VOLUME 40, NUMBER 17 PHYSICAL RKVIK%' LKTTKRS 24 APRIL 1978 Structurally Induced Semimetal-to-Semiconductor Transition in 1T-TiSe2

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exchange" and correlation' Hamiltonian, in
which all non-muffin-tin contributions to the po-
tential are fully retained and a nonlinearly opti-
mized numerical basis set consisting of Ti 1s to
4p and Se 1s to 4d orbitals is used. In the first
stage of self-consistency we iteratively modify the electronic orbital configuration of the con-stituent atoms, so as to minimize

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% CHANGE IN Ti-Se BOND
—2 0 +2

—30—

- +
r
3

h

6.0— I
+

.. r,

M — l
6.5— r

C3K
LLJ

—7.0 ~

—8.0

—8.5

+
r
3

—9.5—

—IO.O—

0.220 0.230 0.240 0.250 0.260

ening of the Ti-Se bond length by 0.08 A (3.3%) due to distortions in the positions of a majority

FIG. 1. Dependence of various band energies in TiSe2 on the parameter z. Full lines indicate valence bands while dashed lines correspond to conduction bands. The shaded area indicates the metallic region while the cross-hatched region denotes the semicon-ducting region. Full dots correspond to calculated points.

(i.e., 75/p) of atoms, while the rest of the atoms do not move. '

If one is to simply simulate the ef-
fect of the average bond shortening (2.4%%d) on the electronic structure of the CDW state by consid-ering a normal phase with a similar bond short-ening (i.e., z = 0.232), the results of Fig. 1 indi-
cate a tmnsition to a semiconductor, very close
to this z value. These results suggest that an artificial reduction of z by means of defects or applied shear would act to suppress the CDW transition temperature. It is observed' that the bond shortening in the CDW phase is accompa-nied by an increase in the resistivity and a de-
crease in the magnetic susceptibility, suggest-
ing that a higher-resistance state has been formed, in agreement with our model. The low-z regime is further characterized by a large bonding-antibonding gap in the nonmetal s-p man-ifold and by an enhanced triagonal splitting of the t,

g

levels and indicates a considerable increase
in the covalency of the system.
(iii) In the high-z regime, z) 0.260, the metal
d electrons tend to localize as the atoms are fur-ther

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bility' (in that a continuous distorted cylindrical
electron surface at J-M is unlikely to nest with
the small double hole pocket at I') and is thus
predicted to lead to an absence of a superlattice
transition. This can be directly examined in a
combined low-energy electron diffraction and
angle-resolved photoemission study of the sur-
face which is underway.

"

We note that the ex-

istence of such a fundamental sensitivity of the
electronic and transport properties to the struc-ture parameter z is found to be unique to the
group-IV 1T-dichalcogenides; since the Fermi-
surface-induced structural instabilities in the group-V IT-dichalcogenides are related prirna-rily to electron-hole coupling uitkin a single con-nected surface, a modulation of the bond does not lead to the disappearance of the instability.

"

In line with this, we note the experimental evi-dence for the occurrence of the surface superlat-tice in the group-V Ta dichalcogenides.

"

In conclusion, we feel that although more com-plex patterns of atomic displacement which lead to a Ti-Se bond shortening might also produce similar effects, our model configuration change involving the variation of a single structural pa-rameter provides a physically appealing interpre-tation to the variation in the conducting states and yields a quantitatively correct deformation pa-rameter. As we have seen, energy-band results based on variation of z yields the essential ele-ments of the relations between the structure and the conduction state of the material. The exis-tence of such a band-overlay modulation so sen-sitive to particular atomic displacements might
lead to important experiments, including the ef--
fect of intercalation and pressure on the conduc-tion properties as well as the prediction of the absence of a surface superlattice due to atomic relaxation at the surface.

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