Structurally Induced Semimetal-to-Semiconductor Transition in 1*T*-$TiSe_2$

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We show that observed changes in the nature of the conducting state of 1*T*-$TiSe_2$ in going from the normal semimetallic state to the charge-density–wave semiconducting state can be successfully modeled by variation of a single structural parameter, z, which modulates the Ti-Se bond length. These *ab initio* band-structure results lead to a number of interesting experimental consequences.

Current interest in charge-density–wave (CDW) phenomena in metals, especially the layered dichalcogenides of the transition series, remains high, particularly as regards their origin and the physical properties which accompany the transition to the CDW state.[1-4] Recent advances in *ab initio* band-structure theory avoid the approximations underlying the more conventional approaches to the one-electron problem (e.g., muffin-tin approximations, lack of self-consistency, shortcomings in the basis-set representations, etc.), and have been found to describe accurately the properties of the normal state of these compounds. In particular, the nature of the conducting state of TiS_2[5,6] and $TiSe_2$[7] (semiconductor and semimetal, respectively), which had been highly controversial for some time,[8] has now been correctly predicted; even more strikingly, these calculations were able to predict the dimensions of the electron and hole pockets in $TiSe_2$,[7] in excellent agreement both with transport measurements[9] and with recent angle-resolved photoemission data.[9] Similar studies on TiS_2[5] and VSe_2[10] were used to analyze successfully a wealth of experimental data, including x-ray and uv photoemission, optical reflectivity, infrared effective charge, appearance-potential spectra, and transport properties, and have provided a coherent microscopic picture of the chemical bonding in these systems.

Questions pertaining to the electronic properties of the CDW state, however, remain largely unresolved. Although the basic phenomena involving phonon-mediated interactions between the electron and hole pieces of the Fermi surface (FS) have been phenomenologically understood for some time on the basis of simple momentum-conserving geometrical FS models, a theoretical description of the underlying changes in the electronic structure of the CDW state is still lacking. This has a simple practical reason. Unlike the unit cell of the normal phase, which contains a tractable number of atoms, the CDW state is extremely complex (e.g., in $TiSe_2$ it contains 24 atoms and 128 of its 720 electrons are in valence states) and so cannot be treated by the present generation one-electron methods with an accuracy comparable to the relevant band overlaps and band gaps (0.1–0.2 eV).[11] In particular, the large number of internal structural degrees of freedom in the CDW phase, makes it practically impossible to establish a direct correlation between the structural deformations accompanying the CDW formation and the pertinent electronic properties.

We have isolated a simple structural variable in 1*T*-$TiSe_2$ that allows the electronic response to the observed complex pattern of lattice distortions in the CDW state to be modeled in a simple and direct way. This simple structural degree of freedom is the internal crystal parameter[12] z that modulates the Ti-Se bond length and determines the height of the Se atoms above the metal-layer planes. The simplicity of the model permits a detailed study of the electronic response to such structural deformations and provides a direct characterization of the conducting states of the material in terms of its electronic structure. Among other results, variations of this parameter in a first-principles energy-band calculation are found to transform the system from a semimetallic state to a semiconductinglike state characteristic of the CDW phase. The results of these energy-band studies lead to a number of interesting, and possibly important, experimental consequences, including the effect of pressure on the conduction properties and the prediction of the absence of a surface superlattice due to atomic relaxation at the surface.

The band calculations were performed with use of the numerical–basis-set linear combination of atomic orbitals (LCAO) method described previously[5,12]; briefly, it consists of a first-principles LCAO approach to the local-density-functional exchange[13] and correlation[14] Hamiltonian, in which all non–muffin-tin contributions to the potential are fully retained and a nonlinearly optimized 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 constituent atoms, so as to minimize in the least-squares sense the deviation $\Delta\rho(\vec{r})$ between the variationally determined charge density $\rho(\vec{r})$ and the configuration-dependent superposition density.[12] We find that in this system the single-site excitations already provide most of the charge redistribution effects characteristic of the bulk (six iterations are used). The second stage of self-consistency consists of a direct incorporation of the residual–charge-density anisotropy term $\Delta\rho(\vec{r})$ into the crystal potential. Since we find that, in $\mathrm{TiSe_2}$, $\Delta\rho(\vec{r}) \ll \rho(\vec{r})$ over the entire unit-cell space, only a single iteration appears to be sufficient for this final stage. The resulting band structure for the observed z value[7] (0.25) shows a characteristic semimetallic behavior with a hole pocket around Γ and an electron pocket around L. The *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 $\Gamma_3^- - M_1^+$ and $\Gamma_3^- - \Gamma_3^+$ indirect and direct bands *gaps* are 0.15 ± 0.03 eV and 0.35 ± 0.03 eV, respectively. The dimensions of the electron pocket around L (as a percentage 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 $(7\text{–}8) \times 10^{20}$ conduction electrons per cubic centimeter in the perfect crystal, in very good agreement with the independently reported transport[1] (see modified results quoted in Ref. 9) and angle-resolved photoemission[9] experiments.

