

Synthesis and Characterization of Nearly Stoichiometric Titanium Disulfide*

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Nearly stoichiometric titanium disulfide has been synthesized by direct reaction between the elements using an optimal procedure and characterized by thermogravimetric and chemical analyses, ammonia intercalation rate, magnetic susceptibility measurements, and X-ray diffraction. The most nearly stoichiometric TiS_2 that can be prepared is $\text{Ti}_{1.0021 \pm 0.0010}\text{S}_2$, so that a slight excess of titanium is always present. This excess titanium inhibits the initial opening of the van der Waals gap during ammonia intercalation. The small titanium excess is the primary source of conduction electrons in TiS_2 , which supports the view that TiS_2 is an extrinsic semiconductor rather than a semimetal. © 1987 Academic Press, Inc.

Introduction

TiS_2 was first shown to exist through the Ti-S phase-diagram studies undertaken by Biltz *et al.* (1). In 1963, Benard and Jeannin (2) concluded from the direct reaction of the elements at high temperatures (800 and 1000°C) that the stoichiometric disulfide was impossible to isolate at these temperatures, with the resulting disulfide always forming the metal-rich compounds $\text{Ti}_{1+x}\text{S}_2$. In 1975, Thompson *et al.* (3) lowered the synthesis temperature to 600°C and obtained apparently stoichiometric TiS_2 . Shortly thereafter, the work of Winn and Steele (4) confirmed the existence of this compound. Subsequently, several methods for preparing the stoichiometric disulfide by

direct reaction of the elements have been published (5-8).

TiS_2 is an important material for practicing intercalation chemistry (9, 10) as well as for cathodes in secondary batteries (11, 12). In this regard, several factors need to be considered in the synthesis of high-quality TiS_2 suitable for use as a host for intercalation reactions or as a battery cathode material. The formation of the stoichiometric disulfide is particularly important, since any excess Ti residing in the van der Waals (vdW) gap (2) apparently pins the host layers together, slowing, if not preventing, intercalation (3). Similarly, it is desirable to avoid exciting Ti atoms into the vdW gap via the formation of titanium vacancy-interstitial pairs ($V_{\text{Ti}}I_{\text{Ti}}$), which are created during high-temperature synthesis (1000°C) (13). TiS_2 prepared at lower temperatures (600°C) shows no evidence of such defect formation (13, 14). In addition

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to keeping the vdW gap vacant, care must also be taken to avoid TiS_3 formation, which can occur at the higher sulfur pressures required to minimize the excess Ti present. TiS_2 in the presence of liquid sulfur cannot form TiS_3 above the temperature range 630–632°C (6–8). Consequently, syntheses using a liquid-sulfur bath above this range followed by quenching from the reaction temperature effectively avoid TiS_3 formation.

In addition to its desirable properties for intercalation chemistry and battery technology, TiS_2 also exhibits unusual electronic properties that have been disputed actively during the past decade. The nature of the controversy is whether apparently stoichiometric TiS_2 , which exhibits metallic behavior with a conduction-electron concentration of 2×10^{20} el/cm³, is an extrinsic semiconductor or a semimetal. With the former possibility there is an indirect energy gap between the sulfur 3*p* valence band and the titanium 3*d* conduction band, whereas in the latter case there is a small indirect overlap between these bands. Although there have been several band-structure calculations for TiS_2 , they give contradictory results. Most of these calculations predict a band gap (15–19), but a more recent theoretical study has predicted band overlaps as large as 0.7 eV (20). However, experimentally there is a growing body of convincing evidence favoring the extrinsic-semiconductor model. This evidence includes the invariance of the Hall coefficient with pressure up to 20 kbar (21), the direct proportionality between carrier concentrations derived from electrical transport and reflectivity measurements (22, 23), and angle-resolved photoemission studies indicating a band gap of about 0.3 eV (24, 25). The most recent work (26) has indicated that below 40 kbar the transport properties of TiS_2 may be understood in terms of an extrinsic-semiconductor model with strong electron-phonon scattering. The band gap

at ambient pressure was estimated to be 0.18 ± 0.06 eV (26).

