35 ELECTRONIC STRUCTURE OF M3Sb-TYPE FILLED... 3953

P M3 Sb (M= Li,K,Cs) in the ordered cubic D 03 struc-
ture. In this crystal structure (inset to Fig. 1), four simple
face-centered sublattices are mutually displaced along the
body diagonal such that a11 nearest-neighbor distances
equal 4 of this diagonal. There are two different types of
crystallographically inequivalent cations in this structure: M& with eight M» cation as nearest neighbors, and M» with four cations and four anions as nearest neighbors. The primitive lattice vectors are

a, =(0, —,

, —,)a, 1

a2 ——(—,

,0, —,)a, 1 I

tegration. The basis set consists of about 200 functions (a basis set of about 300 functions was, however, needed for the calculations which treat Cs Sp states as valence states, see below). Eigenvalues of the valence states are con-verged to better than 0.03 eV (0.2 mRy). Finally, the den-sity of states (DOS) is calculated using the tetrahedral in-tegration method with a square broadening scheme (with a width of 0.16 eV, or 12 mRy) and eight primary k points.
III. RESULTS AND DISCUSSION

A. Total-energy and ground-state properties

a3 ——(—,

, —,

,0)a, 1 1

and the atomic site coordinates are as follows: Sb at

r) ——(0,0,0)a,
M» at

I 1 1

2 4 4 4

M, at

(2)

The total and cohesive energies as a function of lattice parameter were calculated for Li3Sb, K3Sb, and Cs3Sb in
the cubic (P) D03 structure and are depicted in Fig. 1.
The calculated total energies using the signer' interpola-
tion formula at three values of the lattice parameter were fitted to a quadratic form and interpolated to obtain the zero-temperature equilibrium lattice constant a,q

and

bulk modulus B. The cohesive energies, using the Von Barth —Heding spin-polarized exchange correlation poten-tial (in the Hedin-Lundquist paramagnetic limit), are ob-tained by subtracting the spin-unrestricted atomic total

and M» at

where a is the cubic lattice constant.

From total-energy calculations we have obtained the ground-state properties of these systems. The band

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TABLE I. Calculated [using the Wigner (Ref. 19) exchange-correlation functional] equilibrium lattice constants {a,q

), bulk moduli
(B), cohesive energy per four atoms (E,) and spin-orbit splitting of the valence-band maximum (Ap) of Li3Sb, K3Sb, and Cs3Sb in the D03 structure, compared with experimental data and the LMTO results of Christensen (Ref. 11) [using the Ceperley-Alder (Ref. 21) exchange correlation].

Properties

a,q

(A)
B (kbar)
E, (eV)
Ap (eV)

Present
calc.

6.497
344
I 1.3
0.62

Li3Sb

LMTO'.

6.631
343

Exptl.

6.572'

9.32

8.357
148
8. 1
0.43

8.493'

7 50

K3Sb
Present

calc. Exptl ~

Present
calc.

9.063
140
8.3
0.42

Cs3Sb

LMTO'

9 415
151

Exptl ~

9.128'

'Reference 11.

These rather large lattice parameters are the results published in Ref. 11, where the calculations were performed in the atomic-sphere approximation (ASA). Christensen believes (Ref. 29) that upon improving this approximation, the lattice parameters of Li3Sb and

0

Cs3Sb would be reduced to 6.52 and 9.24 A, respectively.
'Reference 4.
Reference 25.
'Reference 5.
Reference 6.

energies (including spin-polarization corrections which are 0.37, 0.25, 0.21, and 1.35 eV for Li, K, Cs, and Sb, respec-tively) from the crystal total energies. The calculated cohesive energies are assumed to be independent of specif-ic correlation form. These resu1ts are summarized in

Table I where they are compared with the experimental data and with the linear —muffin-tin-orbital (LMTO) results of Christensen" for Li3Sb and Cs3Sb. In our calculation for Cs3Sb we treat the partially delocalized Cs 5p states as variational valence-band states, i.e., on the
sy

35 CTRONIC STRUCTURE Q M3sb- TYPE FILLED 3955

L3c

Lic

2 -::=::::::::::::::=:::::::::;:;:.

, L3c;-:::::.:::::::;.:::::::::-;:::.

