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Ionization threshold of crystalline LiF

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The ionization threshold for crystalline LiF is calculated using a cluster embedded model. The experimental ionization threshold is 9.8 eV; however, previous band and cluster model calculations gave 14–15 eV. These earlier calculations used a crystal having a perfect lattice. In the present work, a crystal with lattice defects is introduced. The calculated surface and bulk ionization thresholds are 8.1 and 8.7 eV, respectively, showing good correspondence with experiment. The electron affinity and other band parameters are also studied. [S0163-1829(99)03730-3]

I. INTRODUCTION

Many experimental[1–10] and theoretical investigations[11–28] have been performed on crystalline LiF; these are summarized in Table I. Experimental band gaps between the valence and conduction bands are 13.6 eV (Refs. 4 and 5) and 14.2 eV.[6] There are two types of theoretical calculation: a band calculation and a cluster model calculation in which a large cluster is embedded in an ionic cage. The band calculation, with correction for electron correlation, gives the band gap as 13.9 eV (Ref. 24) and 14.0 eV,[25] while the cluster model gives 13.9 eV.[28] Agreement between these theoretical calculations and experiment is almost perfect. Pong and Inouye (quoted in Ref. 24) observed exciton photoemission at ~12.6 eV relative to the ground state level (the top of the valence band), while Gallon[9] observed the exciton at ~13.5 eV using electron-energy-loss spectroscopy (EELS). The bulk exciton states calculated by the band theory and the cluster model with the electron correlation correction are located at 11.7 eV (Ref. 24), and 13.4 eV (Ref. 28) above the ground state, so that the result of the cluster model accords well with the EELS result. The surface exciton has also been observed by EELS;[9] the excitation energy is 3 eV less than that of the bulk exciton, and is accurately predicted by the cluster model. All the observations mentioned so far are well explained by theoretical calculations, and especially by the embedded cluster model. Exceptions are the ionization threshold (I_t) and the total bandwidth of the fluorine ion band.

We first discuss the ionization threshold I_t. Poole and co-workers[4,5] undertook ultraviolet-photoelectron-spectroscopy (UPS) observation. They obtained I_t as

$$I_t = E_b^{\mathrm{exp}}(\mathrm{F}^-) - 0.5E_{\mathrm{tw}}(\mathrm{F}^-), \tag{1}$$

where $E_b^{\mathrm{exp}}(\mathrm{F}^-)$ is the arithmetic midpoint of the valence fluorine ion band, and $E_{\mathrm{tw}}(\mathrm{F}^-)$ is the total width of this band; the values found for these are 12.85 and 6.1 eV, so that $I_t = 9.8\,\mathrm{eV}$.[4,5] Poole and co-workers stated that ''Taylor and Hartman[1] tentatively placed the valence band of LiF 13 eV below the vacuum level on the basis of the edge in the photoelectric yield curve. However, their yield curve continues to fall rapidly at lower energies, and this may be interpreted as a threshold of approximately 10 eV, which compares favorably with present estimates of 9.8 eV for this quantity.'' The calculated I_t values corrected for electron correlation are up to 14.3–14.6 eV irrespective of the calculational method, and are far from experimental values.[4] Furthermore, if we

TABLE I. Summary of previous results for band structure of LiF (all in eV).

Method	Ionization threshold	Band Gap	Band width F 2*p*	Exciton Bulk	Exciton Surface
Band theory					
LDF[a]	11.7	10.5	2.8		
LDF with correlation (periodic cluster Δ SCF)[a]	14.3	13.9	2.8	11.7	
LDF with correlation[b]		14.0	2.0		
Embedded cluster (surface and bulk)[c]					
ΔSCF	12.5–13.1	11.8	2.7	11.3	9.4
Δ SCF with correlation correction	14.6–15.2	13.9	2.7	13.4	11.5
Expt.	9.8[d]–13[e]	13.6[d]	6.1	13.5[g]	10.3[g]
		14.2[f]		12.6[h]	

[a] See Ref. 24.

[b] See Ref. 25.

[c] See Ref. 28.

[d] See Refs. 4 and 5.

[e] See Refs. 1 and 2.

[f] See Ref. 6.

[g] See Ref. 9.

[h] W. Poing and C. S. Inouye, as quoted in Ref. 24.

use the UPS spectra given by Poole and co-workers (Fig. 2),[4] we obtain a smaller I_t of $\sim$7.5 eV. This is only one half of the calculated result.

We now discuss the total bandwidth of the fluorine ion band, $E_{\mathrm{tw}}(\mathrm{F}^-)$. Poole and co-workers [4] experimentally found this to be 6.1 eV, while the band theory 2.0 eV (Ref. 25)–2.8 eV,[24] and the cluster model 2.7 eV,[28] respectively. The value of $E_{\mathrm{tw}}(\mathrm{F}^-)$ given by Poole and co-workers is directly related to I_t through Eq. (1). Therefore, if we can discern why the experimental I_t is small, we can also understand why $E_{\mathrm{tw}}(\mathrm{F}^-)$ is so large.

For the perfect lattice, the ionization threshold (I_t) should fall between 14 and 15 eV and the total bandwidth of the fluorine ion should be less than 6.1 eV, since the calculated energetics agree well with experiment except for these two quantities. The onset of the ionization threshold is very low ($\sim$7.5 eV).[4] If a lattice defect is assumed to be at the position of the Li cation, we expect that the neighboring F^- is considerably destabilized, reducing I_t. This paper investigates the effect of lattice defect(s) on I_t and on the total bandwidth of the fluorine ion $E_{\mathrm{tw}}(\mathrm{F}^-)$. In Sec. II the method of calculation is set out. The band structure of LiF, including I_t, is given in Sec. III, and the results are discussed and conclusions set out in Sec. IV.