If TiS_2 is indeed an extrinsic semiconductor with a band gap of ≈ 0.2 eV, then what is the origin of the metallic behavior and rather large conduction-electron concentrations in the nominally stoichiometric material? There are four distinct possibilities which could account for the observed metallic properties (27): (1) a small excess of Ti in the vdW gap to form $\text{Ti}_{1+x}\text{S}_2$, with four electrons being contributed to the conduction band per excess Ti atom; (2) simple displacement defects $V_{\text{Ti}}\text{I}_{\text{Ti}}$, in which two electrons are donated to the conduction band and two destabilized sulfur 3*p* states remain unoccupied; (3) displacement defects induced by the presence of excess Ti, where eight electrons are transferred to the conduction band and four destabilized sulfur 3*p* states are empty; and (4) ionized impurities in the vdW gap.

Clearly, the actual stoichiometry of TiS_2 is of critical importance in deciding among the various possibilities for the source of its conduction electrons. The lack of a precise determination of the TiS_2 stoichiometry in previous work (3, 4, 8, 28) has motivated us to synthesize the most stoichiometric TiS_2 possible by direct reaction between the elements followed by detailed characterization and compositional analysis. The results of this study demonstrate that a small excess of Ti is always present in nominally stoichiometric TiS_2 and that this excess is sufficient to account for the metallic behavior of this material.

Experimental

1. Synthesis

An optimal procedure was used to prepare TiS_2 as close to stoichiometry as possible by direct reaction between the elements. This procedure was developed on the basis of numerous reports in the litera-

ture on the preparation of stoichiometric TiS₂ (1–8, 13, 14) as well as from information obtained from our own detailed studies of this material (29, 30). A summary of the synthetic procedure is given below.

All glassware used in this investigation was cleaned using an HF cleaning solution consisting of 88 ml of 48% hydrofluoric acid, 332 ml of 70% nitric acid, 405 ml of distilled water, and 20 g of Alconox. Both acids were reagent grade from the J. T. Baker Chemical Company. The glassware was exposed to the solution for 3 min, rinsed at least 25 times with distilled water, and subsequently rinsed 5 additional times with deionized, doubly distilled water which had been passed through an organic contaminant filter. The glassware was then dried at 110°C.

Polycrystalline samples of TiS₂ were prepared by two direct reactions between the elements. Marz-grade titanium wire was purchased from Materials Research Corporation and had a stated purity of 99.93%, with O (500 ppm), Fe (50 ppm), Ni (30 ppm), C (30 ppm), Cr (20 ppm), Pb (20 ppm), Sn (20 ppm), Al (15 ppm), N (10 ppm), Ag (<10 ppm), Cu (<10 ppm), Mn (<10 ppm), V (<5 ppm), Ca (<5 ppm), Mg (<5 ppm), Si (<5 ppm), and H (3 ppm) being the measured impurities by weight. The Ti wire was degreased by sonicating twice in Baker AR grade trichloroethylene (evaporation residue $\leq 0.0001\%$) followed by three sonications in Baker AR-grade toluene (evaporation residue $\leq 0.00001\%$), with each sonication taking about 15 min. Gold Label sulfur powder (99.999%) was purchased from the Aldrich Chemical Company, with the measured impurities being Fe (0.1–0.5 ppm) and Si (0.1–0.5 ppm), and was used as received.

Stoichiometric amounts of Ti and S plus an additional 5 mg/cm³ excess S were placed in quartz ampoules and the upper, empty two-thirds of these ampoules was heated under vacuum to 400–500°C with a

flame to remove any residual water. The ampoules were then sealed in quartz ampoules at 10⁻⁴ Torr. The ampoules were heated to 450°C for one day, and the temperature then increased approximately 50°C per day, in two 25°C steps, to 640°C. The temperature was held at 640°C for 3 days, and the ampoules were subsequently air cooled to ambient temperature. The excess S was vapor transported to the opposite end of the ampoule from the disulfide by holding the disulfide-containing end of the ampoule at 350°C and the opposite end near ambient temperature. The ampoule was scratched in the middle with a glass knife and wrapped with parafilm. It was carefully snapped in a helium-containing Vacuum Atmospheres Model MO-40-1H Dri-Train dry box (<1 ppm H₂O and O₂) to avoid both sudden implosion and quartz-chip impurities. Since TiS₂ is mildly air sensitive, it was always handled in the dry box and was only removed in leak-checked, sealed containers. The resulting disulfide was crushed in an agate mortar and pestle and transferred, along with 5, 20, or 40 mg/cm³ excess S, to a quartz ampoule. The ampoule was sealed at 10⁻⁴ Torr, heated at 640 \pm 1°C for 3 days, and then water quenched to avoid TiS₃ formation. The excess sulfur was vapor transported to the opposite end of the ampoule from the TiS₂, again using a 350°C to near ambient-temperature gradient, this time with occasional agitation of the disulfide to remove any trapped S (30).

