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Scanning tunneling microscopy and spectroscopy of Na intercalation in VSe_2

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Abstract. We have used an ultrahigh vacuum variable-temperature scanning tunneling microscope to study in situ Na intercalation in $1T$-VSe_2. At room temperature the clean surface showed large flat areas and a trigonal atomic arrangement. Tunneling spectroscopy revealed the known state at 100 mV below E_F. At 60 K the clean surface showed a 4×4 charge density wave and the spectra showed a CDW gap $\Delta \approx 80$ mV. When evaporating ≤ 1 ML Na at room temperature, the intercalated Na were distributed non-uniformly, giving bright areas of increased topographic height where Na was intercalated. In the intercalated material the VSe_2 state was seen in the tunneling spectra, and was slightly shifted towards E_F. Preliminary spectroscopy of the intercalated material at 60 K showed two different types of spectra. One type showed the VSe_2 peak clearly, but had no sign of the CDW gap, while the other type showed a gap structure but did not resolve the VSe_2 state. Presently, we can not tell whether these different spectra originate from the differences in the intercalated and non-intercalated areas or not.

The transition metal dichalcogenides (TMDs) are layered materials that are highly anisotropic, leading to rather two-dimensional properties. They consist of one transition metal atom in-between two chalcogen atoms, forming covalently bonded sheets. Different sheets are bonded to each other by weak van der Waals forces, giving a layered structure, similar to graphite. The TMDs serve as model systems for low-dimensional properties. Among the interesting phenomena occurring in these materials are the formation of charge density waves (CDW) and the possibility of intentional modification by intercalation of foreign atoms or molecules in the van der Waals gap between the layers. A CDW is a standing wave of electron density, caused by electron-phonon interaction giving a condensate of electron-hole pairs. The CDW state has similarities to the superconducting state; for example it shows a transition temperature and an energy gap. Usually, different incommensurate (IC) and commensurate (C) phases are found in different temperature ranges. Alkali metals form intercalation compounds with TMDs spontaneously when evaporated in ultrahigh vacuum (UHV) [1, 2], and they have a strong tendency to donate their single valence electron to the host lattice.

$1T$-VSe_2 exhibits a CDW transition at ~ 110 K with a well-known 4×4 structure that is commensurate with the atomic lattice below 80 K [3].

We have studied Na intercalation in $1T$-VSe_2 by scanning tunneling microscopy (STM) and spectroscopy (STS). STM images and STS data of clean $1T$-VSe_2 at 77 K and 4.2 K have been published by Coleman and co-workers [4], showing the 4×4 CDW and an energy gap Δ at 4.2 K of ~ 40 mV. Only a few STM studies of in situ intercalated TMDs have been reported. Silver intercalation has been studied in $1T$-TaS_2 [5] and $2H$-$NbSe_2$ [6]. TaS_2 changes from $1T$-coordination to a $2H$ coordination by Ag intercalation and the transition temperatures for the different TaS_2 phases are lowered. In $2H$-$NbSe_2$ a local $\sqrt{13} \times \sqrt{13}$ CDW is induced at room temperature by the Ag intercalation. Ag intercalation in NbS_2 has also been studied, but NbS_2 does not exhibit a CDW [7]. STM of bulk intercalated $LiTaS_2$ shows a reduction of the CDW wavelength [8]. A strong VSe_2 state is known to exist ~ 100 mV below E_F from photoemission and band calculations [2]. STS around E_F should be able to follow this state during CDW formation and intercalation.

STM and STS studies of in situ intercalation systems open the possibility of investigating local aspects of the formation and modification of CDW.

