Structure of *in vacuo* Rb-intercalated 1*T*-TaS$_2$

P. Schmidt, B. Murphy, J. Kröger,* H. Jensen, and R. Berndt

Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, D-24098 Kiel, Germany
(Received 22 September 2006; published 13 November 2006)

Rubidium adsorption in ultrahigh vacuum on the transition metal dichalcogenide 1*T*-TaS$_2$ is investigated by scanning tunneling microscopy at 9 K and at room temperature. Comparison of step heights on clean and Rb-covered surfaces provides direct evidence that the adsorbed Rb atoms intercalate between the topmost layers of the substrate. This result resolves the current uncertainty about the structure of these widely investigated surfaces. The increase of the van der Waals gap between the substrate layers is discussed on the basis of a sphere model.

Transition-metal dichalcogenides (TMDC's) have attracted considerable attention. These materials can serve as the basis for lubricants,[1] battery systems,[2] and solar cells.[3] Crystals at the nanometer scale were synthesized from TMDC's (Refs. 4 and 5) as well as single-wall nanotubes.[6] Recently, surfaces of TMDC's have been used to fabricate nanostructures.[7,8] From a fundamental point of view TMDC's present a material class with intriguing phase diagrams which include metal-insulator transitions, charge density waves (CDW's), and superconductivity.[9,10] Owing to their peculiar geometric structure consisting of a periodic stacking of van der Waals–bonded TMDC layers, dimensionality effects on the above-mentioned phases can be investigated. By intercalation it is possible to tailor the interlayer spacing in these materials while conserving the structural integrity within the layers.[11] During this process the van der Waals gap between the layers is increased in order to accommodate the intercalated compound. For instance, by preparing reactants in sealed Pyrex tubes or using a solution suspension, *ex situ* insertion of pyridine molecules between TaS$_2$ layers has been achieved. Electron microscopy and diffraction studies report an increase in the interlayer spacing of about 6 Å while superconductivity of the hosting substrate is preserved.[12,13] In other early studies intercalation compounds were prepared during growth or by electrochemical processes.[11,14]

Since the electronic properties can be tuned by introducing intercalate compounds to the host lattice, it is naturally desirable to perform this process *in vacuo* so that dimensionality and electronic properties may be tuned on a local level. Many *in vacuo* photoemission experiments, on alkali-metal adsorption on TMDC materials, show that local changes in the host-metal *d* band are evident upon deposition.[15–17] However, the location of the alkali metal cannot be directly determined from such measurements. For instance, a gradual transformation of the three-dimensional electronic structure of clean VSe$_2$ to an essentially two-dimensional structure of Cs-intercalated VSe$_2$ has been observed.[15] Rossnagel *et al.* have demonstrated by an angle-resolved photoelectron spectroscopy (ARPES) experiment the continuous tuning of electronic correlations by *in vacuo* Rb adsorption on 1*T*-TaS$_2$.[16] Charge transfer from the alkali metal to the substrate and simultaneous modification of the interlayer coupling were suggested to drive a Mott-Hubbard-type transition at the surface.[16]

Scanning tunneling microscopy (STM) studies have shown that the exposure to large amounts of metal adatoms drives the formation of nanostructures on the surface of TiTe$_2$ and similar materials.[7,18,19] These studies have suggested that the alkali-metal atoms remain on the surface forming nanostructures and that no intercalation takes place. Recently published transmission and scanning electron microscopy studies, on the other hand, show that introducing Cu adatoms to VSe$_2$ drives a deformation of the top layers such that a nanofold network formation appears.[8] This point of view is supported by ARPES studies of Rb deposition on 1*T*-TaSe$_2$.[21] Despite the interest devoted to electronic and structural aspects of TMDC surfaces, a real-space analysis with atomic resolution which clearly demonstrates intercalation, or lack of it, for *in vacuo* adsorbed atoms has not been reported. Until now only indirect evidence for intercalation has been given. The aim of this study is to determine if adsorbed Rb stays at the surface of 1*T*-TaS$_2$ or intercalates between the layers.

In this article we present a STM investigation of 1*T*-TaS$_2$ (Fig. 1) and Rb-covered TaS$_2$ at 9 K and at room temperature. By comparing step heights of the clean surface with those of Rb-exposed samples we provide clear evidence that the adsorbed Rb atoms intercalate between the substrate layers. The increase of the step heights of TaS$_2$ is in accordance with Rb atoms occupying adsorption sites within the van der Waals gap of the substrate.