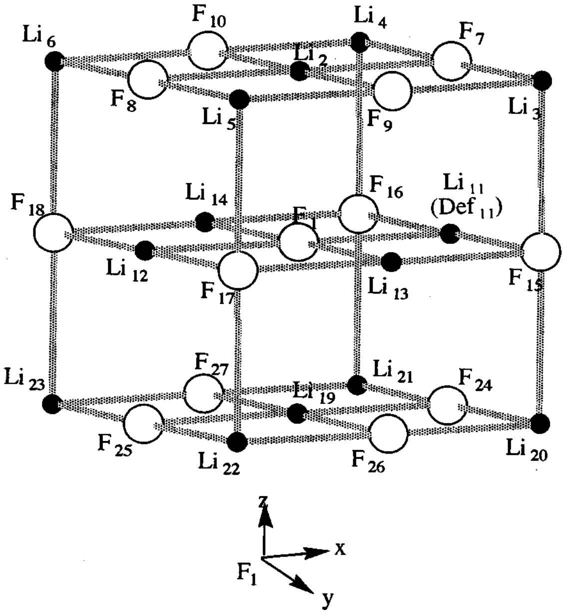

FIG. 1. Geometrical structure of $\mathrm{Li^+}_{14}\,\mathrm{F^-}_{13}$. (a) With the perfect lattice, this cluster is embedded in the ionic cage. (b) With an imperfect lattice, the cluster with a defect at Li_{11} (denoted Def_{11}) is embedded in the ionic cage.

II. METHOD OF CALCULATION

A. Cluster model embedded in ionic cage

As before,[28] we use a cluster model embedded in the ionic cage composed of point charges in which Li^+ and F^- ions are modeled by $+1$ and -1 point charges. To calculate the Madelung potential, Evjen's method[29] was used. It was confirmed that an ionic cage constituting of 3375 point charges gives an accurate Madelung potential of 0.460 37 a.u. In our previous work[28] we replaced the 27 central ions with the cluster $\mathrm{Li^+}_{14}\,\mathrm{F^-}_{13}$ (see Fig. 1) in order to treat the electronic band structure of the bulk material. A similar approximation is made in studying the surface band. The electronic structure of the cluster of these 27 ions is solved by the open-shell self-consistent field (SCF) method proposed by Roothaan and Bagus,[30] in which multicenter Coulomb and exchange integrals, and also the interaction integrals between cluster electrons and cage ions, are calculated exactly within the accuracy of the basis sets.

B. Basis sets

Tatewaki and Huzinaga[31–33] have developed minimal-type basis sets (MINL-i) with contracted Gaussian-type functions (CGTF's) where the exponents and the expansion coefficients of the CGTF's are determined so as to give the optimum total energy. Although the size of the sets is small, they describe the valence orbitals well. A large number of these basis sets are calculated and collected in Ref. 33. Since the sets are minimal type, the valence orbitals should be split in molecular applications. In this paper, part of the set for F^- is split; the set is the double-zeta-type of MIDI-4 (421/31) (Refs. 31 and 32) in which the *s* and *p* SCF orbitals are expanded as three and two contracted Gaussian-type functions, and the respective CGTF's are described by 4, 2, 1, 3, and 1 primitive GTF's. Here, two diffuse *s*-type primitives were added for consistency with our previous work,[28] in which such functions were added to describe transitions corresponding to $\mathrm{F}\,2p \rightarrow \mathrm{F}\,3s$. The total set for F^- is (42111/31). For Li^+, we assembled (421) from (43) and added one *p*-type polarization function, and completed the basis set for Li^+ as (421/1). These are given in the top half of Table II. Total energies of gaseous (free) ions and of ions with other surrounding ions are given in the lower half of Table II. The surrounding point charges destabilize Li^+ by 0.46 a.u. per electron and stabilize F^- by -0.46 a.u. per electron; these values are almost equal to the Madelung potentials for the respective atoms. In the next section it will be shown that the sets for Li^+ and F^- are well suited. We observe that the atomic charge distributions (F^-) with and without the surrounding ions are almost the same as indicated from the coefficients given in Table II. Although we have not shown the results, the same is true for Li^+.

C. Energetics

We employ ΔSCF calculations, where ionization potentials (IP's), electron affinities (EA's), and excitation energies (EX's) for the excitons are calculated as differences of the total energies of the respective states:

$$\begin{aligned}\mathrm{IP}(\Delta\mathrm{SCF}) = {}&\mathrm{TE}_{\mathrm{SCF}}(\text{cluster}^+\text{: ground state})\\ &-\mathrm{TE}_{\mathrm{SCF}}(\text{cluster: ground state}),\end{aligned} \tag{2}$$

$$\begin{aligned}\mathrm{EA}(\Delta\mathrm{SCF}) = {}&\mathrm{TE}_{\mathrm{SCF}}(\text{cluster: ground state})\\ &-\mathrm{TE}_{\mathrm{SCF}}(\text{cluster}^-\text{: ground state}),\end{aligned} \tag{3}$$

and

TABLE II. Basis set for calculating Li^+mF^-n with surrounding ions. (Number of suroundung ions is 3374. Madelung potentials per electron for Li^+ and F^- are 0.460 37 and −0.460 37 a.u., respectively.)

Exponents and expansion coefficients

	Li^+ exp.	coef	F^- exp.	coef
1*s*-CGTF	104.726 13	0.026 110	1040.662 5	0.019 234
	15.662 25	0.137 521	156.684 33	0.133 321
	3.399 55	0.457 142	35.119 88	0.460 998
	0.850 39	0.534 692	9.293 25	0.526 665
2*s*-CGTF1	0.757 53	−0.091 659	13.989 20	−0.079 747
	0.065 90	0.647 001	1.162 29	0.583 900
2*s*-CGTF2	0.025 29	1.0	0.323 18	1.0
3*s*-CGTF1			0.068 31	1.0
3*s*-CGTF2			0.025 55	1.0
2*p*-CGTF1	0.076	1.0	19.106 17	0.052 356
			4.146 32	0.258 527
			1.072 09	0.508 261
2*p*-CGTF2			0.239 85	1.0

Total energies and orbital energies (a.u.)

