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High-pressure semiconductor-semimetal transition in TiS_2

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We present results of high-pressure single-crystal x-ray-diffraction studies and *ab initio* pseudopotential calculations of stoichiometric TiS_2. Neither present any evidence for a structural phase transition; it is shown that the material undergoes an isostructural semiconductor-semimetal phase transition between 4 and 6 GPa. [S0163-1829(98)04106-X]

Due to their outstanding potential for a variety of technological applications there is considerable interest, at both an applied and fundamental level, in the structural, electronic, and optical properties of the transition-metal dichalcogenides and their intercalation compounds.[1,2]

These compounds have the formula TX_2, where T is a transition-metal atom from group IV, V, or VI in the Periodic Table and X is one of the chalcogens: sulfur, selenium, or tellurium. They are highly anisotropic materials, sometimes referred to as two-dimensional solids, because they have strongly (ionic/covalent) bound layers held together by weak dispersion forces.

A variety of electron donors or Lewis bases, such as alkali metals and many organic molecules, can be intercalated between the layers.[1–3] This can often induce rather dramatic changes in the electronic properties of the host lattice, and these changes can be understood in terms of charge transfer and increased interlayer separation. Under appropriate conditions, TiS_2 also shows superionic behavior. Recently, the intercalation and ionic conduction of lithium in TiS_2 has been exploited in its use as a positive electrode in rechargeable lithium batteries.[4,5]

Detailed studies on the electronic structure of pure TiS_2 under ambient conditions, however, have produced conflicting conclusions.[6–10] Some band-structure calculations[8,9] indicate that an indirect p/d band overlap exists with an overlap ranging from 0.2 to 1.5 eV while others infer that TiS_2 is a narrow gap semiconductor. None of these calculations have optimized the atomic structure, and in view of the subtlety of the effects it is clearly important to use a method which consistently optimizes the atomic and electronic structure.

Due to the strong tendency toward nonstoichiometry with titanium excess, all physical measurements performed to define the true nature of TiS_2 (semimetal or semiconductor) have to be considered with great caution. For example, the experimental evidence gathered in photoemission experiments have been interpreted as indicating either semimetallic[9] or semiconducting[8] behavior. Resistivity measurements in highly stoichiometric titanium disulphide indicate a metallic behavior at all temperatures,[11,12] while Hall coefficient and thermoelectric power measurements support the semiconducting hypothesis.[13] More recently, however, Wu *et al.*[10] have combined x-ray-absorption spectroscopy and electron-energy-loss spectroscopy measurements with linear muffin-tin band-structure calculations to conclude that TiS_2 is a metal or semimetal at ambient pressure.

Pressure often causes a closing of the band gap in low dimensional semiconductors,[14] usually associated with a structural phase transition.[15] Measurement of the variation with pressure of the transport properties of TiS_2,[13] show pronounced discontinuities in the pressure dependence of both the Hall coefficient and thermoelectric power at about 4 GPa and at higher pressures, the pressure dependence of the transport properties were found to be similar to those of semimetallic $TiSe_2$. This behavior was shown to be consistent with TiS_2 having a semiconductor-semimetallic phase transition. There is now clearly a need to determine the high-pressure behavior of TiS_2 to establish the true nature of its transport properties. In this paper we present an experimental high-pressure single-crystal x-ray-diffraction study and comparative theoretical *ab initio* pseudopotential calculations of the pressure dependence of both the crystal structure and band structure of TiS_2. We show that the transition in transport properties observed at 4 GPa is not associated with a structural phase transition, but is the result of pressure-induced band-gap closure.

At ambient pressure TiS_2 adopts a characteristic layered structure, with trigonal space group $P\overline{3}m1$, formed from infinite sheets of face-sharing TiS_6 octahedra. The unit cell, of dimensions $a=3.407$ Å $c=5.695$ Å, has titanium atoms at each corner (a sites) and the sulfur atoms are located at interior positions (d sites) given by $(1/3,2/3,z)$ and $(2/3,1/3,\overline{z})$ with $z=0.2493$.[16] The c/a ratio of 1.6703 is sig-

TABLE I. Unit-cell dimensions (Å) and refined fractional coordinate of TiS_2 as a function of pressure. The number of independent reflections (N), the weighted R factor (R_w) and the goodness of fit G_f are also given. There were seven variable parameters in each refinement.

