energy-band calculation should produce reasonable agreement for the energy-band gap E_g, the electron affinity χ, and the total valence-band width $E_{tw}(H^-)$. Band calculations employing a local approximation (Slater exchange) to the exchange potential produce very poor results in comparison with experiment, particularly in regard to the valence-band widths. The method developed by Kunz, Lipari, and Fowler using the Hartree-Fock approximation and taking into account correlation effects in a consistent fashion via the so-called self-energy operator, which includes a screened exchange-potential term and a Coulomb-hole self-energy term, produces excellent agreement for NaBr, KCl, and NaCl and might be expected to produce similar agreement with experiment when complete calculations are made for LiBr and LiCl. Further calculations for the alkali fluorides are suggested along the lines developed by Kunz, Lipari, and Fowler.

For reasons given above it may also be useful to note that when semiempirical calculations are made on strongly ionic crystals, the Coulomb-hole self-energy corrections should be made prior to adjusting the band gap to fit the experimental values.

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