L2c

I 0 g:.::.:

Xic

.L

L2v

i Xsy

:;::::::::.;:.,:.-:::::. -: X ac

Xgy
X4v

CP

4Pc
LU -4-

L2'y X4y

P-K Sb
= 6-572 A ~=8.493 A

p-cs3Sb
~= 9-128 A

-6- (a) (b)
Sb gs

(c)

xiv

-8-
Liy

Li y
I)y

Sb,ss
Xiy

'Iiv

Sb,ss

xiv

- 10
L

Iiv

X X

FIG. 2. Band structur uctures of cubic (a) Li Sb 11 coordinate system is at the Sb
5 ( )b d

nge-correlation at the
g P g
is p ot.

a re . as ed lines

X

ably smaller. Thee 1ower valence b
i a band width o

a

1 b d

'

il 1

Th hi jl va 1ence band (L ~ -P
dispersionless. Th 1 1 td

„„-X,,) is aim t
p' p 'g
e va ence-band maximum (VBM). Our re-

suits, theree ore, do not agree with an est ato o
o e. 30. We find t

p as
e a

d b d E =0
1 1 f 14 V

xper-

"n".f.3-.-"f ose of K3Sb are more complicated due

(a) P-LiaSb a=6.572 A
Sb

(b) P-K, Sb a=8.493 A (c) P-Cs, Sb
20- '

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TABLE II. Calculated [using Wigner's exchange correlation (Ref. 19i] one-electron eigenvalues (in eV} and 1-decomposed local

0 0

charge character (in percentages) inside atomic muffin-tin (MT) spheres of cubic Li3Sb (a=6.572 A, RMT ——1.370 A), K3Sb (a=8.493

0 0 ct 0

A, RMT ——1.767 A, and Cs3Sb (a =9.128 A, RMT ——1.900 A) at high-symmetry points. For each state the I characters are given for Sb (first row), M& (second row), and M&& (third row). The energy zero is at the I »„valence-band maximum.

State

I 25.

X),

Xg,

X5„

X),

X3,

—9.31

7.28

2.98

4.92

—8.42

—2.12

0.74

3.07

—8.67

Li3Sb
S

63
3
5

28
25
10

74

1

0

0
0
11

6
30

0
0
21

70
0
2

57
5
1

0
0

5

4.

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to the presence of the unoccupied K 3d orbitals. These d
orbitals have an

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TABLE III. Comparison of the bandwidths and band gaps of Li3Sb, K3Sb, Cs3Sb

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Ll, Sb
6 572

8

4

K3 Sb
a=8.493 A
I(JQ

/

Cs3Sb

FIG. 5. Calculated valence charge-density contours (in units of 10 '

e/a. u. ') for (a) Li3Sb, (b) K3Sb, and (c) Cs3Sb (without Cs 5p states) on the (110) plane. Successive contours are separated by 4&(10 '

e/ '

e a.u. Plots are drawn wit h theh correct proportion of the lattice parameters. Dashed regions in (a) show Li-Li bond.

[compare Figs. 4(a) and 2(a)].
(ii) The strongly ((')Tj ET -T /Xi7 8.39 Tf 56.11 5120 Td (di(Sb)Tj ETTj T /Xi7 9.08 Tf 344.11 521 Td (dislattice)non-BT /Xi7 8.27 Tf 388.11 524.22 Tdi(S)Tj ET)Tj E

strongly BT /Xi7 7.72 Tf 330.22 595 Td (455states)T BT /Xi7 10.19 Tf(S)Tj 5346(455tes)BT /Xi7 9.39 Tf 80.44 5114.56 T458sy)Tj ET+T /Xi7 9.69 Tf 464. a255contours Li-Li a24(K3Sb,)TjX3BT /Xi7 7.87 Tf (S)Tj 514.3(a24((110))TBT /Xi7 8.25 Tf 42544 5124.22 T44.56 Tj ET BT /Xi7 7.72 Tf 931.33 5273(a$(of)Tj ETj ET BT /Xi7 7.14 Tf 539.78 72(stro4 (e/a.)Tj beTj ingT in110) Sa213of ina the 455sn

ot prximsity 1140(rbief)es)a u a) Cs (withou a2 (figs.)Tj ET BT /Xi70.44 9 Tf(S)Tj 3714033 T404((c))Tj ET BT /Xi7 8.64 Tf4244.13814.33 Td (and)Tj ET BT /Xi798984 Tf 6331j 380.44 T4 2((cET)Tj ET BT /Xi7 9.39 Tf 88 the of C oience a d t th

o
(3the coducrtion a i

f 65 2674.33 Td —u

ch
bon(oj beTj ingT /Xi79.51 Tf 325 ET 2r9n71 Tf 52densiite) wit o

of S

o

1studergly T40chemicf plane. 1T4 (and)Tj E ET BT /10i70.44 TTf 6 3924.22 [Td lane. 1(402K3)Tj ET B BT /Xi7 9.9939f 344.1 3924033 [Td lane.

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Treatment (1) of Table IV of Ref. 17 was used here. The
larger lattice constants obtained by Christensen (Ref. 11) (cf.,
Table I), especially for Cs3Sb, are probably due to the use of
the renormahzed frozen-core approximation. Such an ap-
proximation has been known (see Ref. 17) to exaggerate the
lattice parameter, particularly when one renormalizes and
freezes the rather extended Cs 5p orbitals.
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