Pressure	a(Å)	c(Å)	z	N	R_w	G_f
0	3.4075(3)	5.6969(4)	0.2488(2)	72	5.5	1.39
0	3.4073(3)	5.6973(2)	0.24872(16)	85	3.6	1.24
0.94(1)	3.39351(10)	5.60446(16)	0.25329(17)	77	4.3	1.34
1.49(1)	3.38512(20)	5.56041(25)	0.25524(18)	78	3.8	1.35
2.40(1)	3.3747(4)	5.5013(6)	0.2579(3)	70	5.6	1.22
3.40(1)	3.3626(10)	5.4444(15)	0.2606(2)	74	5.5	1.35
3.93(1)	3.35471(14)	5.4248(22)	0.2621(2)	77	4.7	1.32
4.31(1)	3.35074(9)	5.40969(14)	0.2627(2)	76	4.5	1.36
4.79(1)	3.34495(17)	5.38851(26)	0.2639(2)	77	4.2	1.52
5.53(1)	3.3369(2)	5.36289(18)	0.26522(17)	78	3.8	1.46
6.38(1)	3.3272(5)	5.3324(4)	0.26718(17)	64	2.9	1.20
7.14(1)	3.31913(19)	5.30758(17)	0.26818(15)	63	2.9	1.15
7.62(1)	3.3142(3)	5.2937(2)	0.26924(15)	77	3.0	1.20

nificantly larger than the ideal ratio of 1.633 which one would obtain assuming that the relatively large sulfurs adopted a hexagonal close-packed arrangement. The x-ray-diffraction studies were conducted on a single crystal of TiS_2, with approximate dimensions of 75 μm×50 μm ×20 μm, which was selected from a batch of stoichiometric crystals grown using the method described in Ref. 17. Reflections measured from a series of test scans with a CAD4 four-circle diffractometer were found to give sharp diffraction peaks and, therefore, the crystal was deemed suitable for the high-pressure experiment. An initial intensity data collection was performed over the region $0° < \theta < 30°$ and the refined structure was found to be in excellent agreement with previous structure determinations.[16] The crystal was mounted in a BGI design of a pressure cell[18] with its [0 0 1] axis parallel to the diamond-anvil culets and secured in place using petroleum jelly. As the only refinable structural parameter is the sulfur z coordinate, this orientation allows the highest resolution to be obtained on any pressure-induced structural changes. A tungsten gasket with a 200 μm hole was used to enclose the sample and both the ruby and fluorite single-crystal pressure standards. The pressure cell was mounted on the CAD4 and the sample centered using the four-equivalent-settings procedure with graphite-monochromated Mo$K\alpha$ x rays.

Intensity data were collected with the ω-scan method at the position of least attenuation of the pressure cell, according to the fixed-ϕ technique.[19] All accessible reflections up to a maximum $\sin\theta/\lambda$ of 0.91 Å^{-1} were measured. After applying a correction for both pressure cell[19] and sample absorption, the data were used for a least-squares refinement of the structure, including an extinction correction, using the Prometheus crystallographic programs. The structural parameters of the preceding out-of-cell structure determination were used as starting values and anisotropic thermal parameters were refined for both the Ti and S atoms. Unit-cell parameters were determined using a modified Huber four-circle goniometer which has been described elsewhere.[20] Each reflection in a selected set of 12 strong reflectons were centered in eight positions on the diffractometer following the method of King and Finger[21] to eliminate the effects of diffractometer circle zero offsets, crystal offsets, and abberations in the diffractometer alignment. A subset of fluorite reflections were also measured for subsequent pressure determination.