	Free Li^+ [a]	with surrounding ions	Free F^- [b]	with surrounding ion
Total energy	−7.223 86	−6.303 17	−99.294 35	−103.895 52
$2\varepsilon_{1s}$	−2.787 73	−2.327 50	−25.774 97	−26.232 66
ε_{2s}			−1.051 91	−1.511 11
ε_{2p}			−0.157 14	−0.616 13

Coefficients of SCF orbitals for F^-

	Free F^-			F^- with surrounding ions		
	1*s*	2*s*	2*p*	1*s*	2*s*	2*p*
C1*s*-CGTF	0.993 42	−0.242 99		0.993 41	−0.243 00	
C2*s*-CGTF1	0.316 38	0.574 50		0.031 64	0.574 02	
C2*s*-CGTF2	−0.011 38	0.506 38		−0.011 37	0.507 54	
C3*s*-CGTF1	0.005 28	0.018 42		0.005 26	0.018 26	
C3*s*-CGTF2	−0.002 31	0.000 33		−0.002 30	−0.001 56	
C2*p*-CGTF1			0.710 02			0.710 31
C2*p*-CGTE2			0.462 65			0.462 30

[a] Total energy for the free (gaseous) Li atom calculated with this set is −7.419 94 a.u., giving IP of 5.335 eV.

[b] Total energy for the free (gaseous) F atom calculated with this set is −99.245 94 a.u., giving EA of 1.317 eV.

$$\mathrm{EX}(\Delta\mathrm{SCF})=\mathrm{TE}_{\mathrm{SCF}}(\text{cluster:}\quad\text{excited state})$$
$$-\mathrm{TE}_{\mathrm{SCF}}(\text{cluster:}\quad\text{ground state}),\qquad(4)$$

where TE_{SCF} is the SCF total energy. Next we discuss the dimension of the Fock matrices. As an example we used a symmetry C_1 for the imperfect lattice model calculations. The dimension of the Fock matrices in C_1 for ${Li^+}_m{F^-}_n$ is the total number of CGTF's and is given by $(1\times3+3)\times m+(1\times5+3\times2)\times n$: the dimension of the Fock matrices is 221 for all the states in ${Li_{13}}^+{F_{13}}^-$. The convergence thresholds for the SCF calculations are 5×10^{-6} a.u. and 5×10^{-4} for the total energy and density matrix, respectively; these thresholds are used throughout. The calculation time for a single SCF cycle was about 20 min on an IBM RS6000 3 AT, and up to 200 cycles were required for some states.

III. ELECTRONIC BAND STRUCTURE OF LiF

A. Perfect lattice model

The symmetry D_{4h} was used to treat bulk solid and C_{4v} for the surface states. The cluster ${Li^+}_{14}{F^-}_{13}$ (see Fig. 1) was embedded in the ionic cage[28] in order to treat the bulk states. The total number of CGTF's is 227, and the formal dimension of the Fock matrices is also 227, but these are separated into small matrices of the elements of a_{1g}, a_{2g}, b_{1g}, b_{2g}, $e_g(x)$, $e_g(y)$, a_{1u}, a_{2u}, b_{1u}, b_{2u}, $e_u(x)$, and $e_u(y)$ in D_{4h} and a_1, a_2, b_1, b_2, $e(x)$, and $e(y)$ in C_{4v}. The dimensions of these matrices are 34, 6, 16, 15, 21, 21, 3, 23, 9, 11, 34, and 34 in D_{4h} and 57, 9, 27, 24, 55, and 55 in C_{4v}. As seen in Table I, the cluster model embedded in the ionic cage[28] provides almost perfect agreement with experiment except for the total bandwidth of the fluorine ion $E_{\mathrm{tw}}(\mathrm{F}^-)$ and the ionization threshold I_t. In those calculations a perfect, defect-free lattice was assumed. Here, we pick out and summarize the exciton band. The wave functions of these states are expressed as

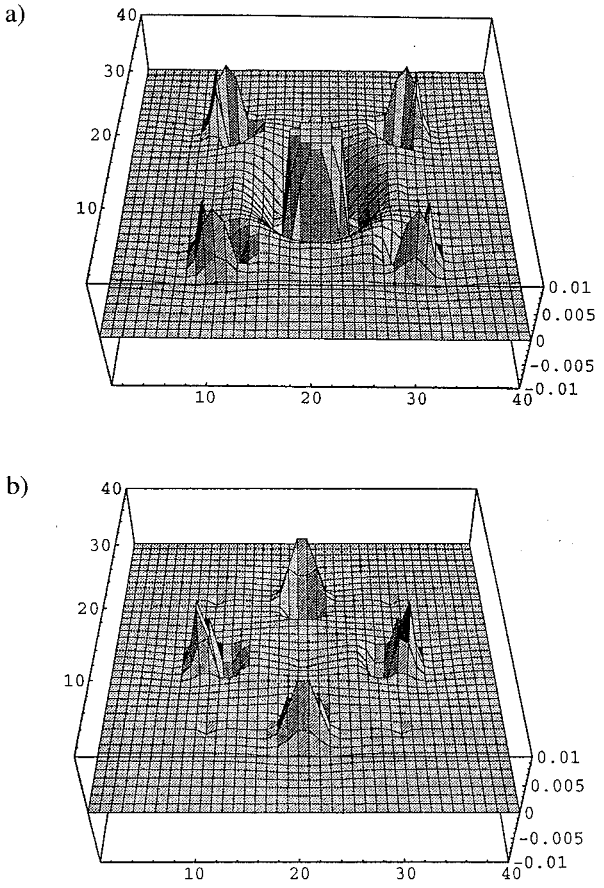

FIG. 2. Shape of the hole in the bulk solid: difference in charge density between ${}^2A_{2u}$ and ${}^1A_{1g}$. (a) On the second layer. (b) On the first (third) layer.

