Spin-orbit coupling in the band structure of reconstructed 1*T*-TaS_2

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Empirical tight-binding simulations of the band structure of 1*T*-TaS_2 reveal that the combination of spin-orbit coupling and the low-temperature $\sqrt{13}\times\sqrt{13}$ reconstruction generates a distinct and very narrow band at the Fermi level. Spin-orbit interaction is therefore important in any understanding of the correlation effects in this material. The states within the split-off band are primarily of $d_{x^2-y^2}$, d_{xy} character and reside preferentially on the central atom of the "Star-of-David" cluster.

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Tantalum is a heavy element and so spin-orbit interaction is expected to be important in the valence band structure of compounds such as the intriguing material 1*T*-TaS_2. The transition-metal dichalcogenides are layered materials that provide a fertile field for the study of correlation effects in the two-dimensional electron gas. At low temperatures 1*T*-TaS_2 displays structural changes associated with charge-density-wave formation and undergoes a metal-insulator transition. The possible importance of spin-orbit coupling in driving these phenomena was suggested many years ago[1] but there appears to have been very little follow-up. In this brief report, we report the results of some empirical tight-binding simulations of the band structure of 1*T*-TaS_2 which show that spin-orbit coupling, in combination with the reconstruction that this material undergoes at low temperature, is indeed important. We find a distinct and very narrow split-off band at the Fermi level that is ripe for a Mott-Hubbard transition. We further find that the states within this band have specific orbital character and atomic location. Thus spin-orbit coupling emerges as an ingredient in any understanding of many-body correlations in 1*T*-TaS_2 and related materials.

Our approach is to extend a simple tight-binding scheme presented earlier.[2] The starting point is a fit of the Slater-Koster parameters, using only Ta 5*d* orbitals and the nearest-neighbor two-center approximation, to an early first-principles band structure calculation by Mattheiss.[3] Spin-orbit coupling is added by inclusion of the intra-atomic matrices M and N of Abate and Asdente[4] and by use of the Herman-Skillman value[5] of the spin-orbit parameter (ξ=0.313 eV). Band structures with and without spin-orbit coupling are illustrated in Fig. 1(a) for the unreconstructed case. Although there are some large splittings in the bands (e.g., $\approx$0.6 eV in the lowest state at Γ), the effect on the Fermi surface and its topology is very small. At first sight, the effects of spin-orbit interaction could easily be dismissed. But, as we shall show below, it is not just spin-orbit coupling but rather the *combination* of spin-orbit coupling and the reconstruction that leads to dramatic effects. The occupied valence band is sometimes loosely referred to as the Ta d_{z^2} band. This is misleading. The mean energies in the crystal-field diagram of Fig. 1(b) indicate comparable importance for the $d_{x^2-y^2}$ and d_{xy} orbitals giving a foretaste of the results to come.

At low temperatures, 1*T*-TaS_2 undergoes a commensurate reconstruction into a $\sqrt{13}\times\sqrt{13}$ rotated unit cell containing 13 Ta atoms as illustrated in Fig. 2. There are three inequivalent types of Ta atoms in the unit cell designated as "a," "b," and "c." Clusters centered on atoms of type "a" have a "Star-of-David" structure characterized by a shrinkage of the ab and bc interatomic distances by 6.4 and 3.2 %, respectively.[6]

Our tight-binding simulation of the effects of the reconstruction starts as previously described.[2] The Hamiltonian of the unreconstructed case was opened out into the larger unit cell. To simulate the reconstruction, the Slater-Koster hopping integrals $dd\sigma$, $dd\pi$, and $dd\delta$ were scaled as R^{-5} where R is the Ta-Ta distance.[7] Bonds within the Star-of-David