For the high-pressure structure determinations an ethanol-methanol pressure transmitting fluid was introduced into the gasket hole. The high-pressure data collections were undertaken following the strategy outlined above for the 0 GPa structure determination. At each pressure the unit cells of the

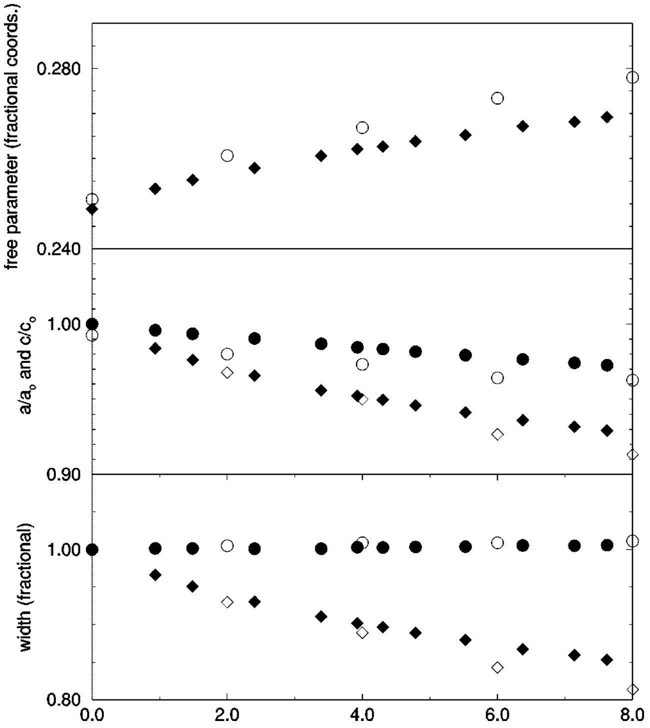

FIG. 1. Variation of the a/a_0 and c/c_0 lattice parameters, the sulfur free parameter (fractional coordinate) and the layer and interlayer thicknesses with pressure (in GPa) in TiS_2. Where a_0 and c_0 are the experimental ambient values. The empty symbols are *ab initio* results, the filled experimental (uncertainties are smaller than the symbols). In the lower two graphs, the circles refer to the a parameter and the diamonds to the c parameter.

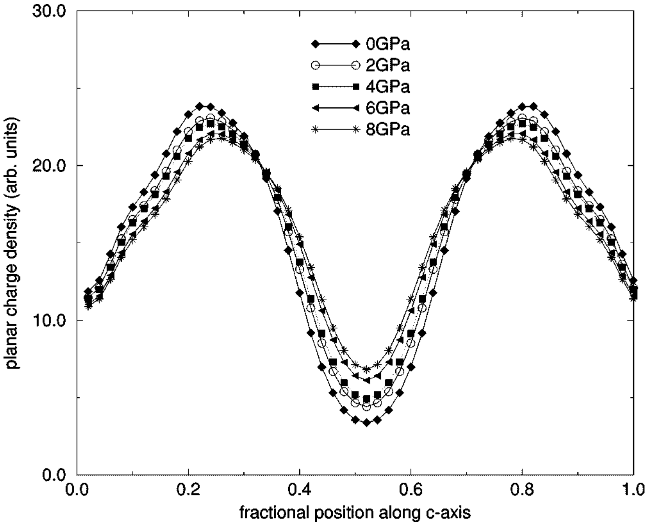

FIG. 2. Valence charge density averaged across the plane perpendicular to the c axis for the five different pressures of the simulations.

sample and fluorite pressure standard were measured accurately with the Huber diffractometer. The pressures were determined using the fluorite unit-cell volumes and the previously determined equation of state. The experimental results are in Table I (see Ref. 22 for definitions).

The simulations were performed using first-principles density-functional theory (DFT) within the pseudopotential approximation which is well documented elsewhere.[23] Nonlocal Kleinmann-Bylander[24] pseudopotentials were used, generated by the method due to Lin *et al.*[25] The local-density approximation (LDA) for exchange and correlation is used.[26,27] The wave functions are expanded in a plane-wave basis set up to an energy cutoff of 400 eV which converges the total energy to better than 0.1 meV/atom. The Brillouin-zone integrations were performed using a $6\times6\times5$ Monkhorst-Pack set[28] which gave 56 special k points. This converges the total energy of each structure to within 5 meV per atom.

The relaxation of the cell size was performed with the Parinello-Rahman Lagrangian formalism incorporating a Pulay correction[29,30] to the total energy and stresses on the unit cell due to the changing basis set. This allows relaxation of the size and shape of the unit cell to the minimum free energy. Relaxation of the cell and the ions was performed consecutively until the forces were smaller than 0.01 eV/Å and until the total stress was less than 10% of the Pulay correction.