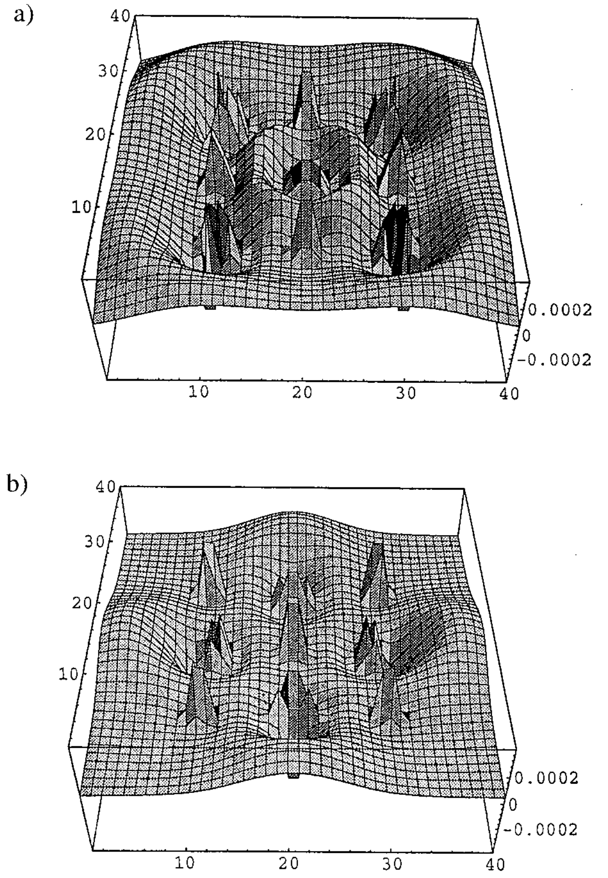

FIG. 3. Shape of the particle in the bulk solid: difference in charge density between ${}^3A_{2u}$ and ${}^2A_{2u}$. (a) On the second layer. (b) On the first (third) layer.

$$\begin{aligned}\phi = {} & C_A|\phi_{\rm Li}(A'B'C'\cdots)\phi_{\rm F}(A^{-1}BC\cdots)\phi_{{\rm exc,F}\,3s(A)+{\rm Li}\,2s}| \\ & + C_B|\phi_{\rm Li}(A'B'C'\cdots)\phi_{\rm F}(AB^{-1}C\cdots)\phi_{{\rm exc,F}\,3s(B)+{\rm Li}\,2s}| \\ & + C_C|\phi_{\rm Li}(A'B'C'\cdots)\phi_{\rm F}(ABC^{-1}\cdots)\phi_{{\rm exc,F}\,3s(C)+{\rm Li}\,2s}| \\ & + \cdots ,\end{aligned} \tag{5}$$

where $\phi_{\rm Li}$ and $\phi_{\rm F}$ symbolically represent all the Li and F electrons in the solid. The first line implies that the p electron at the fluorine ion F_{A^-} is excited into the exciton band orbital $\phi_{{\rm exc,F}\,3s(A)+{\rm Li}\,2s}$, which is constructed mainly from the F 3s of F_{A^-} and six adjacent Li 2s orbitals. Other components of Eq. (5) have similar meanings. Only the first term in Eq. (5) is considered here, assuming H_{ij} $(i\neq j)$ is small. The excitation energy calculated by ΔSCF [see Eq. (3)] is 11.3 eV, while the correlation correction, described at the end of this subsection, yields 13.4 eV, which is close to the EELS value of 13.5 eV. In Figs. 2 and 3 we show the hole that is given as the difference in the total densities between the ionic state with configuration $\phi_{\rm Li}\phi_{\rm F}(A^{-1}BC\cdots)$ and the ground state with $\phi_{\rm Li}\phi_{\rm F}(ABC\cdots)$, and the particle that is the difference between $\phi_{\rm Li}\phi_{\rm F}(A^{-1}BC\cdots)$ $\phi_{{\rm exc,F}\,3s(A)+{\rm Li}\,2s}$ and the ionic state with $\phi_{\rm Li}\phi_{P}(A^{-1}BC\cdots)$. We see that the hole [Fig. 2(a)] is covered by the particle [Fig. 3(a)]. Band theory with correlation corrections gives 11.7 eV (Ref. 24) for this excitation, which is a little less than the EELS value of 13.5 eV. The band theory[24] also employed the locally excited state, using the small-periodic-cluster (SPC) model in which a large crystallographic unit cell with a locally excited state at its center is set up, and the associated Bloch Hamiltonian problem with periodicity imposed via this large super cell is solved. The cluster calculation involves the unrealistic assumption that the hole is perfectly screened by the surrounding electrons of the nearest 26 ions, while the band calculations require that the locally excited state repeats periodically. The difference between the two results is unlikely to be due to working differences in the environment, since the band gaps calculated by the two methods are almost the same; the band calculations give 13.9 (Ref. 24) and 14.0 eV (Ref. 25) while the cluster calculation gives 13.9 eV. The experimental result is 14.2 eV. The difference between the methods for the exciton states may arise from differences in the calculations for the exchange integral, for which the band calculations assume local potentials while the cluster method calculates them exactly. The local potential approximation may be inadequate for interband transition where the excited electron is localized.

Calculations for the negative ion are performed to treat the electron affinity. The subgroup D_{4h} of O_h is used as stated before and the lattice is taken as perfect, with no defects. The total numbers of electrons are 158 for the ground state and 159 for the two affinity states. The ground state ${}^1A_{1g}$ has electron configuration

TABLE III. Electron affinity of bulk LiF calculated with the perfect lattice model.