2. Characterization

The TiS₂ prepared above was characterized by thermogravimetric analysis (TGA) of an oxygen burn to TiO₂ using a Perkin-Elmer TGS-2 system with an ultimate 0.1 μ g sensitivity and 0.01% weight resolution. The mass was calibrated using standard weights. The TGS-2 was thermally calibrated to $\pm 2^\circ\text{C}$ using the following magnetic-transition standards, whose magnetic-transition temperatures are given in

parentheses: Monel (65°C), Alumel (163°C), nickel (354°C), Mumetal (393°C), Nicoseal Deep Draw (438°C), Perkalloy (596°C), iron (780°C), and Hisat 50 (1000°C). The disulfide was transferred from the dry box to the Pt sample pan of the TGS-2, which was preheated to 110°C, as quickly as possible. The gas flow was 40 cm³/min of 99.995%-pure oxygen. Prior to oxidation, the sulfide was held at 110°C for at least 10 min, during which there was no weight fluctuation outside of the normal fluctuation of the balance ($< \pm 0.01\%$ for a typical 40 mg sample). The disulfide was then heated to 2°C/min to 900°C, held at 900°C for 3 hr and cooled back to 110°C to determine the final weight change.

Intercalation-rate experiments for the reaction of liquid NH₃ with TiS₂ were carried out at 20°C. The TiS₂ used for intercalation-rate studies was sieved to obtain a relatively uniform particle size ranging from 40 to 80 mesh (180–425 μm). The disulfide was transferred to one leg of an h-tube in the dry box, as shown in Fig. 1a. The tube was transferred to a vacuum line having a liquid-nitrogen trap, evacuated to 10⁻⁵ Torr, and closed. The vacuum line was then filled with 3.6 liters NH₃ at 300 Torr, previously dried using a Na–NH₃ solution (31), after

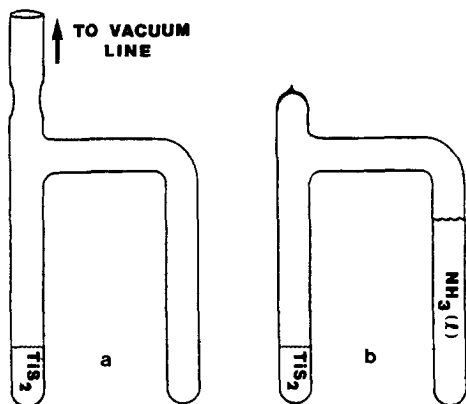


FIG. 1. Schematic drawing of the vessel used for intercalation of TiS₂ with NH₃: (a) the initial h-tube and (b) the final n-tube.

which the Na–NH₃ solution was isolated from the vacuum line. The h-tube was opened to the line, and the NH₃ was condensed into the h-tube leg not containing the disulfide using liquid nitrogen. The h-tube was then evacuated to 10⁻⁴ Torr and sealed with a gas torch to form an n-tube, as shown in Fig. 1b. The NH₃, which was in large excess of the maximum stoichiometry of NH₃TiS₂ (32), was warmed to ambient temperature in less than 10 min and poured onto the TiS₂. The intercalation rate was measured by monitoring the column height as a function of time.

Magnetic measurements were made using a SHE Model VTS-905 SQUID magnetometer with 10⁻¹² emu/g sensitivity and a maximum field of 25 kG. Samples (≈150 mg) were loaded into specially fabricated Delrin buckets in the dry box. Each bucket had a threaded top that was sealed with a thin layer of silicone grease and was leak checked using Na metal. Magnetic susceptibilities were calibrated using the NBS standards Pt and Pd, and sample temperatures were calibrated using the magnetic alloy PdTb₃ as well as Ge and Pt resistance thermometers.