We do not wish to presume *a priori* the conducting nature of the material, i.e., whether semiconducting, semimetallic, or metallic. Therefore all calculations were performed with Gaussian smearing[31] which allows for partial occupancy of the electronic bands and we also include an entropy correction term.[32] Since DFT is a ground-state theory, the value of the band gap may not be given correctly, however the ground state (and its semiconducting or semimetallic character) will be correct. Calculations were performed at zero temperature and five different pressures (0, 2, 4, 6 and 8 GPa).

The results for the a and c lattice parameters can be seen in Fig. 1. The two sets of data shown are the *ab initio* results (empty symbols) and results of x-ray-diffraction experiments (filled symbols). We find the agreement between theory and experiment to be good with the a lattice parameter being consistently underestimated by about 1%. (The LDA has a well documented tendency to overestimate the electron binding leading to an underestimate of the lattice parameters.) At low pressures the agreement with the c direction is excellent, but at higher pressures the discrepancy increases to about 1%. Also plotted is the variation with pressure of the free internal parameter which describes the position of the sulfur atom. It is slightly overestimated which is seen to persist at all pressures. The c/a ratio is also overestimated by just under 1% compared to the experimental data.

For evaluating the band structure we associate the pressure in the calculation directly with the pressure in the experiment, rather than deducing the pressure from comparison of experimental lattice parameters. This ensures that the calculations are fully *ab initio*.

It is clear that the compression is highly anisotropic with the c axis decreasing by 7.1% experimentally and 8.7% from the calculations over the pressure range studied, while the a axis only decreases by 2.7% experimentally and 3.0% theoretically. This can be attributed to the ease with which the volume between the octahedra can be reduced compared to distorting the octahedra which would require considerably more energy.

The thickness of the layers was measured both by the x-ray-diffraction measurements and the calculations. We define the interlayer distance, or van der Waals gap, between sulfur layers along the c axis to be $(1-2z)c$. Similarly the intralayer thickness is $2zc$. The theoretical and experimental results are also plotted in Fig. 1. As can be seen clearly from the graph the interlayer distance undergoes the greatest compression (14.7% experimentally and 18.6% theoretically), this corresponds to decreasing the distance between the sulfur ions in the same cell. The thickness of the layers actually undergoes a slight increase (around 0.5% experimentally and 1.1% from the calculation). This increase of the layer thickness is unexpected but can probably be understood by considering the movement of charge. In Fig. 2 it can be seen that the charge increases in the interlayer region between the sulfurs, corresponding to increasingly metallic rather than van der Waals bonding between the layers.

Band structures were plotted for the structures at the five different pressures studied (only four shown, Fig. 3). The zero-pressure structure is clearly a semiconductor with an indirect band gap of 1.9 eV with the valence maximum along the Γ to M line and the conduction minimum being located at the M point, (1/2, 0, 0). As the pressure increases the maximum of the valence band moves to the Γ point and the gap reduces. Between 4 and 6 GPa the gap remains indirect with the conduction minimum at the M point. The linear muffin-tin-orbital (LMTO) calculations of Wu *et al.*[10] differ from our results: they found that the zero-pressure structure was semimetallic. However no atomic-relaxation was allowed, and the atomic sphere approximation which was used gives a poor description of the interstitial regions into which charge is transferred on metallization.[33] Self-consistent methods as used here or full-potential LMTO (Ref. 34) give a more reliable treatment of the electronic structure.

At a calculated pressure of 6 GPa the band gap is closed. The M and L points are now almost degenerate in energy at