1 Experimental details

Measurements were made in a variable-temperature ultrahigh vacuum STM [9], equipped with a home-built Na evaporation source, calibrated to evaporate ~ 1 monolayer (ML) in 11 min. The base pressure in the system was 4×10^{-11} mbar and the pressure never increased during evaporation. All evaporations were made at room temperature. The VSe_2 sample was cleaved in air and immediately placed in the fast-entry load-lock chamber. It was heated inside the UHV chamber to $\sim 350\,°C$ to remove contamination. Measurements were made at room temperature and at 60 K. The temperature of 60 K ensured that we were measuring well below the IC-C transition at 80 K. Cooling was done using a flowing He cryostat, which was temperature-controlled by counter-resistive heating. The tips used were electrochemically d.c. etched tungsten tips, cleaned by sputtering and heating inside the UHV chamber [10]. The sign of V_{bias} corresponds to the sample bias. Tunneling spectra are measured with a tunneling resistance of the order of GΩ.

2 Results

2.1 *Clean* VSe_2

At room temperature the clean surface showed large (~ 600 nm), flat and mostly defect-free areas, and a trigonal atomic arrangement with a lattice constant close to 3.35 Å, as expected (Fig. 1a). Single as well as multilayer steps were found. STS at room temperature showed a peak 100 mV below E_F (Fig. 2), identified as the VSe_2 state. The state was rather weak in our spectra.

The 4×4 CDW was clearly seen, together with the atomic lattice, in our STM images at 60 K (Fig. 3), and was in good agreement with earlier studies [4]. STS at 60 K showed, along with the VSe_2 peak, a gap structure that was identified as the CDW gap (Fig. 4a). The gap was estimated to be $\Delta \approx 80$ mV, which gives $2\Delta/k_B T_{\text{CDW}} \approx 13.3$.

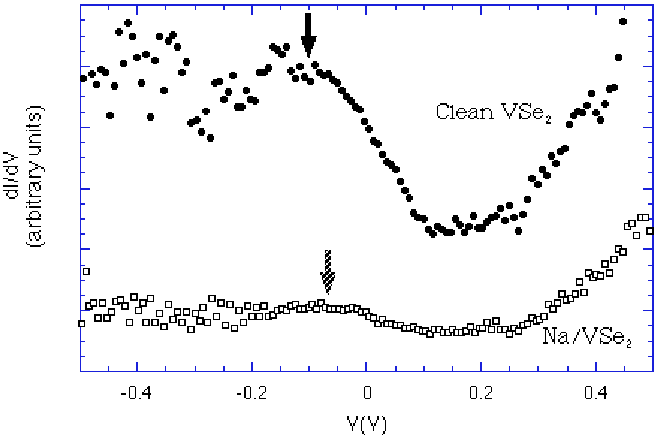

Fig. 2. Room-temperature scanning tunneling spectroscopy showing a peak at 100 mV below E_F on the clean material (dots). When 1 ML Na was evaporated, the peak was slightly shifted, to ~ 60 mV below E_F (squares). The spectra are shifted for clarity

2.2 $NaVSe_2$

When evaporating ≤ 1 ML at room temperature, STM images showed dark and bright areas with a height difference of 1.6 Å (Fig. 1b). This height was much smaller than the expected height from a monolayer step, which is more than 6 Å. Small holes in the bright areas were also found. The holes were ~ 1 Å deep and had a diameter of 1–2 nm. Inside the holes the atomic lattice was undistorted, meaning that the holes were not due to lattice defects.

