Electronic structure of $1T$-TiS_2

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We present state-of-the-art band-structure calculations for the $1T$ phase of TiS_2. We have used the full-potential linear augmented-plane-wave method as embodied in the WIEN97 code. Our calculations show that $1T$-TiS_2 is semimetallic at ambient pressure in agreement with the recent calculations based on the augmented spherical wave (ASW) and the linear-muffin-tin-orbital methods but in disagreement with the more recent pseudopotential calculations. In order to ascertain the effect of lattice parameters on the band structure, we have performed calculations for lattice parameters corresponding to hydrostatic pressures up to 7.6 GPa. Our calculations show that $1T$-TiS_2 remains semimetallic at these pressures. Calculations are also performed for the slab geometry to ascertain whether the band overlap decreases with increasing distance between the TiS_2 layers making it a semiconductor as revealed by the ASW calculations. We find that $1T$-TiS_2 is semimetallic in the slab geometry, too. [S0163-1829(99)01920-7]

The study of the electronic properties of the transition-metal dichalcogenides (TMDC) has been actively pursued during the past three decades due to their potential for a variety of technological applications. The TMDC can exist in various crystallographic structures. These compounds have very anisotropic physical properties so much so that they can be regarded as two-dimensional solids due to the strong covalent bound layers held together by weak Van der Waals forces. As a result of this, the TMDC can be intercalated with foreign atoms and molecules leading to significant and dramatic changes in their electronic properties. For example, the intercalation of lithium in TiS_2 has led to its use in lithium batteries.

TiS_2 is known to exist in two phases, $1T$-TiS_2 (trigonal prismatic) and $2H$-TiS_2 (octahedral coordination). Of these, the $1T$-TiS_2 is the most studied phase experimentally as well as theoretically.[1–16] the electronic band structure of this phase has been clouded with controversy. We address this controversy regarding the electronic band structure of $1T$-TiS_2 (henceforth termed as TiS_2 only) in this paper and try to redress it. The earlier calculations of Umrigar *et al.*[7] using the self-consistent linear augmented-plane-wave (LAPW) scheme showed that TiS_2 is a semimetal. This was in contrast with the optical experiments of Greenway and Nitsche,[1] who suggested that TiS_2 is a semiconductor with a gap of 1–2 eV. The optical experiments of Liang and his co-workers[2,3,6] could not help in resolving this discrepancy as their data did not extend to low energies. From the measurements of the Hall coefficient, thermoelectric power, and resistivity as a function of pressure, Klipstein and Friend[8] concluded that the band overlap increased at a rate 4.5 meV/Kbar. This suggested that TiS_2 is a semiconductor with a gap of around 0.18 eV. Benesch *et al.*[9] calculated the band structure of TiS_2 using the LAPW method, as a function of pressure, and confirmed this increase in band overlap. However, their calculations also gave a semimetallic ground state. In the last two years research activity in TiS_2 has suddenly increased as is evident by the number of papers published.[10–16] Recent measurements of the polarized x-ray-absorption near-edge spectra have further contributed to interest in this compound.[16] Although recent band calculations based on the augmented spherical wave (ASW) method by Fang *et al.*[11] and the linear-muffin-tin-orbital (LMTO) method by Wu *et al.*[10,12] show TiS_2 to be semimetallic, a more recent calculation using the pseudopotential (PP) method shows it to be a semiconductor with an indirect gap of about 2 eV.[15] These authors have measured the lattice parameters of TiS_2 under hydrostatic pressure up to 7.62 GPa. Using their experimentally determined lattice parameters, they have performed