X-ray powder diffraction patterns were recorded at ambient temperature using Ni-filtered CuKα radiation. TiS₂ was loaded into 0.3-mm Pyrex sample capillaries in the dry box and sealed under an atmosphere of helium prior to insertion into a Debye–Scherrer camera, which was previously calibrated using NBS SRM 640 silicon.

Results and Discussion

1. Compositional Analysis of Nearly Stoichiometric Titanium Disulfide

A typical TGA curve for the oxidation of TiS₂ to TiO₂ is shown in Fig. 2. The slight inflection at 620°C is associated with sulfur loss, the details of which will be the subject of a future publication. The compositions

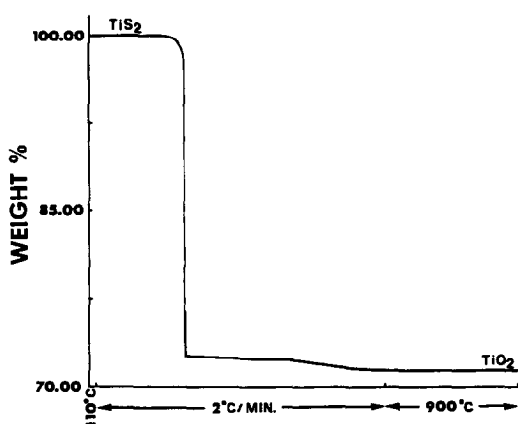


FIG. 2. TGA curve of the oxidation of TiS₂ to TiO₂.

derived from TGA experiments are given in Table I. X-ray diffraction experiments have confirmed that by 900°C all of the TiS₂ has been converted to the rutile form of TiO₂. Each composition was based on at least nine analyses, including independent preparations using the same amount of excess S. More stoichiometric TiS₂ is not expected for S concentrations exceeding 40 mg/cm³, since at this concentration liquid S is present during synthesis at 640°C. Therefore, the most stoichiometric TiS₂ possible according to these experiments is Ti_{1.0032}S₂, with the maximum error in *x* being ±0.0010. The cell constants for this compound (*a* = 3.407 ± 0.002 Å and *c* = 5.695 ± 0.003 Å) are in good agreement with previous work on nominally stoichiometric TiS₂ (13, 14).

The TiO₂ produced from the TGA of Ti_{1.0032}S₂ was analyzed for residual S by Guelph Chemical Laboratories Ltd. The analytical procedure consisted of combusting TiO₂ in the presence of oxygen above 2000°C to completely oxidize any S present. The resulting sulfur-containing gases were dissolved in aqueous hydrogen peroxide to give the sulfate, after which the sulfur content was determined by titration with a standard barium perchlorate solution using Thorin indicator. These analyses

gave 800 ± 30 ppm S by weight. Combining this residual S with the TGA data gives a composition of Ti_{1.0025}S₂ for the most stoichiometric TiS₂. Furthermore, if all of the 500 ppm oxygen in the starting Ti wire resulted in the production of TiO₂, then the TiS₂ nonstoichiometry would be further reduced to Ti_{1.0021}S₂. Oxygen analysis was not performed directly on the TiS₂ because the moderate sensitivity of this compound to oxygen and moisture would have contaminated the sample unless it was analyzed under inert-atmosphere conditions. Therefore, taking into account residual S and O, the composition of the most nearly stoichiometric TiS₂ prepared by direct reaction of the elements can be expressed conservatively as Ti_{1.0021±0.0010}S₂.

The stoichiometry of TiS₂ determined above provides a simple explanation of the origin of the observed conduction electrons in this compound. Carrier concentrations evaluated from Hall-coefficient measurements (23, 26) using a one-band model for three independent specimens of TiS₂ prepared by a procedure similar to that described in this paper are summarized in Table II. Also given in Table II are the stoichiometries of TiS₂ corresponding to these carrier densities assuming four electrons are donated to the conduction band per intercalated Ti atom. These calculated

TABLE I
STOICHIOMETRY OF TiS₂ FOR DIFFERENT
PREPARATIONS DETERMINED BY
THERMOGRAVIMETRIC OXIDATION TO 900°C

Excess sulfur (mg/cm ³)	Weight percent ^a (%)	<i>x</i> in Ti _{1+x} S ₂ ^b
5	71.53	0.0051
20	71.47	0.0037
40	71.45	0.0032

^a Weight percent = (wt TiO₂/wt TiS₂) × 100. Weight percents are the average values for multiple analyses, with the maximum error being ±0.04%.