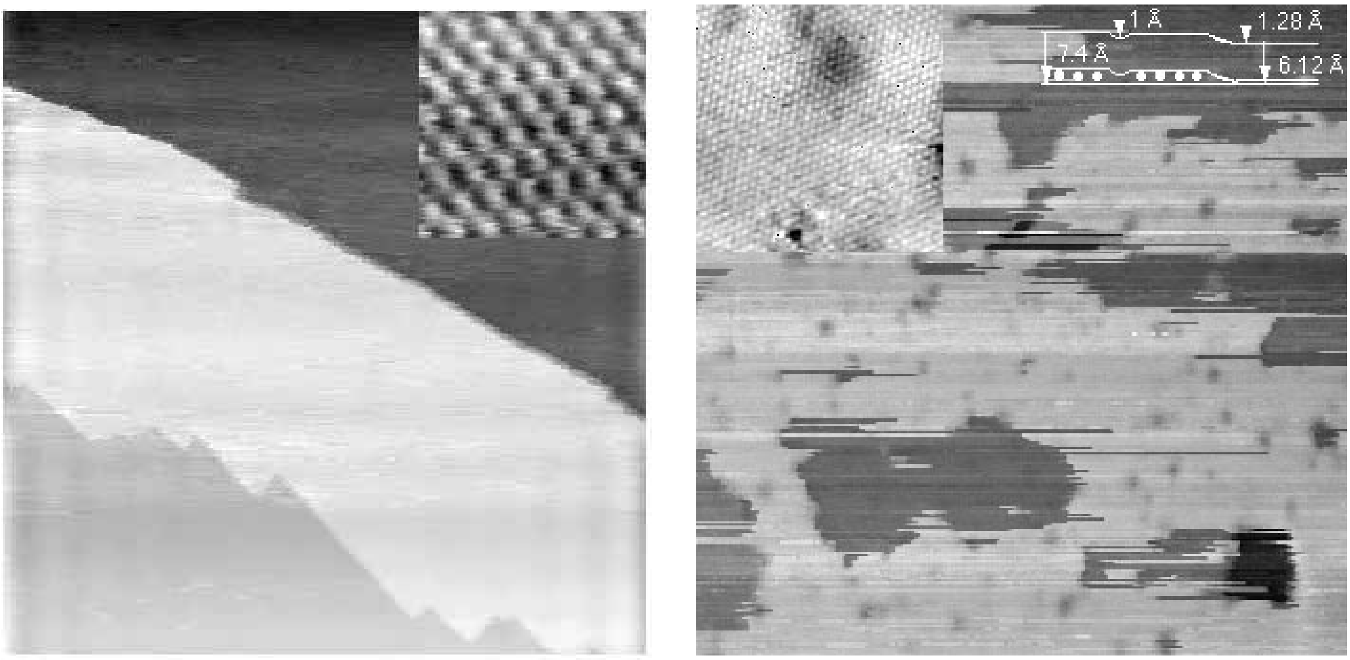

Fig. 1a,b. Room-temperature STM images. **a** Clean VSe_2 surface showing large, flat areas separated by single and multiple steps. $V_{\text{bias}} = -0.13$ V, $I = 0.84$ nA, scan range $800 \times 800\,\text{nm}^2$. Inset: atomic resolution of VSe_2. $V_{\text{bias}} = -0.11$ V, $I = 1.71$ nA, scan range $\sim 2.8 \times 2.8\,\text{nm}^2$. **b** After evaporation of 1 ML Na at room temperature, dark and bright areas and small holes are seen. $V_{\text{bias}} = -0.06$ V, $I = 2.32$ nA, scan range $100 \times 100\,\text{nm}^2$. Inset: inside the holes the atomic lattice is undistorted. A lattice defect can be seen at the bottom of the inset. $V_{\text{bias}} = -0.06$ V, $I = 2.32$ nA, scan range $\sim 9 \times 9\,\text{nm}^2$. The line sketch is a schematic of the interpretation of the bright and dark areas. Below the first layer Na atoms (dots) are present in a non-uniform fashion, leaving steps and holes

