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Electronic structure of 1T-VSe2

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systems and the interesting results obtained es-
pecially for TiSe„we decided to investigate the
electronic structure of its neighboring group-VB
dichalcogenide, namely, 1T-VSe„which has a
number of interesting and anomalous CDW and other
properties.

"'

In this paper, we report results of
two sets of extensive gb initio theoretical studies
of the electronic band structure and properties of
1T-VSe„using our recently reported self co-nsis tent numerical basis set LCAO method. In the first, we discuss some of the resulting electronic properties using results determined with the ob-served lattice parameters. We compare the band-
structure results with the non-self-consistent re-

sults of Woolley and Wexler' and then use them to discuss the optical, appearance potential, x-ray
absorption and photoemission measurements. We
also compare results obtained here for VSe, with
its isoelectronic counterpart TaSe, and with the
IVB systems 1T-TiS, and TiSe,. In the second part, we report a study of the variation of the electronic band structure and properties (notably, the CDW) with variation of several structural pa-
rameters: (i) the sandwich height parameter z,
and (ii) the c/g ratio, which is anomalously high
relative to other 1T compounds. '

II. METHODOLOGY

The self-consistent numerical basis set LCAO
method" has a number of important features
which are especially applicable to studies of
transition-metal compounds such as 1T-VSe,. It
uses an accurate nonlinearly optimized atomic
basis set for all core, valence, and some virtual states of the atoms in the unit cell; all Hamilton-ian interaction and overlap integrals are evaluated accurately using a three-dimensional numerical
Diophantine integration scheme "; full self-con-
sistency is obtained in a scheme that does not restrict the form of the crystalline charge density to any particular shape (viz, cellular or muffin-tin schemes that spherically average the charge den-sity around each site before the next iteration is
attempted). All non-muffin-tin contributions to the
potential are fully retained and the electron local-density correlation functional" is treated as an
intrinsic part of the crystal potential.
We start with an initial guess for the charge den-sity in the form of a population-dependent super-position density p,„,

(r)=g p (r —R„) made up
from the o.'th site atomic (or ionic) charge densi-ties p (r) at the lattice points R„. The single-site
densities p (r) are obtained from self-consistent
(spherically symmetric) numerical solutions of
the local-density single-particle equation for the
n'th atom (or ion), assuming trial occupation num-

bers f„,for the corresponding atomic orbitals, leading to possible non-neutral species when Q

= 2 -P„,f„,WO. These occupation numbers and
charges are used below as variational parameters to define an optimal superposition density. Using

the initial charge density p,„,(r), the crystal poten-tial V[p,

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-2—+

03

3
CUo

4
-5 -'-+

m -6—+
)

g

II FQ

I~
8

Ct

C3
9
R -IO
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-

I

I

-l2
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I)

-20

)-2I

-22

"

r

Mp K3 M M7Ii'W

~

M~ Kg

I

M

T

K

T

LIA

R

vsea~

Lp

LpI

Lp H~
LI

L

S

H

S

A
/
Q2

Qp

P
F/8

~

6

(0, Mi787ii-.„;.mZ2

E
F
-W+

P

Q

P

FIG. 2. Exchange and

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TABLE I. Comparison of bandwidths and major gapg
between the chalcogen p-like and metal d-like bands
(denoted by an asterisk) in TiS2, TiSe2, and VSe2,
Results are given in eV.

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surface-driven instabilities in that 1T-VSe, can
exhibit not only

a nesting of electron and hole
pieces in&ide the d-based bands with wave vectors
parallel to the 1"M directions as

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-5.0

-6.0-

-7.0—

-9.0-

VSe2

+V

+

2c& g +

~3,c

L 1c ~+
1,c
,V
,V
L2,v
M1v

,V

05-

Q4-

0.3-

0.2-

Q.1—

0.0

~ -Q.1-
8
&- -Q.2—
Q

& -0.3-W
LLI

04—

- 10.0— -0.5—

-0.6-

-'11.0 I I I I I I
0.22 0.24 0.26 0.28 z
FIG. 3. Variation of high-symmetry band energies in
1T-USe2 with the sandwich height parameter z. The
dotted area indicates the

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VSep
— 3 ":-----
3,c

+

-4— I3c
+

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