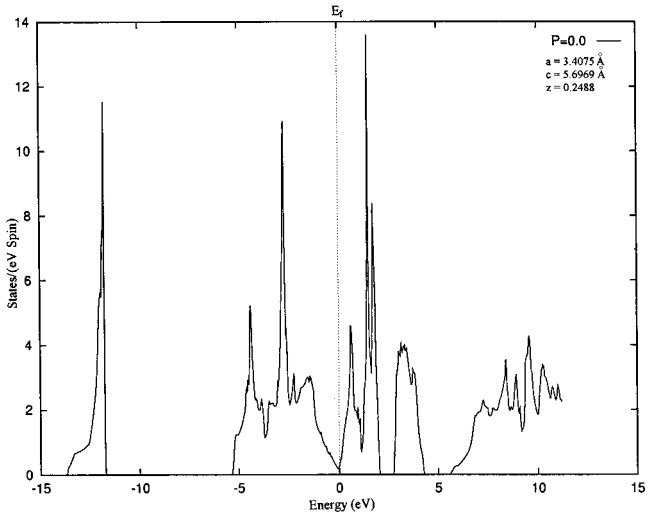

FIG. 1. The density of states of $1T$-TiS_2 at ambient pressure.

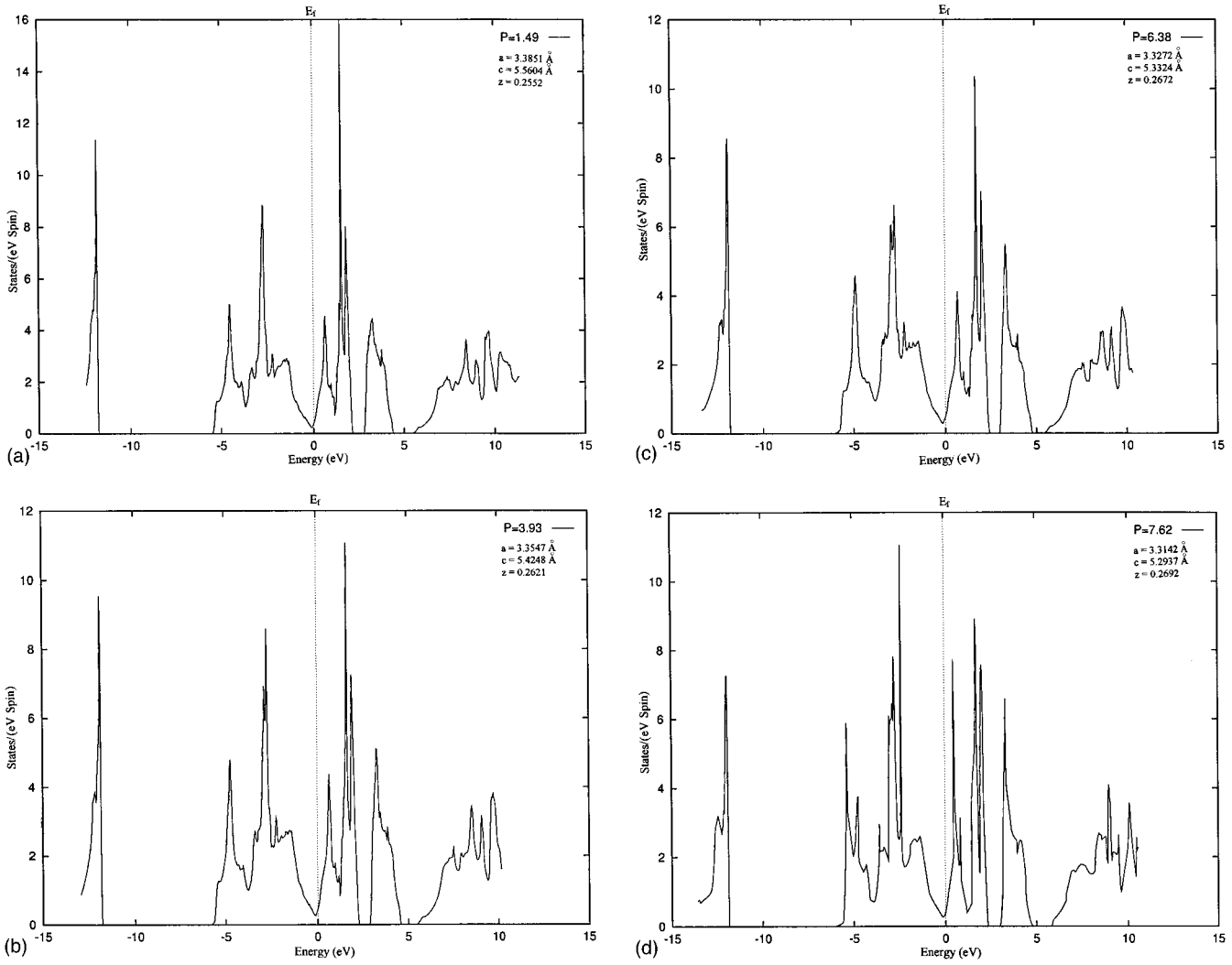

FIG. 2. The density of states of $1T$-TiS_2 at different hydrostatic pressures. The lattice parameters are given in the figure parts. (a) corresponds to 1.49 GPa, (b) to 3.93 GPa, (c) to 6.38 GPa, and (d) to 7.62 GPa.

band calculations using the PP method and find that the energy gap is reduced, as a function of pressure, and around 4–6 GPa TiS_2 becomes semimetallic.

In view of the conflicting results about the ground state of TiS_2 from the PP band calculations compared to those from LAPW, ASW, and LMTO calculations, we have tried to resolve this discrepancy once and for all. The LAPW, ASW, and LMTO calculations suffer from the drawback that they use an approximate potential. It would be worthwhile to calculate the band structure using a potential with no shape approximation. We have performed calculations on TiS_2 using the full-potential linear augmented-plane-wave (FPLAPW) method as incorporated in the WIEN97 code.[17] These are reported in this paper. We have also performed calculations of TiS_2 under hydrostatic pressures up to 7.6 GPa using the measure lattice parameters to ascertain if changing the lattice parameters has any effect on the ground state. Calculations are also performed for TiS_2 in the slab geometry with the aim to study the effect of increasing the interlayer distance of the MX_2 sandwich on the nature of the ground state.

