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Ground- and excited-state properties of LiF in the local-density formalism*

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The band structure, charge density, x-ray scattering factor (and their behavior under pressure),
equilibrium lattice constant, and cohesive energy of the prototype ionic solid LiF were determined using our
recently developed self-consistent numerical basis set (non-muffin-tin) linear-combination-of-atomic-orbitals method, within the

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LRC ——-VXC
VSRC

analogous molecula. r studies'); a large number of
Diophantine integration points (2000 per Li and 3000-4000 per F) together with an improved samp-ling point mapping scheme are needed to obtain an accuracy of 0.5—0.3 eV in the total energy. All our calculated binding energies are given later
with

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r5
l5 l5

IO

Li (2p)
Li (2s)

IO

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0.90
I i

0.80— ———WITH CORREL.

WITHOUT CORREL

0.70—

O

0.60—

0.50— Z
tAJ O

0,40—

0.30—

0.20—

O, IO—

Li
I I I-- I
0 0.2 0.4 0.6 0.8 1.0
Ol STANCE ALONG [

I I I

]

FIG. 6. Total ground-state charge density calculated
in (1) the exchange and correlation model, and (2) the exchange model along the [100] direction in the unit cells. The arrows point to the positions of minimum density in the corresponding models.

F) predict amuchlarger disproportion between the size of the lattice iona (15.3% and 34.7% for Li'
and F, respectively) than do both the observed
and the calculated values in the crystal.
The precise value of the minimum charge density
in the unit cell is difficult to evaluate accurately
from the experimental data since small changes in
the temperature parameters and structure factr/Xi7 9.(exchangeTf 214.1 29f 226.9 Tj ET 8937troduj ET BT /Xi7 9.34 Tf 179.36 5

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TABLE IV. Calculated and observed x-rays scattering factors for LiF.

hkl

200
220
222
400
420
422
440
600
442
111
311
331
333
511

Atomic

(spherical)
HF

7.62
5.71
4.61
3.90
3.41
3.05
2.58
2.41
2.41
4.89
2.36
1.65
1.38
1.38

Atomic

tspherical)
LDF;n 2

7.49
5.65
4.58
3.88
3.40
3.05
2.57
2.40
2.40
4.77
2.38
1.69
1.42
1.42

Atomic

(spherical)
LDF; o.'=1

7.72
5.95
4.86
4 ~ 12

3.60
3.22
2.63
2.45
2.45
4.90
2.55
1.76
1.44
1.44

Atomic

nonspherical
HF

7.72
5.78
4.66
3.94
3.44
3.08
2.60
2.43
2.43
4.96
2.38
1.65
1.37
1.37

Crystal
HFb

7.70
5.72
4.60
3.90
3.40
3.04
2.57
2.41
2.41
4.98
2.36
1.63
1.36
1.37

Crystal
LDF
A=—2
3

7.79
5.69
4.66
4.03
3.48
3.11
2.57
2.40
2.40
4.88
2.39
1 ~ 71
1.43
1.42

Exp

7.72
5.70
4.60
3.99
3.45
3.07
2.57

2.40
4.

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ll) and includmg F 1s, 2s, 2p, 3s, 3p, and 3d and
Li' 1s, 2s, and 2p numerical

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bly very close to this value due to the low electron
affinity of the system.

"

"

No exciton series has
so far been identified for this transition. Similarly, the excitations of this level into the conduction

states [expected to start at about 708 eV

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50 eV. The absorption spectra in the 35-50 eV
region" show no structure. The energy-loss
spectra calculated" from these data show only plasmon peaks at 45 and 50 eV, while the measured energy-loss spectra"" show also two pronounced
structures at 33.

5 and 42 eV and an additional fea-
ture at 51 eV. Absorption in the 50-60 eV region
shows

a flat structure which was tentatively as-
signed to a Li 1s transition. Due to the possible
overlap of the high-energy part of the valence to conduction bands with the low-energy part of the Li 1s transitions, it is difficult to resolve the spec-tra in the 35-50 eV region. The inelastic electron scattering data of Fields et at.