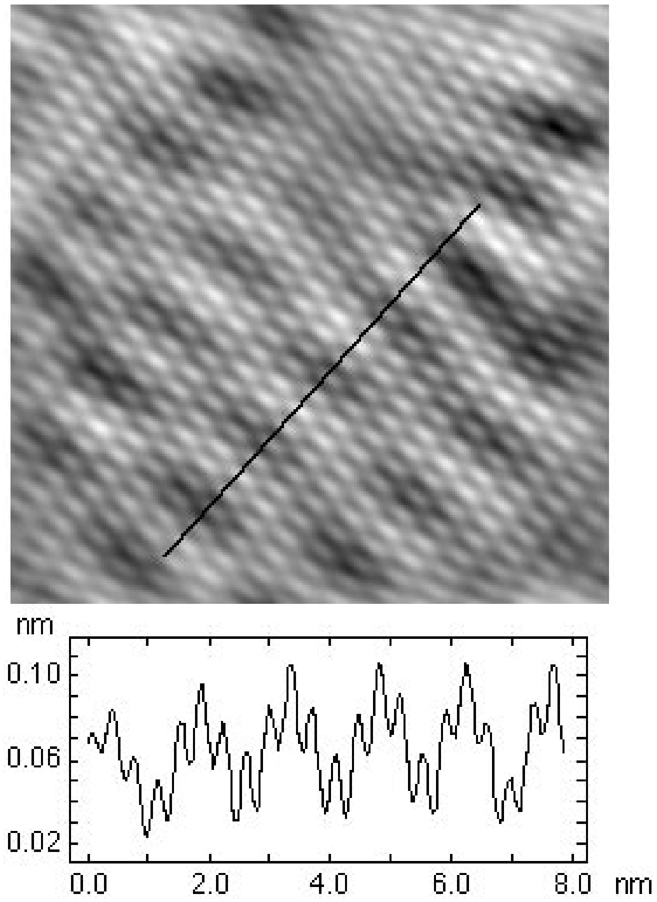

Fig. 3. STM image taken at 60 K of clean VSe$_2$, showing the 4 × 4 CDW that is known to occur below 110 K. The line profile clearly shows that every fourth atom is enhanced. The image is distorted due to lateral drift in the STM, so that the atomic lattice is not perfectly trigonal. $V_{\text{bias}} = 0.034$ V, $I = 1.74$ nA, scan size 10 × 10 nm^2

Room temperature STS of the intercalated material showed the same VSe$_2$ state as in the clean material (Fig. 2). It seems as that the state is slightly shifted compared with the clean material, to about 60 mV below E_F.

At 60 K two different types of spectra were recorded (Fig. 4b). Type 1 spectra showed a very clear, broad VSe$_2$ peak, but no sign of a CDW gap. Type 2 spectra showed a gap structure, but did not resolve the VSe$_2$ state. So far we have not obtained any high-quality topographic images at low temperature of the intercalated material, owing to a malfunction of the *y*-scanning direction that was discovered during the set of low-temperature experiments discussed here.

3 Discussion

Na evaporated in UHV intercalates quickly, and only very small amounts of Na should be present at the surface. The dark and bright areas are therefore interpreted as a non-uniform distribution of intercalated Na. The topographic height is increased when intercalated Na is present below the first VSe$_2$ layer, since Na atoms are too large to fit in the van der Waals gap. This increase in the *c*-lattice parameter is somewhat larger (1.6 Å) than expected (1.28 Å according to Wiegers [11]), but that might be explained by different charge densities in the different areas. The small holes are interpreted as locally missing Na. These holes are less deep than the “step height”, since the lateral extension is too small to restore the layer separation to its original value. A line sketch is shown in Fig. 1b to show the non-uniform distribution schematically.

The intercalated images are rather streaky. Streaks always show up in the scan direction, regardless of the angle of the scan. One could argue that this would originate from tip changes, so that the dark and bright areas mainly show when something happens in the tunneling junction. However, there are many indicators that this is not the case. The distribution of dark and bright areas is reproducible in subsequent scans, although some small parts can change from dark to bright, and vice versa. A tip change caused by Na on top of the sample would not cause any reproducibility in the scans, since that process would occur haphazardly in space. Also, we observe no differences with different polarity that might be expected if Na transfer was involved. We have not investigated the STM sample with any other surface analytical technique, but separately made photoemission ex-