Calculations are performed using the full-potential linear augmented-plane-wave method as implemented in the WIEN97 code, including local orbitals for the high-lying ''semicore'' states. Exchange and correlation are treated within the local-density approximation (LDA) and the scalar-relativistic equations are used to obtain self-consistency. We have used the Barth-Hedin exchange correlation potential.[18] In contrast to previous LDA calculations, no shape approximation to the potential or the charge density is made. This could be the reason for the differences between the ASW, LAPW, and LMTO calculations from the PP calculations. All the calculations are performed using 100 k points in the irreducible Brillouin zone.

TiS_2 crystallizes in the $1T$-type $Cd(OH)_2$ structure (space group $P3m1$). One Ti atom is at $1a$ (origin) and two S atoms at $2d$ $(\frac{1}{3},\frac{2}{3},z)$and $(\frac{2}{3},\frac{1}{3},-z)$ sites. First we performed calculations for TiS_2 at ambient pressure using the lattice parameters given in Fig. 1. Our calculations indicate that TiS_2 is a semimetal in accordance with the recent ASW (Ref. 11) and LMTO (Refs. 10 and 12) calculations, and the earlier LAPW calculations.[7,9] However, this is in contrast to a very recent PP calculation, which predicts TiS_2 to be a semiconductor with an indirect gap of around 2 eV.

