Band structure and lattice instability of TiSe$_2$

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(Received 23 June 1977)

The energy band structure of TiSe$_2$, determined in the local-density approach yields a semimetal (band overlap 0.20 ± 0.05 eV) with holes at Γ and electron pockets only at L. The dimensions of the electron pocket indicate the presence of $(7-8) \times 10^{20}$ carriers/cm^3 in excellent agreement with both transport and angular-resolved photoemission data. The observed charge-density wave is attributed to characteristic "volume" effects, i.e., nesting of parallel electron-hole bands at E_F separated by the Γ-L zone-boundary wave vector.

The nature and unusual properties of the electronic state of TiS$_2$ and TiSe$_2$ have become the subject of intense interest and study. The question as to whether TiS$_2$ (and TiSe$_2$) is a semiconductor or a semimetal is still not resolved and the closely coupled question of the origin of the unusual T^2 temperature dependence of its resistivity is still not understood. The recent observation[1,2] of a $2a_0 \times 2c_0$ lattice instability in TiSe$_2$ at temperatures below 202 °K, coupled with its semimetallic conductivity above this temperature in the most nearly stoichiometric crystals ($\sim 10^{20}$–10^{21} carriers/cm^3), has served to intensify interest and speculation as to its electronic structure. Of particular concern has been the mechanism with which to explain the origin of its charge-density wave (CDW) and the failure to observe such an instability in TiS$_2$. Theory has not added enlightenment. The early non-self-consistent Korringa-Kohn-Rostoker (KKR) muffin-tin band calculation[3] for TiS$_2$ (TiSe$_2$) gave a fundamental gap of 2.0 eV (1.2 eV) at Γ and a smaller indirect gap of 1.4 eV (0.5 eV) between Γ and L; similar semiconducting characteristics have been predicted by empirical tight-binding studies.[4]

Recently, our fully-self-consistent numerical basis set linear combination of atomic orbitals (LCAO) general (non-muffin-tin) potential calculation for TiS$_2$,[5] showed good agreement with optical properties for energies below 16 eV. Contrary to previous expectations, a *small* indirect gap (0.2–0.3 eV) was found to occur at the points L and M in the Brillouin zone, with a larger direct gap (0.8 eV) at Γ. (A recent comprehensive analysis of transport, magnetic susceptibility, Hall effect, resistivity, Seebeck, etc.,[6] data yielded a gap of 0.2–0.5 eV, in agreement with our predictions.) Since extrapolation of our results for TiS$_2$ to the case of TiSe$_2$ is crude at best, and since muffin-

tin[3] or semiempirical models[4] are not able to resolve these questions, we undertook an *ab initio* study of the electronic band structure of TiSe$_2$ in order to understand its various measured properties. Of direct interest was to compare with the first angle-resolved photoemission studies of Bachrach *et al.*,[7] which showed conduction-band overlap of the valence band along the Γ-M direction by at least 0.5 eV.

The band structure was calculated in the local-density functional (LDF) approach, using our previously published numerical basis set LCAO discrete variational method.[5,8] We find that TiSe$_2$ is a semimetal with an indirect *negative* gap (0.20 eV) between Γ and L; contrary to some previous expectations,[2] no electron pocket was found at M. The dimensions of the electron pocket at L ($0.20LH$, $0.25LA$, and $0.5LM$) indicate the presence of $(7-8) \times 10^{20}$ conduction-band carriers/cm^3 in the perfect crystal. This is in very good agreement with the independently reported transport[1] and angle-resolved photoemission experiments.[9]

In our calculations, the linear basis set consisted of Ti 1s to 4p orbitals and Se 1s to 4d orbitals, obtained as accurate self-consistent (numerical) solutions to the corresponding single-site LDF one-particle equations. About 3500–4000 Diophantine integration points per unit cell, together with a cutoff distance of 27 a.u. for the direct space lattice sums, were needed (as was the inclusion of the Se 4d and Ti 4p virtual orbitals) in order to obtain a numerical accuracy of 2–3 mRy in the band eigenvalues for energies below $\epsilon_F + 7$ eV. The initial crystal potential was constructed from an overlapping superposition charge density made up from atomic Ti 3$d^2$4s^2 and Se 4$s^2$4p^4 solutions of the LDF equations. The potential included the local exchange $\rho^{1/3}$ (with a 2/3 coefficient) and the nongradient correlation contribution.[10] All

non-muffin-tin contributions to the crystal density and potential [found to be sizable in TiS_2 (Ref. 5) and to account for differences as much as 1–2 eV in the band structure and to produce a band overlap in $TiSe_2$] were fully retained; linearization of the exchange and correlation functions with respect to the single-site charge densities was avoided. Eigenvalues were first calculated at 24 $\vec{k}$ points in the irreducible Brillouin zone (BZ) along the three parallel planes Γ-M-K-Γ, A-Q-P-A, and A-L-H-A. The resulting band structure (Fig. 1) shows a characteristic semimetallic behavior with a hole pocket around Γ and an electron pocket around L. The band *overlap* between the valence-band maxima at Γ_3^- and the conduction band minima at L_1^+ is 0.18 ± 0.03 eV, while the Γ_3^--M_1^+ and Γ_3^--Γ_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 distance to the nearest-neighbor high-symmetry $\vec{k}$ points) are 20% along L-H, 25% along L-A, and 48% along L-M; this indicates the presence of about $(7-8) \times 10^{20}$ conduction electrons/cm^3 in the perfect crystal.