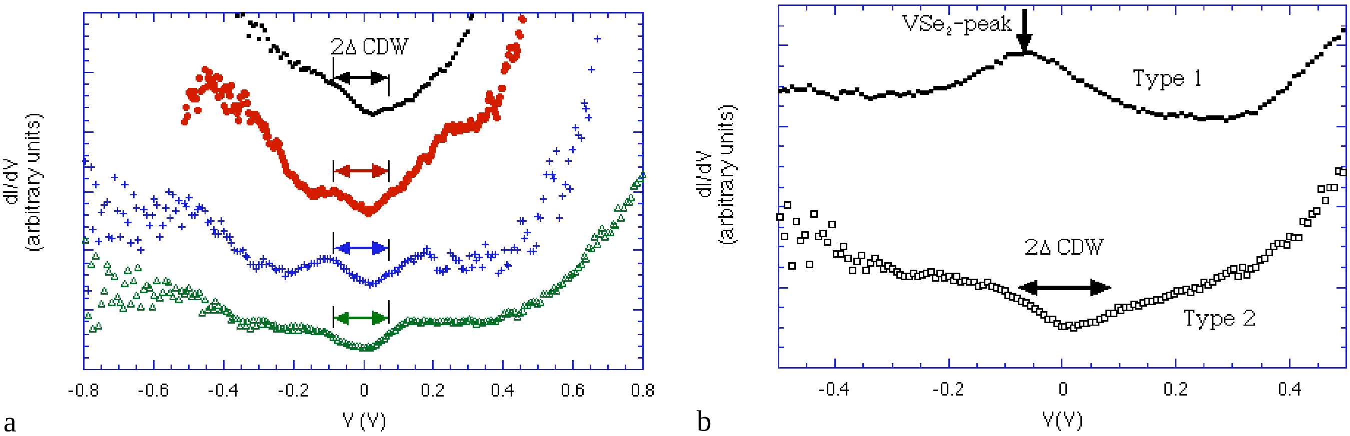

Fig. 4a,b. Spectra taken at 60 K. **a** Four different spectra taken from a clean surface, with different tips and samples, showing a CDW gap $\Delta \approx 80$ mV. The spectra are shifted for clarity. **b** In the intercalated sample two types of spectra are seen. Type 1 shows a broad VSe$_2$ peak but no CDW gap, and type 2 shows a CDW gap but no VSe$_2$-peak. The spectra are shifted for clarity periments on the same kind of samples show that only a very small amount of Na is present on the surface [12]. Photoemission also shows that the amount of contaminants is very small, due to the inert VSe_2 surface. Transfer of Na, or other atoms, between the tip and the sample is therefore not very likely. The tunneling current would also be unstable if alkali atoms were to jump repeatedly in the junction, but we have clear atomic resolution in the entire images. Since STM investigations of intercalated TMDs are rare and, to our knowledge, no in situ alkali-intercalated TMDs have been studied, this type of image has not been observed before. However, diffusion of alkali along the layers is known to occur and have a diffusion coefficient of the order of $10^{-8}\,\mathrm{cm}^2/\mathrm{s}$ [13]. We therefore believe that the streaks could be due to mobile Na below the first layer. This phenomenon has been observed at overlayers and is a consequence of the scanning speed being comparable to the atomic motion [14], leading to atoms moving during the time it takes to record the image. Our atomically resolved images seem to show atomic resolution even at the steps, so that the moving atoms are not dominating the observed surface structure. The atomic motion could possibly be induced by the presence of the tunneling tip. With slightly higher tunneling resistance we see no differences in the appearance of the images, but a systematic variation is needed to clarify whether the interaction between the tip and sample is the origin of mobility of intercalated material.

Intercalation often leads to structure changes in the host material. $NaVSe_2$ has two possible coordinations of Na, depending on the concentration. A trigonal prismatic structure, $3R$(I) is reported for lower concentrations, while an octahedral structure $3R$(II) is reported for high concentrations [11]. On the basis of photoemission studies, showing a stoichiometry of $Na_{0.2}VSe_2$ [12] and the increase in interlayer distance, it is likely that we have the $3R$(I) structure. The room temperature imaging of Na/VSe_2, together with photoemission results, is more thoroughly discussed in [12].

