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non-muffin-tin contributions to the crystal density
and potential [found to be sizable in TiS, (Ref. 5) and to account for differences as much as 1-2 eV in the band structure and to produce aband overlap in TiSe,] were fully retained; linearization of the ex-change and correlation functions with respect to the single-site charge densities was avoided. Ei-genvalues were first calculated at 24 R points in
the irreducible Brillouin zone (BE) along the three
parallel planes I'-M-E-I', & Q

I'-n-, a-nd A-I.-H-
A. The resulting band structure (Fig. 1}shows a
characteristic semimetallic behavior with a hole

pocket around I' and @n electron pocket around L.
The band OverhxP between the valence-band max-ima at I'~ and the conduction band minima at L~

is

0.18+0.03 eV, while the I',-M, amd I',-I'3 indirect and direct band gaps are 0.15+0.03 eV and 0.35
+0.03 eV, respectively. The dimensions of the
electron pocket around L (as a percent of the dis-tance to the nearest-neighbor high-symmetry R points} are 20% along J. H, 25%-along I,-A, and 48% along I-M; this indicates the presence of about (I-8) && 10" conduction electrons/cm' in the per-fect crystal.
The lowest Se-4s-derived valence band as well

as the upper Se-4P, 4s- Ti-4P, M valence bands
(denoted as VB2 and VB1, respectively, in Fig. 1)
are somewhat narrower ln TlSe2 in accordance
with the large basal-plane interatomic separation

in the former case 'x The V81-VBR gap is simi-larly about 0.16 eV smaller in TiS, (6.76 eV) than in TiSe, (6.92 eV). It is interesting to note that the atomic s-P separation in sulphur is about 0.15 eV smaller than the corresponding separation in Se when calculated with the same local density func-tionals used for the crystal calculations. The splitting between the two components of the Ti-M-derived conduction bands (C Bl and C82 in Fig. 1) is reduced from 2.3 eV in gi8, to 2.1 eV in TiSe, and the overall conduction-band width is slightly +educed in TiSe, relative to TiS,. These general trends are consistent with the higher electroneg-ativity of sulphur and with the increased basal plane spacing in TiSe, relative to TiS,. The
changes in the major valence to conduction gaps in
going from TiS, to TiSe, are, however, nonuni-
form, e.g.,

the direct gaps at I' and L, differ by
0.52 eV and 0.31 eV, respectively.
the As a test of possible role of seU-consistency, we have calculated the non-self-consistent correc-

tion (i.e.,

difference p(r the n) between the crystal
density p„,(r), and the input superposition densi-
„,) ty, p, (r and its effect on the band structure.
Figure 2 shows the dispersion of p(k, r) plotted at
a few points along the Ti-Se bond direction, as

weil as the average value p „,(r), obtained by
summing over a discrete set of nearest-volume

weights and k, points. It is seen that p„,(r } thus

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FIG. X. Energy-band structure of Tise& in the local exchange and correlation model.

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the corresponding functionals directly to p, (r) + A p(r). The resulting band structure showed a rigid