^b The maximum error in *x* is ±0.0010.

TABLE II
CARRIER DENSITY AND STOICHIOMETRY OF TiS_2
DETERMINED FROM THE HALL COEFFICIENT USING
A ONE-BAND MODEL AND ASSUMING FOUR
CARRIERS PER EXCESS TI ATOM

Carrier concentration (el/cm ³)	x in $\text{Ti}_{1+x}\text{S}_2$
$(1.4 \pm 0.1) \times 10^{20}$	0.0020 ± 0.0002^a
$(2.0 \pm 0.2) \times 10^{20}$	0.0029 ± 0.0003^a
$(2.2 \pm 0.3) \times 10^{20}$	0.0032 ± 0.0004^b

^a Value taken from Ref. (26).

^b Value taken from Ref. (23).

stoichiometries are in excellent agreement with our experimental determination of the composition of TiS_2 . In particular, the calculated stoichiometry associated with the lowest carrier concentration ($\text{Ti}_{1.0020}\text{S}_2$), which presumably represents the most stoichiometric TiS_2 , is identical within experimental error to our measured value after correction for residual S and O ($\text{Ti}_{1.0021}\text{S}_2$). This finding not only suggests that there are four carriers per excess Ti atom down to $x = 0.002$, but also indicates that the origin of the metallic behavior observed in TiS_2 is excess Ti in the vdW gap rather than displacement defects or ionized impurities.

2. Intercalation Rate

The intercalation rate of liquid NH_3 at 20°C is extremely sensitive to the stoichiometry of the TiS_2 host. However, care must be exercised in attempting to quantify such measurements because the intercalation rate of TiS_2 is a function of the host's particle size, with smaller particles intercalating more rapidly due to their greater areas of exposed layers. Consequently, the TiS_2 used for intercalation-rate studies had the same particle size (40–80 mesh) used in a previous study (3, 30).

In Fig. 3 the height of a cylindrical column of ammonia-intercalated TiS_2 , which is proportional to its volume, is plotted as a function of intercalation time for

the most stoichiometric TiS_2 prepared with a 40 mg/cm^3 S excess. Meticulous care was taken to minimize the effects of gas evolution on the column height due to redox reactions accompanying the formation of the intercalation compounds $(\text{NH}_4^+)_y(\text{NH}_3)_y\text{TiS}_2^{y'-}$ (32). The observed decrease in particle size as intercalation tears up the host has a small effect on the column height, since the observed 49% increase in column height is about 90% of that anticipated based on the expansion of the cell parameters on intercalation (3, 30, 33). Also, differences in particle packing can lead to a small random variation about a constant column height.

Intercalation was complete in about 2 hr for the most stoichiometric TiS_2 , which is faster than the intercalation time of about $2\frac{1}{2}$ hr found in a previous study of nominally stoichiometric TiS_2 (3). The short induction period (≈ 10 min) and intercalation time reflect the near stoichiometry of our TiS_2 . Presumably, these times would be further reduced in even more stoichiometric material. In contrast, with 5 mg/cm^3 S excess ($\text{Ti}_{1.0051}\text{S}_2$ by TGA), the intercalation time increased to about $3\frac{1}{3}$ hr. Moreover, the induction period increased to about 70 min before any noticeable swelling of the host occurred. These observations suggest

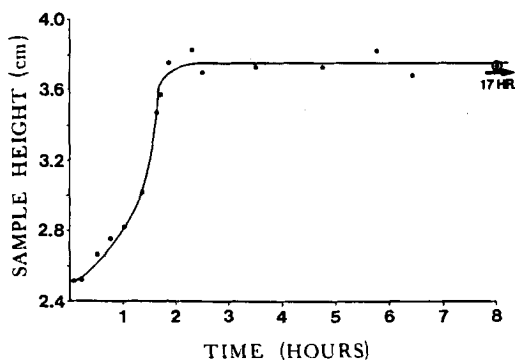


FIG. 3. Height of a column of NH_3 -intercalated TiS_2 as a function of intercalation time for the most stoichiometric TiS_2 . The TiS_2 was 40–80 mesh and the temperature was 20°C .

that the presence of excess Ti, at least for a small excess of Ti, slows intercalation primarily by inhibiting the initial opening of the vdW gap.