Cluster embedded	$\mathrm{Li^+}_{14}\mathrm{F^-}_{13}$		
Number of cage ions	3348		
Number of CGTF's	227		
Symmetry	D_{4h}		
Number (n) of electrons and total energy (te) (a.u.)			
	Ground state	First affinity state	Second affinity state
n	158	159	159
te	−1384.362 06	−1384.329 16	−1384.315 77
Electron configuration	$\cdots(12a_{1g}^2)\cdots(8a_{2u}^2)\cdots(12e_u^4)$	(ground state)+$(13a_g^1)$	(ground state)+$(9a_{2u}^1)$
Electron affinity without correlation correction (eV)		−0.90	−1.26
Electron affinity with correlation correction (eV)		−0.8	−1.2

Madelung potential and gross atomic orbital population (GAOP)

Atom	Madelung (a.u.)	GAOP Ground state	GAOP of the added electron First affinity state	GAOP of the added electron Second affinity state
First layers (and third layer)				
Li 2(19)	−0.4604	1.92	−0.32	0.38
Li 3(20)	−0.4604	1.95	0.34	0.41
Li 4(21)	−0.4604	1.95	0.34	0.41
Li 5(22)	−0.4604	1.95	0.34	0.41
Li 6(23)	−0.4604	1.95	0.34	0.41
F 7(24)	0.4604	10.11	0.09	−0.38
F 8(25)	0.4604	10.11	0.09	−0.38
F 9(26)	0.4604	10.11	0.09	−0.38
F 10(27)	0.4604	10.11	0.09	−0.38
Second layer				
Li 11	−0.4604	1.92	−0.33	−0.00
Li 12	−0.4604	1.92	−0.33	−0.00
Li 13	−0.4604	1.92	−0.33	−0.00
Li 14	−0.4604	1.92	−0.33	−0.00
F 1	0.4604	9.62	−0.83	−0.00
F 15	0.4604	10.11	0.09	0.00
F 16	0.4604	10.11	0.09	0.00
F 17	0.4604	10.11	0.09	0.00
F 18	0.4604	10.11	0.09	0.00

$$(\ldots 12a_{1g}^2)(\ldots 2a_{2g}^2)(\ldots 6b_{1g}^2)(\ldots 5b_{2g}^2)(\ldots 7e_g^4)(1a_{1u}^2) \times(\ldots 8a_{2u}^2)(\ldots 3b_{1u}^2)(\ldots 4b_{2u}^2)(\ldots 12e_u^4). \tag{6}$$

Calculated total energies, electron affinities by ΔSCF [see Eq. (3)] and gross atomic orbital populations[34] (GAOP's) are shown in Table III. The electron configuration for the two affinity states is of the form (ground-state configuration+affinity orbital). Since GAOP's for the ground configurations are almost the same for the ground state and two affinity states, GAOP's are shown for the ground state, and for the affinity orbitals for negatively ionized states. The first affinity state is ${}^2A_{1g}$, with one electron in $13a_{1g}$. By ΔSCF calculations, the electron affinity is −0.9 eV.

Turn now to the characteristics of the $13a_{1g}$ orbital, using the GAOP's in Table III. All corner Li atoms placed in the regular hexahedron have large positive GAOP's, indicating large electron densities on these atoms. On the other hand, six Li's that constitute an octahedron, and F_1 at the center of the octahedron, have large negative GAOP's. This results from large overlaps between the orbitals of the octahedron atoms and those of the corner Li atoms. The electron distributions at the eight hexahedron corners therefore penetrate into the intermediate region spanned by the Li octahedron and the central F_1 atom. Although an added electron is distributed among the whole cluster, larger densities are found around the corner Li $2s$ orbitals.

Since the added electron mainly occupies Li corner $2s$ orbitals, we infer that the electron correlation between the added electron and F^- electrons is negligible. The electron correlation between the Li^+ cores and this added electron therefore stands. Since the added electron is distributed around the entire cluster, and since the Li^+ cores in the clus-

TABLE IV. Ionization threshold of bulk LiF calculated with lattice defect model. With no lattice defects, the Madelung potentials at F and Li are +0.4604 and −0.4604 a.u. The numbers in parentheses are gross atomic orbital populations without lattice defects.

Cluster embedded	$\mathrm{Li^+}_{13}\mathrm{F^-}_{13}$		
Number of cage ions	3348		
Number of CGTF's	221		
Symmetry	C_1		
Number (n) of electrons and total (te) (a.u.)			
	Ground state	First ionized state	Second ionized state
n	156	155	155
te	−1377.109 96	−1376.869 17	−1376.790 66
Electron configuration	$\cdots(78_a^2)$	$\cdots(52_a^1)\cdots(78_a^2)$	$\cdots(52_a^1)\cdots(78_a^2)$
Ionization potential without correlation correction (eV)		6.55	8.69
Ionization potential with correlation correction (eV)		8.7	10.8

Madelung potential and total gross atomic orbital population (GAOP)

Atom	Madelung (a.u.)	GAOP Ground state	GAOP relative to ground state First ion	Second ion
First layer (and third layer)				
Li 2(19)	−0.6467	1.94(1.92)	0.03	−0.01
Li 3(20)	−0.6467	1.96(1.95)	−0.01	0.01
Li 4(21)	−0.6467	1.96(1.95)	−0.01	0.01
Li 5(22)	−0.5679	1.96(1.95)	0.00	−0.01
Li 6(23)	−0.5679	1.96(1.95)	0.00	−0.01
F 7(24)	0.1969	10.03(10.11)	0.00	−0.23
F 8(25)	0.3426	10.10(10.11)	−0.02	0.00
F 9(26)	0.3083	10.08(10.11)	−0.01	0.00
F 10(27)	0.3083	10.08(10.11)	−0.01	0.00
Second layer				
Def. 11	−0.4604	(1.92)		
Li 12	−0.5921	1.93(1.92)	0.04	−0.01
Li 13	−0.6467	1.94(1.92)	0.03	−0.01
Li 14	−0.6467	1.94(1.92)	0.03	−0.01
F 1	0.1969	9.82(9.62)	−1.00	−0.03
F 15	0.1969	10.03(10.11)	0.00	−0.23
F 16	0.1969	10.03(10.11)	0.00	−0.23
F 17	0.3426	10.10(10.11)	−0.02	0.00
F 18	0.3426	10.10(10.11)	−0.02	0.00

ters are very close to an atomic (gaseous) Li^+, the correlation energy between one Li^+ core and the added electron would be about $1/n$ of the atomic $1s$-$2s$ correlation energy $[E_{\mathrm{corr}}(1s\text{-}2s{:}\mathrm{Li})]$, where n is the number of corner Li^+ ions in the crystal. It follows that the correlation correction for the affinity state is approximately $E_{\mathrm{corr}}(1s\text{-}2s{:}\mathrm{Li})$. This can be estimated from the present ΔSCF (5.34 eV) and the experimental[35] (5.39 eV) ionization potentials (IP) of the gaseous (free) Li (see footnote b in Table II).