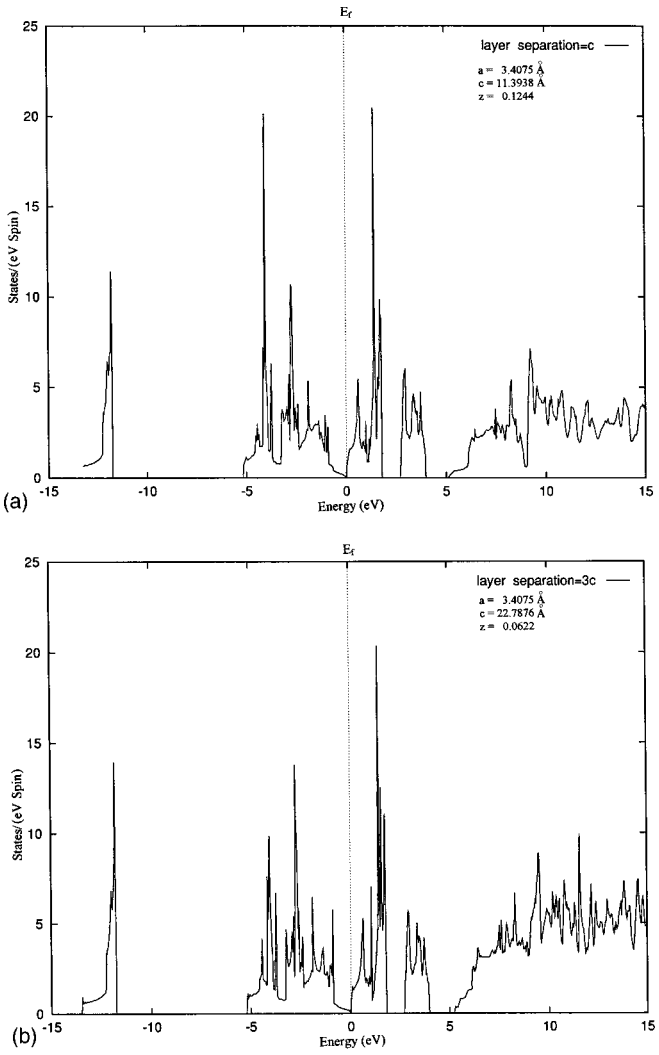

FIG. 3. The density of states of $1T$-TiS_2 in the slab geometry. (a) corresponds to a lattice parameter twice the ambient pressure value and (b) to four times. Lattice parameters are given in the figures.

The density of states (DOS) from our calculations is shown in Fig. 1. From the partial DOS we are able to identify the angular moment character of the various structures. The sharp peak around -11.8 eV is mainly due to the S-s states, the peak around -4.4 and -2.0 eV due to S-p states, and the -2.7 eV peak has contributions from the Ti-d and S-p states. In the conduction bands, the peaks at 0.6, 1.5, and 3.2 eV have mainly Ti-d character while the 10 eV structures contain mixtures of S-p and Ti-spd states. The DOS at Fermi energy (E_F) is controlled by the overlap between the S-p states (valence) and Ti-d states (conduction). This overlap is small resulting in a semimetallic state with a DOS of E_F of 2.3 states/(eV spin).

Since the DOS at E_F is very small, a change in the lattice constant might result in the disappearance of the overlap and in the opening up of an energy gap at E_F. As the lattice parameters of TiS_2 have been measured experimentally[15] under various pressures, we have performed calculations using lattice parameters corresponding to hydrostatic pressure of 1.5, 3.9, 6.4, and 7.6 GPa. The DOS for these is plotted in Fig. 2. Again we find the semimetallic behavior. The DOS at E_F for these pressures is 0.38, 0.43, 0.47, and 0.38 states/(eV spin). This seems to suggest that the overlap is unchanged with pressure. However, some small changes in the DOS as a function of pressure are evident by looking at the figures. Some significant changes are the development of a small secondary peak in the S-s states and the sharp rise in the bottom of the S-p states.

Recently Fang *et al.*[11] have performed calculations for bulk, single slab, and thin films of TiS_2. These calculations show that a single slab of TiS_2 is semiconducting. The single slab calculations were performed for a single layer of TiS_2 separated by three sandwiches of empty spheres. The distance between the slabs is large enough so interaction between the slabs is negligible. Hence surface relaxations are neglected. We have done calculations for two separations of the TiS_2 layers. In the first case the layers are separated by the lattice constant c, i.e., the c lattice constant is twice the ambient pressure value) while in the second case this separation is $3c$ (i.e., the c lattice constant is four times the ambient pressure value). In this way we hope to study the effect of interlayer separation on the overlap between the Ti-d and S-p states. The DOS for both these calculations is shown in Fig. 3. The DOS at E_F is 0.45 and 0.61 states/(eV spin), respectively, indicating a very small change in DOS at E_F as the layer separation is increased. However, there are no dramatic changes in the overall DOS. While the ambient pressure DOS shows one sharp peak in the occupied bands, the slab DOS shows a peakier behavior. The unoccupied bands DOS for the slab is similar to the bulk DOS.