3. Magnetic Susceptibility

The magnetic susceptibility and *c* cell parameter are also sensitive to the stoichiometry of TiS₂. The temperature dependence of the magnetic susceptibility (χ) for our most stoichiometric TiS₂ per mole of TiS₂ is displayed in Fig. 4. Due to the small susceptibility of TiS₂, paramagnetic impurities normally make an important contribution to χ at low temperatures, as evidenced by the Curie tail below about 50 K in Fig. 4. At 4.2 K, the magnetization (*M*) does not vary linearly with magnetic field (*H*) at higher fields, and the Curie contribution to χ can be fit quite well with a Brillouin function using an effective $J = 5/2$. This result is consistent with Fe³⁺ being the primary magnetic impurity, since Fe is the main magnetic impurity in the starting Ti wire. The conduction-electron density resulting from about 150 ppm of intercalated Fe³⁺ per mole of TiS₂ is only 0.08 ± 10^{20} e⁻/cm³, which amounts to only about 5% of the measured carrier density in the most nearly stoichiometric material (see Table II). Therefore, paramagnetic impurities do not

contribute a significant fraction of the carriers in nearly stoichiometric TiS₂. It is also noteworthy that the Curie tail is not related to Ti³⁺, since octahedral Ti³⁺ has a very small susceptibility that is nearly temperature independent at low temperatures (34).

The absence of ferromagnetic impurities was demonstrated at 4.2 K by the reversibility of the *M* vs *H* curve. Moreover, at 350 K all of the *M* vs *H* curves were linear, so that no ferromagnetic impurities having Curie temperatures above 350 K could be detected. Above about 25 K the *M* vs *H* curves were all linear up to 25 kG within experimental error. Consequently, χ was obtained from the relation $\chi = M/H$. However, below 25 K the *M* vs *H* curves were not linear, so that it was necessary to determine the low-field susceptibility using a Brillouin function for $J = 5/2$.

The intrinsic susceptibility per mole of TiS₂ was obtained after correcting for the paramagnetic-impurity contribution and is also shown in Fig. 4. TiS₂ displays a very small temperature-independent paramagnetic susceptibility of $9 \pm 2 \times 10^{-6}$ emu/mole, which is in good agreement with that reported in a previous study (3) of nominally stoichiometric TiS₂, where it was found that χ increased rapidly with excess Ti, presumably due to the enhanced Pauli paramagnetism associated with TiS₂ having higher carrier densities.

The origin of the paramagnetism in TiS₂ is unresolved. It is due, at least partially, to the Pauli paramagnetism of conduction electrons arising from the excess Ti in the vdW gap. In addition, Van Vleck temperature-independent paramagnetism, which depends on the host structure and its associated excited electronic states, may also make a significant contribution.

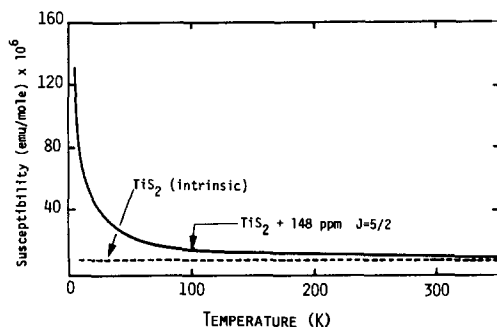


FIG. 4. Temperature dependence of the experimental (solid line) and intrinsic (dashed line) molar magnetic susceptibilities of the most stoichiometric TiS₂. The experimental uncertainty in the susceptibility is $\pm 2 \times 10^{-6}$ emu/mole.

Conclusions

We conclude from the results of this investigation that nominally stoichiometric

TiS₂ is an extrinsic semiconductor because there is always a small excess of Ti present in the vdW gap, even in the most stoichiometric TiS₂ prepared by direct reaction of the elements, and that this excess is sufficient to account for the metallic behavior of this material. The extrinsic-semiconducting nature of TiS₂ is in agreement with recent electron-transport measurements in other laboratories (21–23, 26), but in this study the origin of the conduction electrons has been finally elucidated.

We are currently attempting to synthesize even more stoichiometric TiS₂ by introducing S into the vdW gap.

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