The realization that the essential characteristics of the band structure of the normal phase (e.g., hybridization gap, trigonal splitting of the bottom of the conduction band at Γ, the bonding-antibonding gap, and the p-d band overlap) depend critically on the detailed interplay between the strong s-p metal-nonmetal hybridization on one hand, and the weaker participation of the metal d states in the bond formation on the other hand, led us to choose z as the relevant internal structural parameter for CDW studies. Variations in the Ti-Se bond length and bond angle, effected through changes in z, are directly associated with changes in the relative contributions of d versus s-p orbitals to the bond formation and phase stabilization (e.g., by modifying the degree of localization of the d states and enhancing s-d hybridization). We have consequently carried out detailed band-structure calculations for bulk $\mathrm{TiSe_2}$ as a function of z in order to establish the effect of atomic rearrangement of its electronic structure. Calculations were performed for eight values of z which is related to the Ti-Se distance R by $R = (\frac{1}{3}a^2 + z^2c^2)^{1/2}$, where a and c are the lattice constants. The variation in the energy bands in the vicinity of the Fermi level with z, for z ranging between 0.220 and 0.265, is depicted in Fig. 1.

The lower states Γ_3^+, M_1^-, L_1^-, and L_2^- (full lines in Fig. 1) belong to the occupied bands and represent in-plane (x-y) bonding combinations of the σ-type s, p, and d states. Their energies decrease as the bond length is reduced as a result of the enhanced intersite overlap. On the other hand, the upper L_1^+, M_1^+, Γ_3^+, and Γ_1^+ states (dashed lines) represent nonbonding and antibonding conduction d and s states and are substantially destabilized by reducing the bond length. One observes that as z increases, the overall width of the d-based conduction band ($L_1^+ - \Gamma_3^+$) drops rapidly and both the trigonal splitting $\Gamma_1^+ - \Gamma_3^+$ of the "t_{2g}" state and the "$t_{2g} - e_g$" hybridization gap (Γ_1^+ with upper Γ_3^+) is drastically reduced, suggesting enhanced localization of the d states. There are three different regimes in the conduction characteristics of the system, as a function of z:

(i) In the intermediate-z region, $0.238 \lesssim z \lesssim 0.260$, the L_1^+ conduction state is more stable than the Γ_3^- and Γ_2^- valence states, leading to the semimetallic behavior observed in the bulk[1,2,9] with an *isolated* electron surface around L in the Brillouin zone (extending only about half-way to M in the L–M direction) and a double hole surface around Γ.

(ii) In the low-z regime, $z \lesssim 0.235$, the L_1^+ state has acquired antibonding character (by hybridizing with the out-of-plane p_z states of Se) and has consequently increased its energy to cross the Γ_3^- (x-y) valence states, *producing a semiconductor* (cross-hatched region in Fig. 1). The electrons now tend to occupy the Γ_3^- and Γ_2^- states which are deeper in energy, leading to a possibly more stable state of the system in the dimerized phase. This may be viewed as a simple two-dimensional analog of a Peierls-type transition.

The displacement pattern actually observed in the CDW state of $\mathrm{TiSe_2}$ produces an average short-