"
reveal

a forbidden

F 2s exciton at 35 eV (i.e.

, 2.6-eV binding energy)
which is probably due to

a

F (2s)-Li'(2s) pair below
the conduction band threshold.

(iv) The fundamental valence-conduction region. Roessler and Walker" measured the reflectance of LiF in the 10-20 eV region and analyzed the data
in terms

C'

R

0

U

N

D

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A

N

D F,

X

C

I

T F.

D

-

S

T

A

T F, PROPERTIES

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tempted to calculate the relaxation-polarization
self-energy and the electron-hole interactions in
solids. Those involve either atomic models"

"

(in which the corresponding effects are calculated
in atoms and then added as a constant to the band-

structure estimate of Aq») or more extensive
solid-state approaches" (that involve a model
treatment of the exchange screening and electron-
hole interaction). One notes that in the former
approach one assumes that the relaxation effects
in the crystal are unscreened relative to the free-
ions and that the unperturbed extended crystal
states 96 /Xi15 900 /Xi15 9.48 Tf 98t BTj ET BT /Xi15 8.74 Tf 81 57

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„(z,r) =Q e'"'"y,(r- „r—d,), (13)

where y denotes a wave vector in the (small) BZ
constructed from the large direct-space supercell
(in the case of an unperturbed SPC, each of these
g's is reducible to N values of I(. in the primitive
zone, e.g., for 4 molecules per cell, K =0 corre-sponds to 'i + 3X in the small BZ representation) and T„denotes a direct lattice vector for the super-cell. To allow for greater flexibility of our basis,

we compute the set y,(r - d) self-consistently (and numerically) for the free-ion species assumed in our initial potential construction (e.g., for the local ionization of a Li' 1s electron from the solid our basis set contains orbitals computed self-

final states, respectively. Using these initial crystal potentials we perform a fully self-con-sistent band-structure calculation subject to the constraint that the (lowest) Li Is band contains, on the average, one hole (i.e., 2' —

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0

a

O
LJJ

O
z-0.5
LLJ

K
IJJ

LJ

LJ.
CL

I-
z

-I.O
LJ)
Cl

Li 1s HOLE

~np Iar

-I.5
0

I

1.0

I I

2.0
DISTANCE (o.u.)

FIG. 10. Core charge density differences due to Li 1s hole formation in the solid. c5pNFt(r) and &p'sc(r) denote the results obtained in non-SC and SC calculations, re-spectively, while 4p'~~(r) is the core free-ion hole den-sity.

laxation effects and become substantially more localized than in the unperturbed ion. Vfhereas the orbital relaxation effects shown in Fig. 9 are totally neglected in the band-structure approach" to excitation energies, free-ion models"

"
at the

other extreme, assume that this free-ion &p(r) persists in the solid in an unscreened fashion. Figure 10 shows the calculated difference in the crystal 1s radial charge density along the [100] direction, obtained from two independent [non-SC and SC) supercell calculations (curves labeled
n, porc(r) and dLp,'P(r), respectively]. To facilitate comparison with the free-ion case, only

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window between the conduction threshold at 38 eV

and about 50 eV where a weak structure occurs. ~ "
Although previously attributed to the Li 1s sp~.c-
tra, '"'""""our present study suggests that this
might be a F 2~ -to-conduction interband transition. The correlated HF calculations of Kunz" predict an F (2s) exciton at 37.6 eV (i.e., only 0.3-eV binding energy relative to the conduction thr shold, in poor agreement with both our calculation and with ex-periment). It is interesting to note that even a sim-ple free-ion model using the observed F (2s) ion-ization potential (24 eV)"" and the point-ion field at the F site (12.45 eV) yields a reasonable result for the F (2s) ionization limit in the solid (36.4 eV compared with the &SCF result 37.2 eV and the ob-served value 37.6 eV).
The F (ls) ionization limit is calculated to be at 694.2 eV (observed:693. 2 eV) and the interband spec-tra for this state are expected to start at about 708 eV. As seen from Table V, the band- structure and DISCI" results for these transition energies differ by about
37 eV. Interestingly, while the n =1 exchange band
model shows a somewhat better agreement with the observed transition energies than does the a = -', ex-change and correlation band model, it leads to much poorer agreement in the final MCF limit [i.e., 720. 1 eV compared with 694.5 eV for the
F (ls) ionization energy and 74.7 eV compared with 63.5 eV for the Li'(ls) ionization energy for o. = 1
and —',
, respectively]. The fact that the choice of
n =1 yields larger eigenvalue separations in the band limit (and hence better agreement with ex-periment), has led many workers to favor this