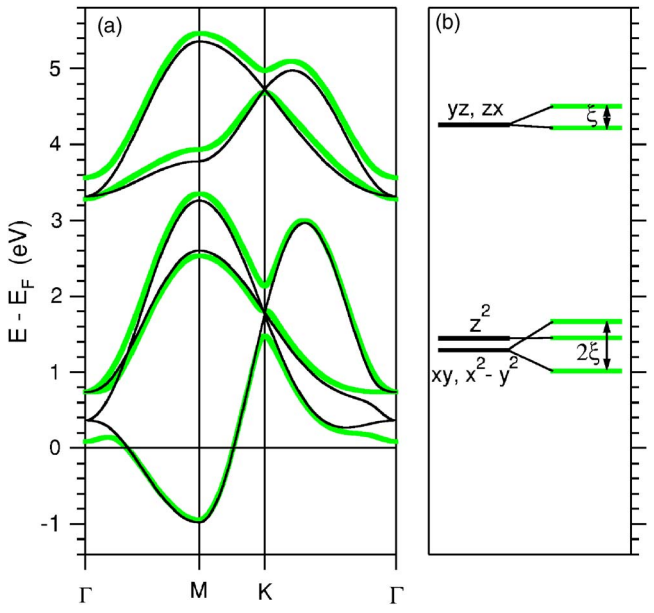

FIG. 1. (Color online) (a) Band structure of 1*T*-TaS_2 both with [bold green (light gray) curves] and without (thinner black curves) the Ta 5*d* spin-orbit coupling. (b) Crystal-field diagram showing the mean energies of the z^2, x^2-y^2/xy, and yz/zx orbitals. The energy scales have been adjusted to bring the Fermi levels into alignment.

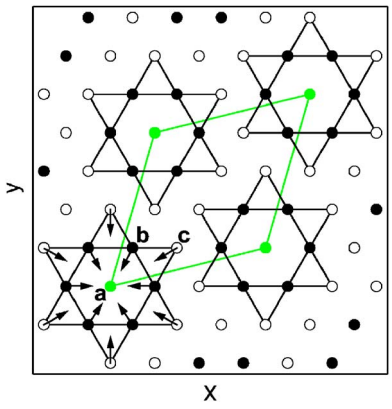

FIG. 2. (Color online) Unit cell of the $\sqrt{13}\times\sqrt{13}$ reconstruction of $1T$-TaS_2 showing the "Star-of-David" clusters having inequivalent "a," "b," and "c" Ta atoms. The arrows indicate the displacements of the Ta atoms from their original positions.

clusters are thereby strengthened and other bonds are weakened. The bond-length changes are known, so from hereon there are no further disposable parameters. (At this level of approximation, we ignore the slight nonradial movements[6] in the formation of the clusters.)

Figure 3 summarizes our results by showing the progressive effects of inclusion of reconstruction and spin-orbit interaction. Figure 3(a) shows the effect of opening out into the 13-atom unit cell; the bold green curves are the original bands and the thinner black curves are the Umklapp or "shadow" bands obtained by translation through the reciprocal lattice vectors of the smaller Brillouin zone.

The effect of introducing the bond strengthenings and weakenings is illustrated in Fig. 3(b). The band structure collapses into submanifolds.[2] There are two low-lying three-band submanifolds each containing six electrons. The "13th" electron (each Ta atom has one $5d$ valence electron) resides at the bottom of a messy-looking set of bands sometimes referred to as "spaghetti." The existence of the submanifolds has been confirmed by angle-resolved photoemission spectroscopy (ARPES) measurements[2,8] and some of the substructure within the submanifolds has been resolved.[9] Our model is two dimensional. First-principles calculations of the reconstructed band structure[10] indicate that three-dimensional interlayer interactions are significant. Band dispersion in the z direction would be very easy to incorporate in our model but is deferred for future study since we wish to highlight here spin-orbit effects. The main effect of z dispersion is a slight broadening of the density-of-states features[3] which arises through a $dd\sigma$-type coupling between Ta d_{z^2} orbitals in adjacent layers.

The combined effects of reconstruction and spin-orbit coupling are shown in Fig. 3(c). The changes within the low-lying three-band submanifolds are relatively minor, consisting of some liftings of degeneracies and some second-order energy shifts. The really striking effect is the conspicuous emergence of a distinct and very narrow band at the Fermi level shown in bold green in Fig. 3(c). We offer this effect as the principal result of this brief report. Reconstruction generates a gap just below the spaghetti; spin-orbit coupling splits off a band into this gap. The band has a very small width ($\approx$80 meV) and is therefore susceptible to a Mott-Hubbard transition, as proposed by Fazekas and