Experiments were performed in ultrahigh vacuum (UHV) with a base pressure of 10^{-9} Pa. Data were acquired at different substrate surfaces by scanning tunneling microscopes
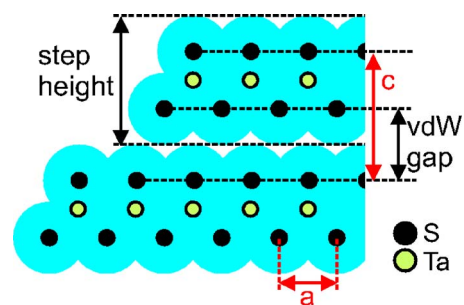

FIG. 1. (Color online) Sketch of two adjacent layers of 1*T*-TaS$_2$ with indicated van der Waals gap, lattice constants *a* and *c*, and step height (identical to *c*).
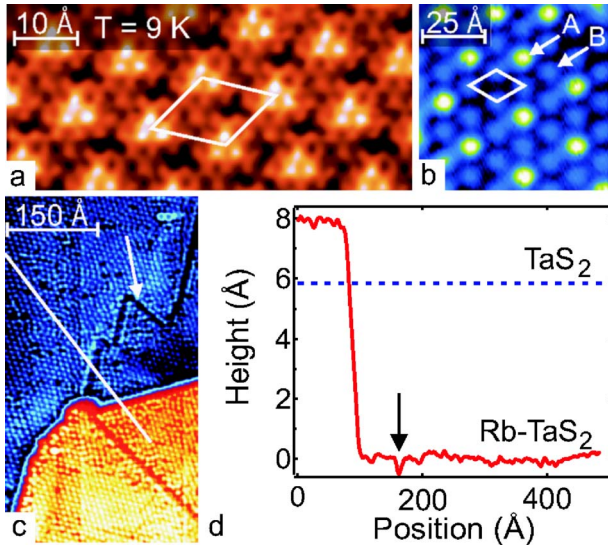
FIG. 2. (Color online) Constant-current STM images of clean and Rb-covered $1T$-TaS_2 at 9 K. (a) Atomically resolved pristine surface (sample voltage $V=850$ mV, current $I=480$ pA). Maxima with 12.1 Å periodicity are due to the CDW which gives rise to the commensurate $\sqrt{13} \times \sqrt{13}$ superstructure. The lozenge indicates the CDW unit cell. (b) Rb-exposed surface with single Rb adatoms (arrow A) residing at some of the CDW maxima indicated by arrow B ($V=870$ mV, $I=370$ pA). The lozenge indicates the CDW unit cell. (c) Two adjacent terraces on the Rb-exposed surface (lighter color depicts upper terrace). The arrow indicates disruption as frequently observed at low temperature. ($V=700$ mV, $I=210$ pA). (d) Profile across adjacent terraces along the line marked in (c). The dashed line indicates the step height of the clean crystal.

FIG. 3. (Color online) STM images of $1T$-TaS_2 at room temperature (RT). (a) Atomically resolved STM image of the clean surface. The lozenge indicates the $p(\sqrt{13} \times \sqrt{13})R13.9°$ CDW unit cell ($V=75$ mV, $I=140$ pA). (b) Adjacent terraces on clean $1T$-TaS_2 with the upper one appearing on the left-hand side ($V=75$ mV, $I=5$ pA). (c) STM image of Rb-covered TaS_2. (d) Profiles across two adjacent terraces on the clean (lower curve) and on the Rb-covered (upper curve) surface.

optimized for operation at 9 K and at room temperature. Crystalline order of $1T$-TaS_2 surfaces cleaved in UHV was monitored using STM and low-energy electron diffraction (LEED). Consistent with previous reports, room-temperature LEED of freshly cleaved $1T$-TaS_2 surfaces exhibited a commensurate $p(\sqrt{13} \times \sqrt{13})R13.9°$ CDW pattern.[16] Rubidium was deposited onto a clean $1T$-TaS_2 substrate surface by thermal evaporation from a commercial dispenser[22] at a rate of 0.9 Å min^{-1}—as monitored by a quartz microbalance—over a deposition time of 5 min. The sample temperature measured during evaporation with a pyrometer was less than 340 K.