Our state-of-the-art full-potential calculations show that at ambient pressure TiS_2 is semimetallic. The conflicting results of the non-full-potential calculations seem to indicate the errors inherent in such calculations. The LAPW, ASW, and LMTO calculations give the correct semimetallic behavior while the PP calculations give a rather large gap of around 2 eV. However, since the LDA is known to underestimate gaps by as much as 50%, it could still be possible to speculate that TiS_2 is a semiconductor with a small energy gap. To study the effect of the pressure on the semimetallic/semiconducting nature of this material, we performed calculations using lattice parameters corresponding to pressures up to 7.6 GPa. These calculations seem to suggest no significant change in the band overlap near E_F as a function of pressure. The calculations of the slab geometry also do not show any significant change in the Ti-d, S-p overlap as the distance between TiS_2 layers in increased. In fact, in contrast to the ASW calculations for the slab geometry which yield a semiconducting behavior, our calculations show that TiS_2 is still semimetallic.

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[1] D. L. Greenway and R. Nitsche, J. Phys. Chem. Solids, **26**, 1445 (1965).
[2] A. R. Beal, J. C. Knights, and W. Y. Liang, J. Phys. C **5**, 3531 (1972).
[3] A. R. Beal and W. Y. Liang, Philos. Mag. **27**, 1397 (1973); J. Phys. C **6**, L482 (1978).
[4] D. W. Fischer, Phys. Rev. B **8**, 3576 (1973).
[5] P. B. Perry, Phys. Rev. B **13**, 5211 (1976).
[6] W. Y. Liang, G. Lucovsky, R. M. White, W. Stutius, and K. R. Pisharody, Philos. Mag. **33**, 492 (1976).
[7] C. Umrigar, D. E. Ellis, D. S. Wang, H. Krakauer, and M. Posternak, Phys. Rev. B **26**, 4935 (1982).
[8] P. C. Klipstein and R. H. Friend, J. Phys. C **17**, 2713 (1984).
[9] G. A. Benesh, A. M. Woolley, and C. Umrigar, J. Phys. C **13**, 1595 (1985).
[10] Z. Y. Zu, G. Ouvrard, S. Lemaux, P. Moreau, P. Gressier, and F. Lemoigno, Phys. Rev. Lett. **77**, 2101 (1996); Z. Y. Wu, F. Lemoigno, P. Gressier, G. Ouvrard, P. Moreau, J. Rouxel, and C. R. Natoli, Phys. Rev. B **54**, R11 009 (1996).
[11] C. M. Fang, R. A. de Groot, and C. Haas, Phys. Rev. B **56**, 4455 (1997).
[12] Z. Y. Wu, G. Ouvrard, P. Moreau, and C. R. Natoli, Phys. Rev. B **55**, 9508 (1997).
[13] F. Mendizabal, R. Contresas, and A. Aizman, J. Phys.: Condens. Matter **9**, 3011 (1997).
[14] A. Simunek, O. Sipr, S. Bocharov, D. Heumann, and G. Drager, Phys. Rev. B **56**, 12 232 (1997).
[15] D. R. Allan, A. A. Kelsey, S. J. Clark, R. J. Angel, and G. J. Ackland, Phys. Rev. B **57**, 5106 (1998).
[16] S. Bocharov, G. Drager, D. Heumann, A. Simunek, and O. Sipr, Phys. Rev. B **58**, 7668 (1998).
[17] P. Blaha, K. Schwarz, and J. Luitz, WIEN97, Vienna University of Technology, 1997 (improved and updated Unix version of the original copywright WIEN code) which was published by P. Blaha, K. Schwartz, P. Sorantin, and S. B. Trickey, Comput. Phys. Commun. **59**, 399 (1990).
[18] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).