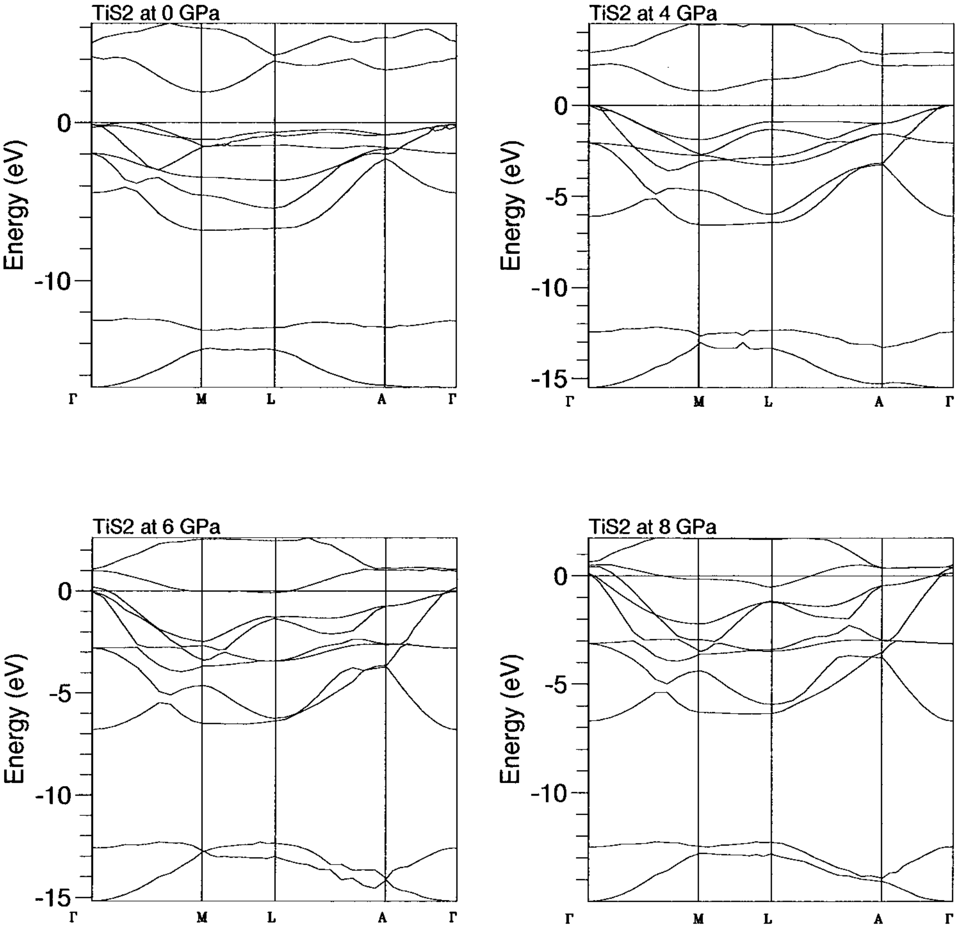

FIG. 3. Variation of band structure with pressure. At zero pressure the top two bands are unoccupied. The band structure for the calculation at 2 GPa is not shown but is intermediate between those for the 0 and 4 GPa simulations.

the highest valence state and slightly lower than the highest point (Γ) in the valence band. The band structure for 8 GPa shows that the lowest point in the conduction band is the *L* point which has a lower energy than the Γ point in the valence band. The conduction band at *L* would now be occupied and the valence band in the neighborhood of the Γ point would be empty.

It is worth noting that this is the behavior that is found experimentally in $TiSe_2$,[16] which is found as a semimetal at ambient pressure with holes at the Γ point and electrons at the *L* point. $TiSe_2$ is the second of the TiX_2 dichalcogenides and possesses the same structure as TiS_2.

The transition from semiconductor to semimetal is not accompanied by any change in structure as indicated by the x-ray-diffraction data. Similarly there is no obvious change in the charge density through the region of the transition. Figure 2 shows the charge density averaged over a plane perpendicular to the *c* axis and plotted against this axis. As the pressure is increased charge moves from the TiS_6 octahedra into the interstitial region between the sulfur ions. This movement of charge accompanied by the reduction in cell volume is sufficient to cause the change from semiconductor to semimetal.

In conclusion, the pressure dependence of the crystal structure and electronic structure of TiS_2 have been studied to 8 GPa using a combination of x-ray-diffraction and *ab initio* pseudopotential calculations. The data reveal that, while there is no structural phase transition or discontinuity in the compression of the TiS_2 structure to 8 GPa, there is a clear band-gap closure between 4 and 6 GPa. This strongly suggests that the TiS_2 changes from a semiconductor to a semimetal in a pressure region where Klipstein and Friend[13] observed discontinuities in the pressure dependence of both the Hall coefficient and thermoelectric power.

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