The lowest Se-$4s$-derived valence band as well as the upper Se-$4p$, $4s$–Ti-$4p$, $3d$ valence bands (denoted as VB2 and VB1, respectively, in Fig. 1) are somewhat narrower in $TiSe_2$ in accordance with the large basal-plane interatomic separation

in the former case.[11] The VB1-VB2 gap is similarly about 0.16 eV smaller in TiS_2 (6.76 eV) than in $TiSe_2$ (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 functionals used for the crystal calculations. The splitting between the two components of the Ti-$3d$-derived conduction bands (CB1 and CB2 in Fig. 1) is reduced from 2.3 eV in TiS_2 to 2.1 eV in $TiSe_2$ and the overall conduction-band width is slightly reduced in $TiSe_2$ relative to TiS_2. These general trends are consistent with the higher electronegativity of sulphur and with the increased basal plane spacing in $TiSe_2$ relative to TiS_2. The changes in the major valence to conduction gaps in going from TiS_2 to $TiSe_2$ are, however, nonuniform, e.g., the direct gaps at Γ and L differ by 0.52 eV and 0.31 eV, respectively.

As a test of the possible role of self-consistency, we have calculated the non-self-consistent correction (i.e., the difference $\Delta\rho(\vec{r})$ between the crystal density $\rho_{cry}(\vec{r})$, and the input superposition density, $\rho_{sup}(\vec{r})$ and its effect on the band structure. Figure 2 shows the dispersion of $\rho(\vec{k}, \vec{r})$ plotted at a few points along the Ti-Se bond direction, as well as the average value $\rho_{cry}(\vec{r})$, obtained by summing over a discrete set of nearest-volume weights and $\vec{k}_i$ points. It is seen that $\rho_{cry}(\vec{r})$ thus
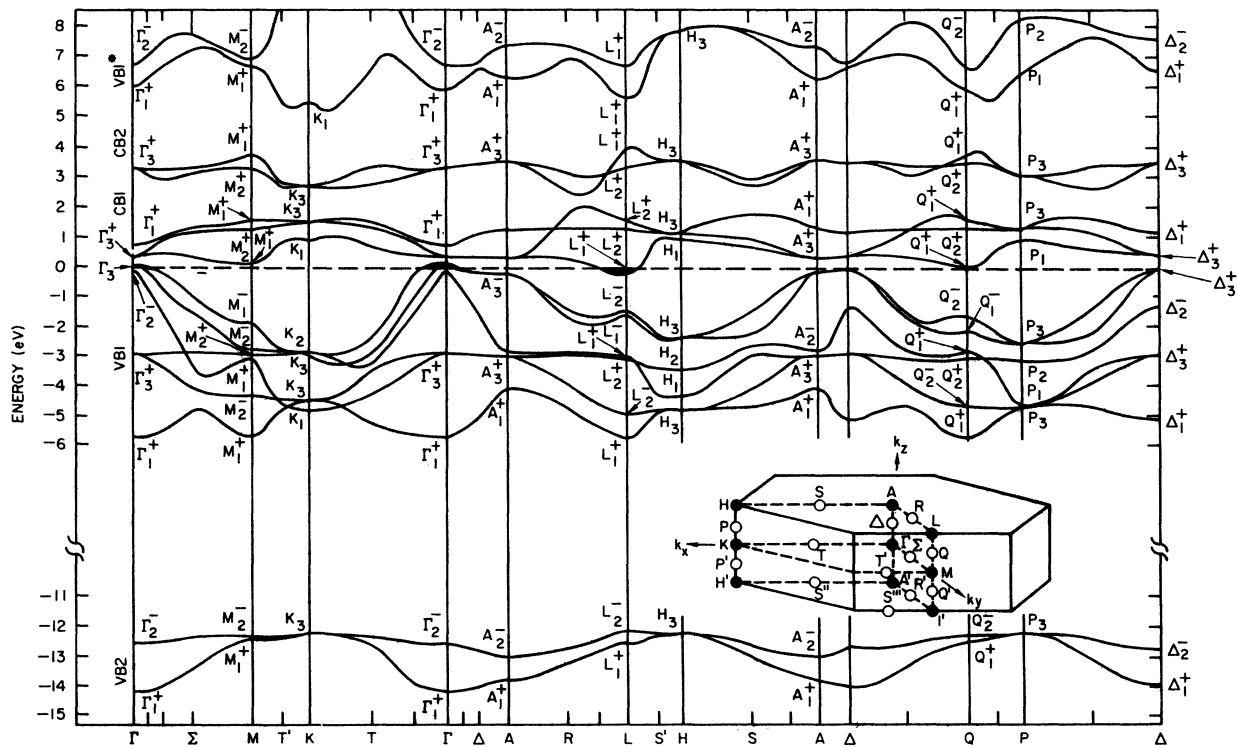