An atomically resolved constant-current STM image of the clean substrate surface at 9 K is shown in Fig. 2(a). The commensurate CDW is indicated by its unit cell (lozenge) with a lattice vector dimension of ≈ 12 Å. A typical constant-current STM image of Rb-covered $1T$-TaS_2 at 9 K is presented in Fig. 2(b). We attribute the highest protrusions (arrow A) to individual Rb atoms which reside on the maxima of the CDW (lower protrusions indicated by arrow B). The apparent height of such a Rb adatom is ≈ 0.9 Å higher than the corresponding height of CDW maxima (≈ 0.3 Å) at the chosen sample voltage and current. While the CDW exhibits the hexagonal symmetry known from the clean surface [Fig. 2(a)] the Rb atoms are not arranged in an ordered superstructure. The minimum mutual Rb distance is $\sqrt{3}$ times the CDW wavelength. The CDW has hexagonal symmetry with the
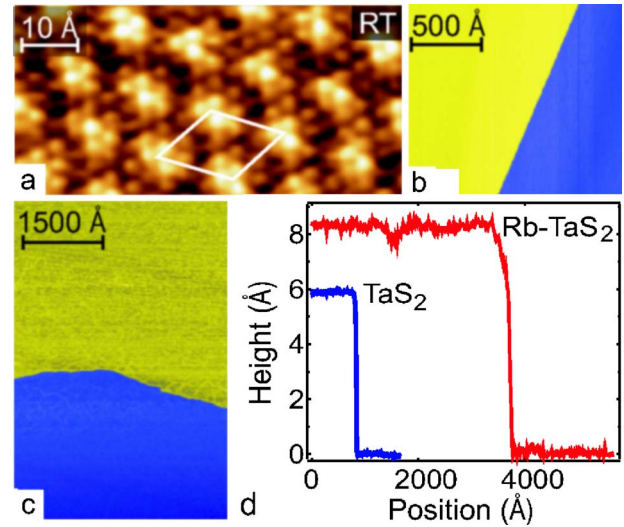
periodicity of the $\sqrt{13} \times \sqrt{13}$ superstructure known from the clean surface showing the sample is in the $1T$ phase.[23] While on pristine $1T$-TaS_2 the surface was flat over lateral distances of 1 μm, apart from corrugations due to substrate atoms and the CDW, at 9 K the terrace width is limited to ≈ 600 Å. On the terraces we occasionally find a lowering of extended areas by some tenths of an Å and defects such as the indicated disruption [arrows in Figs. 2(c) and 2(d)]. Interestingly, assuming that (a) the same amount of Rb was deposited onto the TaS_2 surface as onto the electrode of the quartz microbalance and (b) Rb grows along its (111) bulk crystalline direction, we would expect two to three crystal layers of Rb on TaS_2. From Fig. 2(b) we infer, however, that less than one rubidium atom per ≈ 145 Å^2 is adsorbed on the surface. Figure 2(d) displays a profile across a typical step edge observed at 9 K. From this and many other profiles we measure a step height of (7.9 ± 0.3) Å which is 2 Å higher than the expected clean surface step height of 5.9 Å.[20,24] Intriguingly, the entire top terrace is lifted by $\Delta=(2.0 \pm 0.3)$ Å with respect to the lower one. We interpret this observation as direct evidence for intercalation of Rb.

At room temperature we also observe an increase in the interlayer spacing of the top two layers. A typical constant-current STM image of an atomically resolved pristine $1T$-TaS_2 surface is presented in Fig. 3(a). The lozenge indicates the $p(\sqrt{13} \times \sqrt{13})R13.9°$ CDW unit cell. Figure 3(b) shows an example of a straight step edge separating two terraces. The upper and lower terraces appear as two parallel planes with a mutual distance of 5.9 Å as expected [see the lower profile in Fig. 3(d)]. After depositing Rb onto this surface using the same deposition parameters as in the low temperature experiment, we observed STM images as shown in Fig. 3(c). Characteristics of this surface were flat terraces extend-

ing over more than 1 μm^2. Step edges were scarce and did not reveal the same high degree of straightness as observed for the clean surface. From imaged surface areas we infer that Rb adsorbed on the surface with uniform concentration. In contrast to our observations at low temperatures there is no evidence of layer distortion at room temperature. An observed increase in tunneling current noise is most likely due to diffusing Rb atoms. In Fig. 3(d) cross-sectional profiles across step edges of pristine $1T$-TaS$_2$ (lower curve) and Rb-TaS$_2$ (upper curve) are compared. To present data with reduced noise the data sets show the average over 260 profiles. Compared to the averaged profiles of clean TaS$_2$, the profiles of Rb-TaS$_2$ appear less sharp. This observation is related to an averaging-induced effect. Step edges of Rb-TaS$_2$ are not as straight as those of the clean surface. As a consequence, onsets of step edges appear at slightly different lateral positions. The step edge of the averaged data set then does not show the sharp shape as the individual profile. For the Rb-exposed substrate the step height is increased to (8.3 ± 0.3) Å which corresponds to a lifting of the topmost layer by $\Delta = (2.4 \pm 0.3)$ Å. As in the low-temperature experiment this observation is clear evidence of Rb intercalation into the topmost van der Waals gap. The profile presented in Fig. 3(d) (upper curve) shows that intercalation is not only confined to the vicinity of the step edges but occurs over extended length scales of at least 3000 Å.