Consider now the relation between $E_{\mathrm{corr}}(1s\text{-}2s{:}\mathrm{Li})$ and the experimental and SCF IP's. The experimental atomic total energy ($\mathrm{TE}_{\mathrm{expt}}$) is expressed as the sum of the SCF total energy ($\mathrm{TE}_{\mathrm{SCF}}$), the correlation energy (E_{corr}), and the relativistic energy (E_{rel}). Therefore, the experimental ionization potential ($\mathrm{IP}_{\mathrm{expt}}$) for the atomic Li is given by

$$\begin{aligned}\mathrm{IP}_{\mathrm{expt}}(\mathrm{Li}) &= \mathrm{TE}_{\mathrm{expt}}(\mathrm{Li}^+) - \mathrm{TE}_{\mathrm{expt}}(\mathrm{Li})\\ &= \mathrm{TE}_{\mathrm{SCF}}(\mathrm{Li}^+) + E_{\mathrm{corr}}(\mathrm{Li}^+) + E_{\mathrm{rel}}(\mathrm{Li}^+)\\ &\quad - \{\mathrm{TE}_{\mathrm{SCF}}(\mathrm{Li}) + E_{\mathrm{corr}}(\mathrm{Li}) + E_{\mathrm{rel}}(\mathrm{Li})\}\\ &= \mathrm{IP}(\Delta\mathrm{SCF\,Li}) + \Delta E_{\mathrm{corr}}(\mathrm{Li}^+\text{-}\mathrm{Li}) + \Delta E_{\mathrm{rel}}(\mathrm{Li}^+\text{-}\mathrm{Li})\\ &\approx \mathrm{IP}(\Delta\mathrm{SCF{:}Li}) + \Delta E_{\mathrm{corr}}(\mathrm{Li}^+ - \mathrm{Li})\\ &\approx \mathrm{IP}(\Delta\mathrm{SCF{:}Li}) - E_{\mathrm{corr}}(1s\text{-}2s{:}\mathrm{Li}). \end{aligned} \tag{7}$$

We ignore the relativistic term, because the relativistic energies for Li and Li^+ are small and almost equal. In reaching the last line of Eq. (7), it has been assumed that the $1s$ intrashell correlation energies in Li and Li^+ are the same. Using numerical Hartree-Fock (HF) calculations and perturbation theory, Koga and co-workers[36] found that IP(ΔSCF)'s with and without relativistic effects are, respectively, 5.341 9 2 and 5.341 8 1 eV. The present IP(ΔSCF) is very close to that of the accurate calculation, and the correlation correction, $E_{\rm corr}(1s\text{-}2s{:}\mathrm{Li})$, estimated here is quite reasonable; its value is calculated to be −0.05 eV. In Table III, however, 0.1 eV is added instead of 0.05 eV because the present cluster calculations do not have an accuracy of 0.01 eV. The affinity state may be observed as a resonance state in the continuum. The calculated second affinity state with correlation correction lies 1.2 eV above the ground state.

We now consider the ionization threshold I_t. Poole and co-workers estimated I_t to be 9.8 eV.[4,5] Here two distinct I_t values are discussed, from the surface and in the bulk material, which are, respectively, calculated as 12.5 and 13.1 eV by the ΔSCF method using the perfect lattice approximation. The C_{4v} symmetry is used in calculating I_t's for the surface. The wave function for the ionized states is expressed as

$$\begin{aligned}\phi = {} & C_A|\phi_{\rm Li}(A'B'C'\dots)\phi_{\rm F}(A^{-1}BCD\dots)| \\ & + C_B|\phi_{\rm Li}(A'B'C'\dots)\phi_{\rm F}(AB^{-1}CD\dots)| \\ & + C_C|\phi_{\rm Li}(A'B'C'\dots)\phi_{\rm F}(ABC^{-1}D\dots)| + \cdots, \end{aligned} \tag{8}$$

where X^{-1} implies that a p electron at the ion $\mathrm{F}_X{}^-$ is ionized. Since the atomic ionization process ($\mathrm{F}^- \rightarrow \mathrm{F} + e$) dominates, the atomic correlation correction, which is discussed below, is needed in discussing the ionization threshold qualitatively.

In the (gaseous) atomic case, the electron affinity $[\mathrm{TE_{SCF}(F)} - \mathrm{TE_{SCF}(F^-)}]$ calculated with the present basis is 1.32 eV (see footnote c in Table II), while the experimental value is 3.40 eV.[37] If relativistic differences between F and F^- are ignored, an error of 2.08 eV [the correction $\Delta E_{\rm corr}(\mathrm{F}-\mathrm{F}^-)$] results from the larger electronic correlation in the gaseous negative ion:

$$\begin{aligned}\mathrm{EA_{expt}(F)} &= \mathrm{TE_{expt}(F)} - \mathrm{TE_{expt}(F^-)} \\ &= \mathrm{TE_{SCF}(F)} + E_{\rm corr}(\mathrm{F}) - \{\mathrm{TE_{SCF}(F^-)} + E_{\rm corr}(\mathrm{F^-})\} \\ &= \mathrm{EA}(\Delta\mathrm{SCF{:}F}) + \Delta E_{\rm corr}(\mathrm{F}-\mathrm{F}^-). \end{aligned} \tag{9}$$

Using numerical HF calculations, Koga and co-workers[36] found that EA(ΔSCF:F)'s with and without the relativistic effects are 1.36 and 1.33 eV. The present value of 1.32 eV is close to the accurate EA(ΔSCF:F) of 1.36 eV, showing that the set for F^- is well suited.