FIG. 1. Energy-band structure of $TiSe_2$ in the local exchange and correlation model.
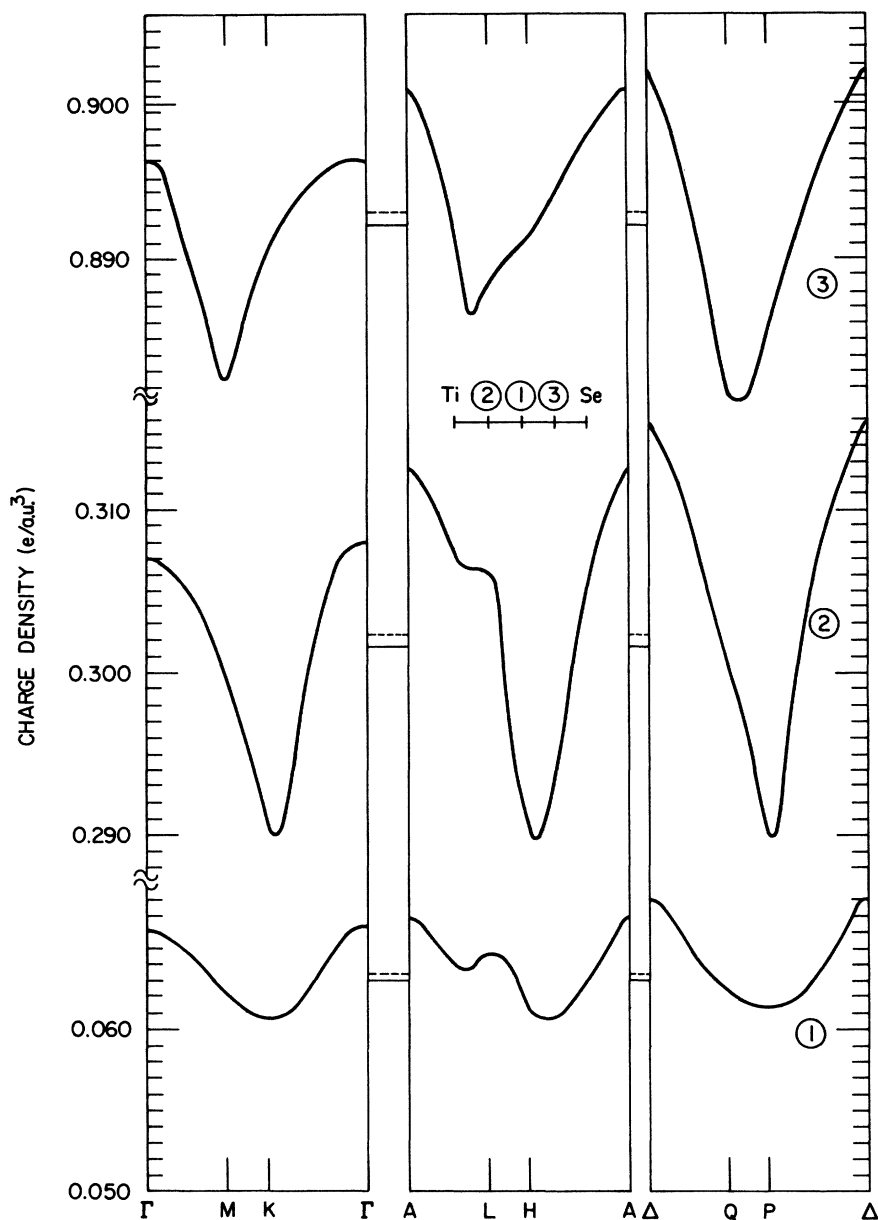
FIG. 2. Dispersion of the charge density under the Fermi energy for three positions along the TiSe bond: (1) bond center, (2) $b/4$ from the Ti site, (3) $b/4$ from the Se site, where b is the bond length. The full horizontal line indicates the average obtained from 9 $\vec{k}$ points while the dashed lines indicate the average obtained from 18 $\vec{k}$ points.