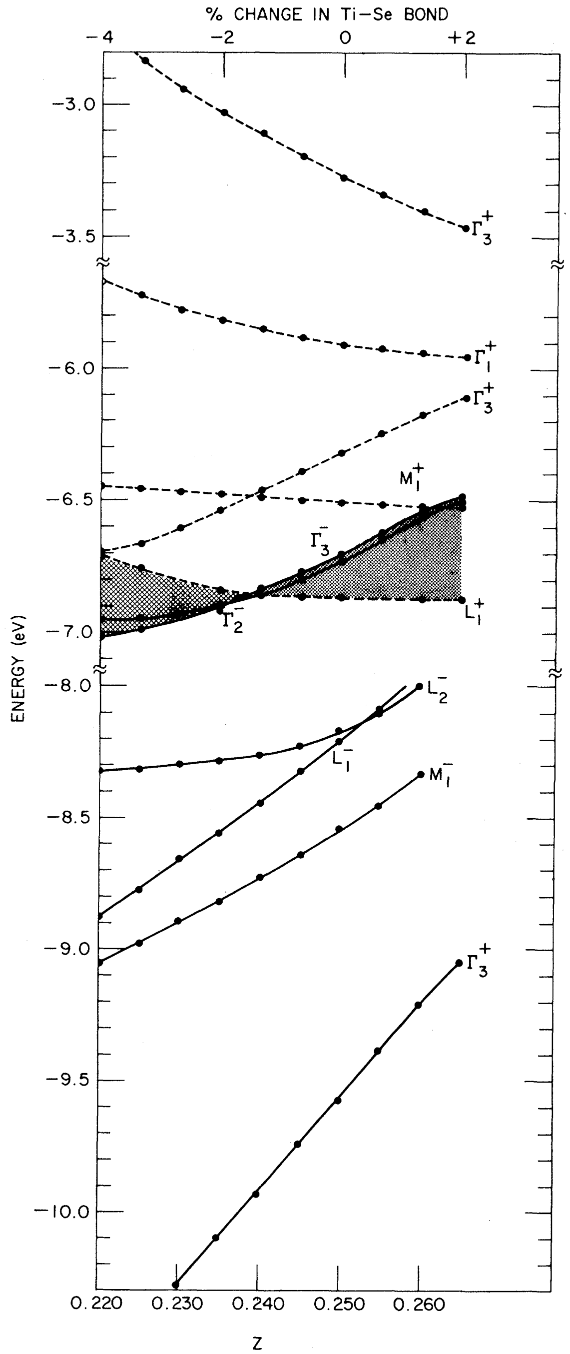

FIG. 1. Dependence of various band energies in $TiSe_2$ on the parameter z. Full lines indicate valence bands while dashed lines correspond to conduction bands. The shaded area indicates the metallic region while the cross-hatched region denotes the semiconducting region. Full dots correspond to calculated points.

ening of the Ti-Se bond length by 0.08 Å (3.3%) due to distortions in the positions of a majority (i.e., 75%) of atoms, while the rest of the atoms do not move.[1] If one is to simply simulate the effect of the average bond shortening (2.4%) on the electronic structure of the CDW state by considering a normal phase with a similar bond shortening (i.e., $z = 0.232$), the results of Fig. 1 indicate *a transition 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[1] that the bond shortening in the CDW phase is accompanied by an increase in the resistivity and a decrease in the magnetic susceptibility, suggesting 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 manifold and by an enhanced trigonal splitting of the t_{2g} levels and indicates a considerable increase in the covalency of the system.

(iii) In the high-z regime, $z \gtrsim 0.260$, the metal d electrons tend to localize as the atoms are further separated; this lowers the repulsive character of the antibonding d-based states at M_1^+ and produces a *continuous* distorted cylindrical electron surface ranging from L to M, instead of the *isolated pocket* at L. The system is now characterized by more atomiclike d states, presumably with lower mobilities and a resulting narrow conduction band with reduced hybridization and crystal-field gaps. Unlike the case of low z, the covalency of the system is reduced as the bonding-antibonding gap, which accommodates the d-based conduction band, is reduced. An increase in the parameter z corresponds also to a decrease[15] of the distance between nearest-neighbor sandwiches (van der Waals gap). On the basis of the softness of the crystal towards squeezing this gap, one would expect that the large-z regime would also simulate the effect of an applied external pressure. A recent study by Friend *et al.*[11] has indeed shown that the in-plane resistivity of the normal phase decreases with pressure. Our model provides a simple physical explanation of this effect in terms of the formation of a larger Fermi-surface area due to the stabilization of the d-based conduction states. Finally, we note that because of atomic relaxation at the surface, an expansion of z may well take place near the surface of a sample.[16] The change of electron Fermi surface which accompanies an increase in z would destroy the electron-hole nesting responsible for the CDW instability[7] (in that a continuous distorted cylindrical electron surface at $L-M$ is unlikely to nest with the small double hole pocket at Γ) 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 surface which is underway.[16] We note that the existence of such a fundamental sensitivity of the electronic and transport properties to the structure parameter z is found to be unique to the group-IV $1T$-dichalcogenides; since the Fermi-surface–induced structural instabilities in the group-V $1T$-dichalcogenides are related primarily to electron-hole coupling *within* a single connected surface, a modulation of the bond does not lead to the disappearance of the instability.[10] In line with this, we note the experimental evidence for the occurrence of the surface superlattice in the group-V Ta dichalcogenides.[17]

In conclusion, we feel that although more complex 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 parameter provides a physically appealing interpretation to the variation in the conducting states and yields a quantitatively correct deformation parameter. As we have seen, energy-band results based on variation of z yields the essential elements of the relations between the structure and the conduction state of the material. The existence of such a band-overlap modulation so sensitive to particular atomic displacements might lead to important experiments, including the effect of intercalation and pressure on the conduction properties as well as the prediction of the absence of a *surface* superlattice due to atomic relaxation at the surface.

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