value. "~" It is gratifying that when a proper MCI'
treatment is done, the results of the more 388i20 10.52 Tf 495.795.76

the796(po)Tj ET T BT /Xi20 9.78 Tf 262137 68652 Td ((this)Tj ETj E)Tj ET /Xi20 8.66 Tf 92.099 6866an 4 (ths)Tj ET BT /Xi20 9.35 Tf 217.89 38 (1) Td (ths)Tj ET oBT /Xi20 9.49 Tf

FeV66point-ionwelT /Xi20 8.68 Tf 100.01 596.92Td (point-ionw BT /Xi20 8.92 Tf 135.62 45873969d (and)Tj ET BT /Xi20 9.38 Tf 275.18 60

obm-

6

', Td (6)Tj ET B BT /Xi20 9.29 Tf 93.338 60387 Td (6)Tj ET Bground-ET BT /Xi20 10 Tf 1410.23 5874469 Td 22he is 388i20dej ET eBT /Xi20 11.32 Tf 17.89 38 1,(

34

(Td 68n

InterestiBT /Xi20 9.28 Tf 275.18 4366pr2Td (Inrgies)negligible BT /Xi20 9.05 Tf 77001 534163 Td (Interesti BT /Xi20 9.6 Tf 182..14 334328 Td (band)Tj EcurBT /Xi20 9. eVtowith (and=)7T0.56e se.596.55reementIE th7d8463j ET BwT /Xi20 9.05 Tf 269.75 384(4)T68obat eVen-en-then-of1tLi'4d1.25th isoflculatiTj ET BT 8.98 Tf 379793 6735289Td (ei)Tj ET slT BTBT /Xi20 10.97 Tf 76.27 68646945d (the)Tj ETflattenBT /Xi20 8.32 T th62T8ob-

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F

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and v =(1,0, 0) differ by 0.13 eV, indicating that re-
sidual interaction is still present in our superlat-
tit."e model. This is undoubtedly caused by the ex-
tended tail of the valence hole density (compare
Fig. 12) and can be treated by significantly enlar-
ging the supercell's size. This demonstrates the inherent difficulty in describing such a perturbed crystal state (intermediate between a core exciton and a Bloch band) which has a pronounced charge localization near the perturbed site but a nonvan-

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different x-ray scattering factors than those obtained from ionic HF orbitals 35 and are substantially more

diffuse spatially than the n=1 local-density ionic o bitals. These latter orbitals result in a substantially
different crystal superposition density than that ob-tained from HF orbitals. ' These differences manifest
themselves in

a large difference in the computed band
gap in the non-SC limit (15.

2 eV with HF orbitals and
12.

2 eV with local density orbitals compared with 10.

5

eV at the convergence limit). It would hence seem that a rather sizable atomic HF basis set would be required
to obtain reasonable convergence in the solution of the local density Harniltonian in ionic materials.

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computed band gap. We indeed find that this is the
case in the LiF crystal. (cf.Table V} and suspect that
this might also be the case in other narrow-band
materials like rare-gas crystals. On the other hand,
the computed Hartree-Fock one-electron energy gaps
are usually much larger than the observed ones (e.g.,

18.5 eV for Ar and 23.1 eU for KC1) and self-energy terms that tend to reduce these values are indeed the

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