Our observations are consistent with a structural model of expected adsorption sites for Rb atoms intercalated in the van der Waals gap. Below we relate the measured step height increase to Rb-induced opening of the van der Waals gap. Figure 4(a) shows a sketch of two adjacent S layers embracing the van der Waals gap. Possible Rb adsorption sites between these sulfur layers are depicted by large circles. The top adsorption site (t) is coordinated by three sulfur atoms in the lower layer and by a single sulfur atom of the top layer; the hollow site (h) is coordinated by six S atoms (three each in the lower and upper layer); the bridge site is positioned between two S atoms of the lower level. The width of the van der Waals gap is defined as the distance between these adjacent sulfur layers. While the S atoms are described as spheres with a radius of 1.67 Å,[25] the radius of the sphere representing the Rb ion is varied such as to give the experimentally observed increase of the step height. Using simple geometric considerations and keeping the in-plane lattice parameter of 3.36 Å as suggested by recent theoretical work,[20,26] we calculate the step height increase within the sphere model of S and Rb atoms for the different adsorption sites within the van der Waals gap. Three curves [Fig. 4(b)] correspond to Rb occupation of the three high-symmetry sites shown in Fig. 4(c). At 9 K the experimentally observed increase in layer spacing is $\Delta = (2.0 \pm 0.3)$ Å which is consistent with Rb atoms occupying the h site and revealing a sphere radius of (1.5 ± 0.1) Å. This result is in agreement with an ion radius of Rb of 1.49 Å.[25] The Rb atom is known to transfer much of its valence electron to the d band of the substrate.[11,14] using the ion radius of Rb obtained for

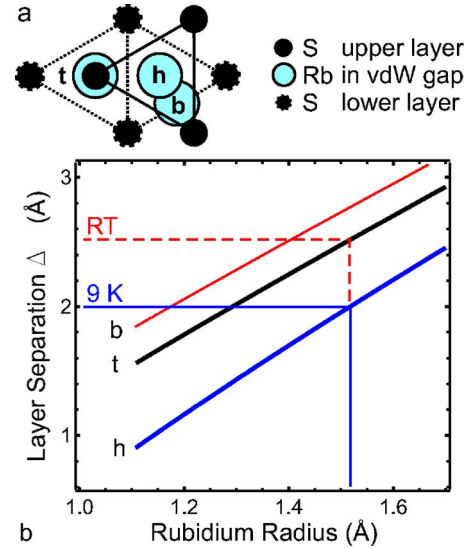
FIG. 4. (Color online) (a) Top view of three high-symmetry adsorption sites within the van der Waals gap of $1T$-TaS$_2$ between the top layer (solid lines) and lower layer (dashed lines). Small circles denote S atoms, large circles denote Rb atoms occupying (h) hollow, (t) top, and (b) bridge sites. (b) Calculated layer separation Δ vs Rb radius for high-symmetry adsorption sites at room temperature (RT) and 9 K.

the low-temperature situation the layer lifting of $\Delta = (2.4 \pm 0.3)$ Å at room temperature can be reproduced, if we assume that Rb additionally resides at the t sites within the van der Waals gap. Lacking data for the energy required to lift a layer of TaS$_2$, we estimate the interlayer binding energy using calculated results for MoS$_2$.[27] In order to increase the interlayer separation necessary to occupy t sites a barrier of approximately 15 meV has to be overcome per unit cell. This very small difference suggests that, at room temperature, Rb atoms diffusing within the van der Waals gap can occupy h and t sites simultaneously, while at 9 K only the h sites are predominantly occupied.