Since electrons in the ionic crystal are well localized at each ionic site in the ground state, and the ionization described by Eq. (8) is essentially a local process, the correlation effect for the present ionization process (neutralization of the F^- ion) in the cluster should be similar to that for the electron affinity mentioned above. Therefore the value of 2.1 eV is used as the correlation correction for the ionization process with a localized hole in the cluster. The correlation-corrected surface and bulk I_t values are, therefore 14.6 and 15.2 eV, and are far from the experimental value given by Poole and co-workers.[4] Recall that the band calculation[24] also gives 14.3 eV for I_t. Provided that LiF has a perfect lattice structure, the bulk I_t should lie between 14 and 15 eV.

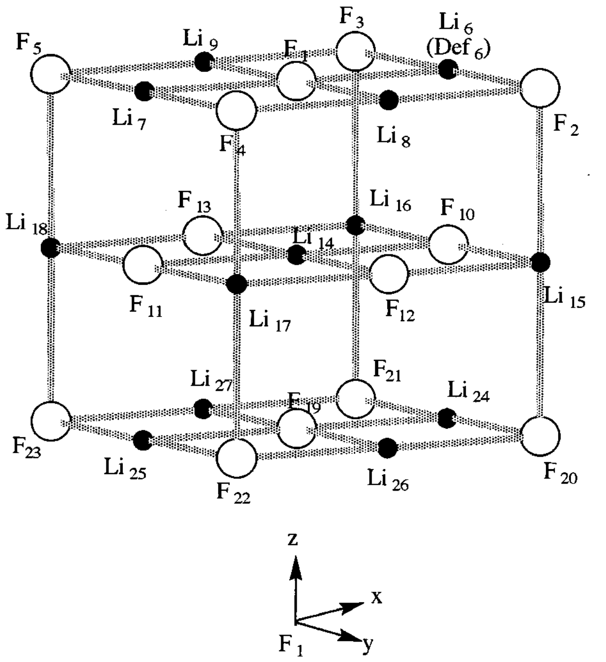

FIG. 4. Geometrical structure of $\mathrm{Li^+}_{13}\mathrm{F^-}_{14}$. (a) With the perfect lattice, this cluster is placed at the surface of the ionic cage. (b) With an imperfect lattice, the cluster with a defect at Li_6 (denoted Def_6) is placed at the surface of the ionic cage.

B. Imperfect lattice model

Since Li^+ ions provide the positive field that stabilizes electrons at F^-, and since the experimental value of I_t is much smaller than the calculated values, it is natural to suppose that there exist lattice defects at Li^+ sites that should be taken into account. In the present work a lattice defect is introduced at the position of Li_{11} (see Fig. 1), and this cluster ($\mathrm{Li^+}_{13}\mathrm{F^-}_{13}$) is embedded in the same ionic cage as in the perfect lattice model. The molecular symmetry is C_s, but C_1 is now employed. The number of CGTF's is 221 and is equal to the dimension of the Fock matrix. The number of electrons for the ground state is 156, instead of 158 in the perfect lattice. SCF calculations were performed for the neutral and ionized states. The total energies, the ionization threshold (I_t), and the electronic configurations for the ground state and two ionized states are listed in Table IV, together with the GAOP's. The calculated value of I_t is now 6.6 eV by ΔSCF, and 8.7 eV after correlation correction, which is close to the experimental estimate of 9.8 eV and the onset I_t of ~7.5 eV. In this state the electron on the central F is removed. The state is not described by a hopping model as in Eq. (8), but is approximately given by the first term of Eq. (8). If another defect exists in a sphere of radius ≤25 a.u., this may lead to a smaller value of I_t (≤7.5 eV). The second ionized state lies 10.8 eV above the ground state. The electronic hole of this state is spread through the solid, as is suggested by the GAOP's.

To discuss lattice defects on the surface, a cluster with a defect at Li_6 of $\mathrm{Li}_{13}{}^+\mathrm{F}_{14}{}^-$ (see Fig. 4) is placed at the center of the surface of a perfect ionic cage consisting of 2025 point charges; 27 point charges of the 2025 are replaced by the cations, anions, and a lattice defect. The molecular symmetry is C_1, the number of CGTF's is 226, and the number of

TABLE V. Ionization threshold of surface LiF calculated with lattice defect model. With no lattice defects, the Madelung potentials at F and Li of the first layer are +0.4429 and -0.4430 au. Madelung potentials of the second and third layers are almost the same as the those of bulk values of ±0.4604; the difference is at most ±0.0002 a.u. The numbers in parentheses are gross atomic orbital population without lattice defect. The ground GAOP's for the third layer are not listed where GAOP's for the ground state and the affinity states are almost the same. The difference was at most −0.02.

Cluster embedded	$Li^{+}{}_{12}F^{-}{}_{14}$			
Number of cage ions	1998			
Number of CGTF's	226			
Symmetry	C1			
Number (n) of electrons and total (e) (a.u.)				
	Ground state	First ionized state	Second ionized state	Third ionized state
n	164	163	163	163
te	−1503.580 34	−1503.360 63	−1503.353 47	−1503.348 58
Electron configurations	$\cdots(82_a^2)$	$\cdots(41_a^1)\cdots(82_a^2)$	$\cdots(41_a^1)\cdots(82_a^2)$	$\cdots(41_a^1)\cdots(82_a^2)$
Ionization potential without correlation correction (eV)		5.98	6.17	6.31
Ionization potential with correlation correction (eV)		8.1	8.3	8.4

Madelung potential and total gross atomic orbital population (GAOP)