obtained is stabilized to within 0.8% when the Γ-M-K, A-L-H, and Δ-Q-P densities are included, relative to a calculation that incorporates the additional S-T-S'', R-Σ-R', and the S'-T'-S''' contributions. $\Delta\rho(\vec{r})$ is found to be rather small over a substantial part of the unit-cell volume, suggesting that the use of a variational basis set and a potential obtained simultaneously from accurate self-consistent solutions to the single-site one-particle equations with the same LDF used in the crystal calculation provides an approximately self-consistent solution. (In our previous study of TiS$_2$, stronger non-self-consistency deviations were found, due to the more pronounced interatomic

charge transfer. While the effective electronic configuration that minimized $\Delta\rho(\vec{r})$ over the unit-cell space in TiS$_2$ was Ti$^{+0.42}$S$^{-0.21}$, we estimate the corresponding configuration in TiSe$_2$ as Ti$^{-0.1}$Se$^{-.05}$.) To examine the effect of $\Delta\rho(\vec{r})$, we have repeated the calculation for the high symmetry points Γ, M, K and A, L, H incorporating the effect of $\Delta\rho(\vec{r})$ on the crystal potential. This was done by expanding the latter in a Fourier series (using the first 32 reciprocal-lattice vectors) and obtaining the correction $\Delta V(\vec{r})$ to the interelectronic Coulomb potential by solving the associated Poisson equation in reciprocal space. The updated exchange and correlation potentials were obtained by applying

the corresponding functionals directly to $\rho_{\text{sub}}(\vec{r})$ + $\Delta\rho(\vec{r})$. The resulting band structure showed a rigid upwards shift of 0.92 eV, while the $\vec{k}$-dependent shifts were rather small: the $\Gamma_3^- - \Gamma_3^+$ band overlap *increased* to 0.20 ± 0.05 eV while the $\Gamma_3^- - M_1^+$ and the $\Gamma_3^- - \Gamma_3^+$ gaps decreased to 0.12 ± 0.05 eV and 0.32 ± 0.05 eV. The integral of $|\Delta\rho(\vec{r})|^2$ over the unit cell, calculated from the Δ, M, K, A, L, and H points, is reduced from 0.44% to 0.12% of the total unit-cell charge in the second iteration and indicates near self-consistency.

What may be said about the origin of the CDW? The several mechanisms proposed[1,2] involve one or another forms of "nesting" of electron-electron or electron-hole Fermi surfaces. This includes the "exciton-insulator" mechanism which, as emphasized by Wilson and Mahajan,[1] is akin to the large scale "electron-hole" nesting present in Cr and responsible for its spin density wave. Because of the degeneracy of the hole bands along Γ-A and their near degeneracy along Γ-M and Γ-K, the volume of the hole pocket is substantially smaller than that of the singly degenerate electron surface and hence direct "nesting" of these surfaces would seem difficult to achieve. It is possible, however, that large peaks in the generalized susceptibility $\chi(\vec{q})$, arising from characteristic "volume effects" (i.e., two parallel electron-hole bands crossing the Fermi surface) provides the overscreening in these strong electron-phonon coupled systems which drives the observed instability. Plausible candidates in $TiSe_2$ are the very nearly parallel $K_3 - \Gamma_3^-$ and the $L_1^+ - H_1$ bands (cf. Fig. 1) which are separated by a zone-boundary wave vector. Parallel bands, not necessarily crossing E_F, are not peculiar to $TiSe_2$ alone but prevail in many similar compounds such as TiS_2, TaS_2, $TaSe_2$, and VSe_2. Indeed, a major peak in $\chi(\vec{q})$ was found[12] in $1T$-TaS_2 and $1T$-$TaSe_2$ to be caused almost entirely by "volume" effects. It therefore seems highly likely to us that this same mechanism drives the CDW instability in $TiSe_2$. Expressed in terms of the bonding in the system, such an instability can be described as a partially screened interaction between the electrons at L (with their wave-function amplitudes predominantly on the Ti site) and the holes at Γ (with wave-function amplitudes predominantly on the Se site) with a zone boundary phonon supplying the coupling momentum and carrying out the structural change (e.g., shortening of the Ti-Se bond). Finally, whereas the phenomenological correlation between the observed instability temperature and the c/a ratio (or lattice ionicity)[13] works remarkably well for many layered dichalcogenides, including $TiSe_2$, it predicts an instability temperature in excess of 100 °K for TiS_2. Our analysis also suggests an explanation of the failure to observe such an instability in TiS_2: although both TiS_2 and $TiSe_2$ fulfill the volume effect condition, slight differences in the ionicities between them, which are not reflected in a dramatic change in the c/a ratio, are sufficient to place this "nesting" in a *gap* region in TiS_2 and in a *semimetallic* region in $TiSe_2$.

ACKNOWLEDGMENTS

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