In summary, on the basis of STM data the key question of where Rb atoms are located following *in vacuo* adsorption on $1T$-TaS$_2$ has been answered. The increase in interlayer spacing observed in the STM data is clear evidence that Rb intercalates into the van der Waals gap between the topmost layers. This evidence is confirmed within a geometric model of the atomic layers. Small differences in the spacing between room-temperature and low-temperature data are consistent with Rb atoms residing at different high-symmetry sites within the van der Waals gap. As the behavior of alkali-metal or metal adatoms on TMDC's is generally similar, we propose that our results are also valid for this class of materials in general.

*Electronic address: kroeger@physik.uni-kiel.de

[1] L. Rapoport, Y. Bilik, Y. Feldman, M. Homyonfer, S. R. Cohen, and R. Tenne, Nature (London) **387**, 791 (1997).

[2] M. S. Whittingham, Science **192**, 1126 (1976).

[3] H. Tributsch, Faraday Discuss. Chem. Soc. **70**, 189 (1980).

[4] L. Margulis, G. Salitra, R. Tenne, and M. Talianker, Nature (London) **365**, 113 (1993).

[5] P. A. Parilla, A. C. Dillon, K. M. Jones, G. Riker, D. L. Schulz, D. S. Ginley, and M. J. Heben, Nature (London) **397**, 114 (1999).

[6] M. Remskar, A. Mrzel, Z. Skraba, A. Jesih, M. Ceh, J. Demšar, P. Stadelmann, F. Lévy, and D. Mihailovic, Science **292**, 479 (2001).

[7] R. Adelung, J. Brandt, K. Rossnagel, O. Seifarth, L. Kipp, M. Skibowski, C. Ramírez, T. Strasser, and W. Schattke, Phys. Rev. Lett. **86**, 1303 (2001).

[8] E. Spiecker, A. K. Schmid, A. M. Minor, U. Dahmen, S. Hollensteiner, and W. Jäger, Phys. Rev. Lett. **96**, 086401 (2006).

[9] V. Grasso, *Electronic Structure and Electronic Transitions in Layered Materials* (Reidel, Dordrecht, 1986).

[10] J. A. Wilson, F. J. DiSalvo, and S. Mahajan, Adv. Phys. **24**, 117 (1975).

[11] R. H. Friend and A. D. Yoffe, Adv. Phys. **36**, 1 (1987).

[12] F. R. Gamble, F. J. DiSalvo, R. A. Klemm, and T. H. Geballe, Science **168**, 568 (1970).

[13] H. Fernández-Morán, M. Ohstuki, A. Hubino, and C. Hough, Science **174**, 498 (1971).

[14] W. Y. Liang, in *Intercalation in Layered Materials: Proceedings of the 10th Course of the Erice Summer School*, edited by M. S. Dresselhaus, (Plenum, New York, 1986), Vol. 148, p 31.

[15] H. I. Starnberg, H. E. Brauer, L. J. Holleboom, and H. P. Hughes, Phys. Rev. Lett. **70**, 3111 (1993).

[16] K. Rossnagel, E. Rotenberg, H. Koh, N. V. Smith, and L. Kipp, Phys. Rev. Lett. **95**, 126403 (2005).

[17] C. Pettenkofer and W. Jaegermann, Phys. Rev. B **50**, 8816 (1994).

[18] R. Adelung, J. Brandt, L. Kipp, and M. Skibowski, Phys. Rev. B **63**, 165327 (2001).

[19] R. Adelung, L. Kipp, J. Brandt, L. Tarcak, M. Traving, C. Kreis, and M. Skibowski, Appl. Phys. Lett. **74**, 3053 (1999).

[20] A. Spijkerman, J. L. de Boer, A. Meetsma, G. A. Wiegers, and S. van Smaalen, Phys. Rev. B **56**, 13757 (1997).

[21] S. E. Stoltz, H. I. Starnberg, and L. J. Holleboom, Phys. Rev. B **67**, 125107 (2003).

[22] SAES Getters, Cologne, Germany.

[23] J. A. Wilson, F. J. DiSalvo, and S. Mahajan, Phys. Rev. Lett. **32**, 882 (1974).

[24] J. A. Wilson and A. D. Yoffe, Adv. Phys. **18**, 193 (1969).

[25] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart and Winston, New York, 1976).

[26] C. Ramirez, R. Adelung, R. Kunz, L. Kipp, and W. Schattke, Phys. Rev. B **71**, 035426 (2005).

[27] H. Rydberg, M. Dion, N. Jacobson, E. Schroder, P. Hyldgaard, S. I. Simak, D. C. Langreth, and B. I. Lundqvist, Phys. Rev. Lett. **91**, 126402 (2003).