Atom	Madelung (a.u.)	GAOP Ground	GAOP relative to ground state First ion	Second ion	Third ion
First layer					
F 1	0.1795	10.15(9.24)	−0.86	0.00	0.03
F 2	0.1795	9.99(9.97)	0.00	0.01	0.00
F 3	0.1795	9.99(9.97)	0.00	−0.89	0.00
F 4	0.3251	10.02(9.97)	−0.01	0.00	0.00
F 5	0.3251	10.02(9.97)	−0.01	0.00	0.00
Def. 6	−0.4430	(2.27)			
Li 7	−0.5748	2.00(2.27)	−0.01	−0.02	−0.03
Li 8	−0.6293	2.00(2.27)	0.01	−0.01	−0.02
Li 9	−0.6293	2.00(2.27)	0.01	−0.02	−0.02
Second layer					
F 10	0.1971	10.22(10.22)	0.01	0.00	−0.89
F 11	0.3427	10.25(10.22)	−0.01	0.00	−0.02
F 12	0.384	10.25(10.22)	0.00	0.00	0.01
F 13	0.3084	10.25(10.22)	0.00	0.01	0.01
Li 14	−0.6469	0.76(0.71)	−0.03	−0.01	−0.07
Li 15	−0.6469	1.97(1.99)	−0.02	−0.01	0.02
Li 16	−0.6469	1.97(1.99)	−0.02	−0.02	0.02
Li 17	−0.5682	1.96(1.99)	−0.01	0.00	−0.01
Li 18	−0.5682	1.96(1.99)	−0.01	−0.01	−0.01

electrons for the ground state is 164. The total energies, the ionization threshold (I_t), and the electronic configurations for the ground state and two ionized states are shown in Table V, together with the GAOP's. The electronic configurations for the ionized states are $\cdots(41a^1)\cdots(82a^2)$. The value of I_t from the surface is 6.0 eV according to ΔSCF, and 8.1 eV with correlation corrections. The correlation-corrected result is very close to the experimental value. It is therefore possible that the observed small I_t arises from lattice defects in the bulk solid and at the surface.

Poole and co-workers[4,5] used their UPS spectra to obtain the total width of the halide-ion band, $E_{\mathrm{tw}}(\mathrm{F}^-)$. This probably includes contributions from the effects discussed above; the calculated $E_{\mathrm{tw}}(\mathrm{F}^-)$ corresponding to the value of 6.1 eV of Poole and co-workers is 9.8 eV. This is obtained as the difference between the maximum[28] IP(ΔSCF: 15.8 eV) + correlation correction (2.1 eV) and the surface I_t (8.1 eV). Although the value of 9.8 eV is different from the value (6.1 eV) of Poole and co-workers, it is quite close to the band width of 10.5 eV that can be directly read from their UPS results.[4] The two band calculations with a perfect lattice give 2.8 eV (Ref. 24) and 2.0 eV,[25] and the previous cluster calculation with perfect lattice also gives 2.7 eV for $E_{\mathrm{tw}}(\mathrm{F}^-)$ (evaluated from Table II in Ref. 28). The calculated and

TABLE VI. Summary of electronic band structure of LiF.

	Ionization Threshold (eV)				Band (eV)			Excition (eV)		
	surface	bulk	surface	bulk	Gap	Band width (F 2p)		Bulk	Surface	Affinity
Method/lattice	Imperfect		Perfect		Perfect	Imperfect	Perfect	Perfect		
Band theory										
LDF[a]				11.7	10.5		2.8			
LDF with correlation (Periodic cluster ΔSCF)[a]				14.3	13.9		2.8		11.7	
LDF with correlation[b]					14.0		2.0			
Embedded cluster[c]										
ΔSCF	6.0	6.6	12.5	13.1	11.8		2.7	11.3	9.4	−0.9
ΔSCF with correlation correction	8.1	8.7	14.6	15.2	13.9	9.8	2.7	13.4	11.5	−0.8
Expt.	~7.5 (9.8)[d]			13.0[e]	13.6[d]	~10.5(6.1)[d]		13.5[h]	10.3[f]	<0.0
					14.2[g]		3.5[h]	12.6[i]		

[a] See Ref. 24.
[b] See Ref. 25.
[c] See Ref. 28.
[d] See Refs. 4 and 5.
[e] See Refs. 1 and 2.
[f] See Ref. 9.
[g] See Ref. 6.
[h] See Ref. 38.
[i] Pong and C. S. Inouye as quoted in Ref. 24.

experimental $E_{\mathrm{tw}}(\mathrm{F}^-)s$ are so different that it would be interesting to remeasure the $E_{\mathrm{tw}}(\mathrm{F}^-)$ and to discuss $E_{\mathrm{tw}}(\mathrm{F}^-)$ from the perfect lattice.

IV. DISCUSSION AND CONCLUSION

The results discussed above are collected in Table VI. Four ionization thresholds (I_t's) are given: the surface and bulk I_t's are calculated with both imperfect and perfect lattice models. The calculated I_t values with electron correlation corrections from the surface and bulk with a lattice defect are 8.1 and 8.7 eV, respectively, which shows good agreement with the onset of UPS, ~ 7.5 eV. The observed value[4] (9.8 eV) will include the defect contamination inevitably present in the solids. The value of $I_t = 13.0$ eV given by Taylor and Hartman[1] is close to the theoretical values calculated for the perfect lattice with correlations (14.3 and 15.2 eV), which may be due to limitations of sensitivity in the 1950s instruments used. The theoretical total band widths for F^- with the perfect lattice lie in the range 2.0–2.8 eV, and compare favorably with the early value (3.5 eV) of O'Bryan and Skinner.[38] Modern UPS (Ref. 4) gave a band width of 6.1 or ~10.5 eV, the lower value (6.1 eV) was given by Poole and co-workers[4] and the larger one is read from their UPS results, and these incorporate contributions from lattice defects in the bulk and the surface because of greater instrumental sensitivity. Other energetics are well explained by the perfect lattice model, implying that contributions from lattice defects are small.

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