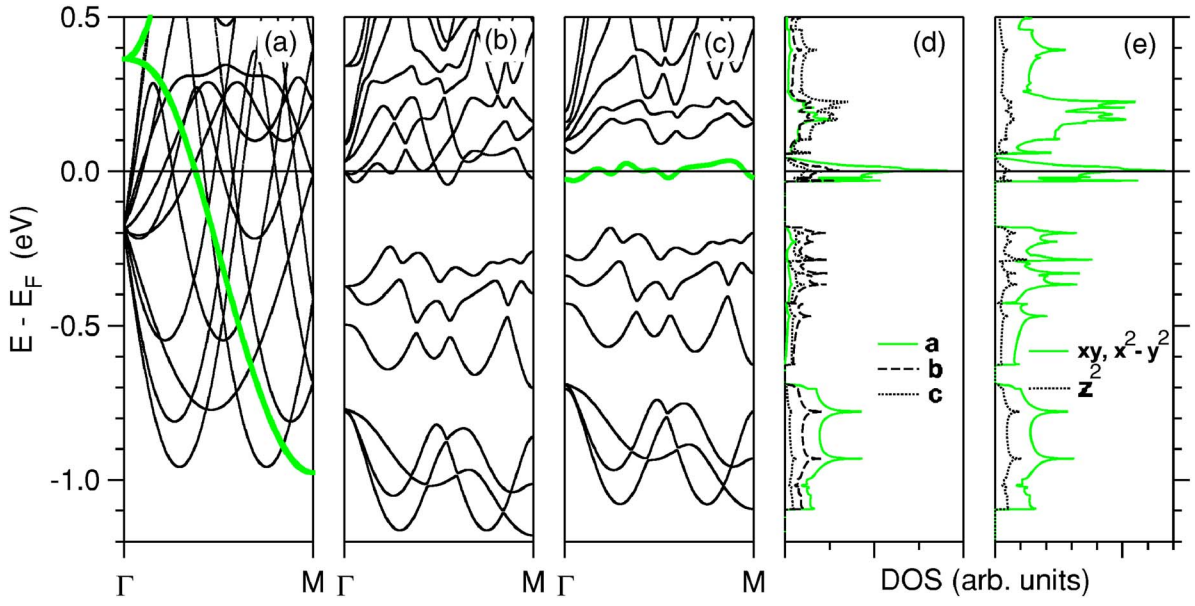

FIG. 3. (Color online) (a) Band structure of $1T$-TaS_2 in the unreconstructed case [bold green (light gray) curves] and the Umklapp bands (thinner black curves) generated by translation through the reciprocal lattice vectors of the reconstructed Brillouin zone. (b) Reconstructed band structure with inclusion of the bond strengthenings within the Star-of-David as described in the text. (c) Reconstructed band structure with inclusion of Ta spin-orbit coupling revealing [bold green (light gray) curve] a single distinct split-off band. (d) Atom-projected densities of states showing that the states in the split-off band reside primarily on the "a" atoms at the center of the cluster. (e) Orbital-projected densities of states showing that the states in the split-off band are primarily of x^2-y^2/xy character. The energy scales have been adjusted to bring the respective Fermi levels into alignment.

Tosatti.[1] Reconstruction and spin-orbit interaction are both essential for this effect to occur.

Our tight-binding model generates information on atomic location and orbital content of the electron states. Atom-projected and orbital-projected densities of states are shown, respectively, in Figs. 3(d) and 3(e). It is seen that the states in the narrow split-off band are located preferentially on the central "a" atom of the Star-of David cluster and are primarily of $d_{x^2-y^2}$ and d_{xy} character with only very weak admixture of d_{z^2} character. The z dispersion of this band should therefore be very small. This information should be of use to many-body theorists seeking a minimal orbital set for Mott-Hubbard type models.[11] Specifically, the orbitals of concern are the degenerate $(d_{x^2-y^2}+id_{xy})\alpha$ and $(d_{x^2-y^2}-id_{xy})\beta$ wave functions where α and β are the usual up and down spin functions.

In closing, we have argued that spin-orbit coupling is essential to any understanding of the intriguing properties of $1T$-TaS_2. We have focused here only on spin-orbit splitting within the Ta-derived valence band. Clerc *et al.*[12] have recently reported ARPES measurements which resolve the spin-orbit splitting within the chalcogen p-derived bands in both $1T$-TaS_2 and $1T$-$TaSe_2$. They point out that the larger spin-orbit splitting in Se and its greater hybridization with the Ta d bands could be implicated in the different physical properties of these isostructural materials. The need for further theoretical and experimental scrutiny of the role of spin-orbit interaction in these and related materials is clearly desirable.

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