The shift of the VSe_2 peak 100 mV below E_F in the intercalated material cannot be explained by band calculations. Band calculations around the Γ point, that is, the k vectors that are mainly involved in STM imaging, predict a shift away from E_F in the intercalated material [15]. However, it should be noted that these band calculations are in less agreement with photoemission experiments around E_F than with measurements of lower-lying valence bands. The shift is below the limit of resolution in the photoemission experiments done, and can therefore not be confirmed in photoemission studies. It might also be a question of the resolution in our STS data, especially when considering that the peak is rather broad. However, the shift is the same at room temperature and at 60 K, and these are reproducible with different tips and samples.

STM images of the CDW in clean $1T$-VSe_2 are in good agreement with earlier work. The 4×4 CDW that should exist with low corrugation is seen together with the atomic lattice, as expected. Our estimation of the energy gap is larger than the energy gap reported by Wang et al. [16] at 4.2 K. They report a gap $\Delta \approx 40\,\mathrm{mV}$, giving $2\Delta/k_B T_{CDW} \approx 8.4$. CDW energy gaps are considered to follow a BCS-like behavior, with increasing gaps at lower temperatures. This means that our gap value is in contradiction to the value measured by Wang et al. It might be difficult to directly compare the gaps. Wang et al. measure with a voltage range of less then ± 100 mV and therefore do not resolve the VSe_2 state. That we see the VSe_2 peak ensures that we reflect at least a part of the band structure, although the width of the VSe_2 state complicates our estimation of the energy gap. The peak structure defining the gap below E_F is hardly detected, since it is concealed by the VSe_2 peak. Considering this difficulty, our gap estimation might be a slight overestimation. However, the peak structure above E_F is clearly seen in the spectra, and it is not controversial to assume a symmetric gap. The spectra are reproducible with different tips and samples, as seen in Fig. 4a. Since our VSe_2 peak is broad, one could expect, although it is not necessary, to see a tail of the peak in the spectra of Wang et al., but no structure is seen apart from the gap. To our knowledge, the value reported by Wang et al. is so far the only published energy gap value for VSe_2. However, the interpretation of STS spectra is far from simple, and it is worth noting that measurements of energy gaps in high-T_c superconductors have been showing large differences [17]. More experiments are needed to clarify this issue; in particular, a temperature-dependent study from the transition temperature down to low temperatures would be useful.

Our value of $2\Delta/k_B T_{CDW} = 13.3$ is comparable to the energy gaps in the $2H$-phase Ta compounds (15.4 for $2H$-TaS_2 and 15.2 for $2H$-$TaSe_2$), in agreement with that fact that $1T$-VSe_2 behaves more like the $2H$-compounds, with lower CDW corrugation (of the same order as the atomic corrugation) and no rotation of the CDW superlattice compared with the atomic lattice. VSe_2 does not exist in the $2H$-phase, but only in the $1T$-phase. $1T$-phase Ta compounds have much larger CDW corrugation (2–4 Å), a rotated $\sqrt{13} \times \sqrt{13}$ CDW superlattice, higher onset temperature (well above room temperature) and energy gaps $2\Delta/k_B T_{CDW} = 6$.

It is not possible to judge whether the two types of low-temperature spectra measured on the intercalated material originate from differences in the intercalated and non-intercalated areas, or are simply are due to tip changes. The induced $\sqrt{13} \times \sqrt{13}$ CDW superlattice at room temperature in Ag-intercalated $NbSe_2$ is local and seen at small areas across the surface [6]. It is therefore likely that intercalated atoms can change the electronic properties of the material locally, not giving any effects in the non-intercalated areas. The electron donation changes the Fermi surface and could therefore largely affect the CDW state and induce, as well as suppress a CDW, depending on the exact Fermi surface change. Our STS data are taken in grids across areas about 10 nm × 10 nm, and are then averaged over this area. It is possible that only one type of area (intercalated or non-intercalated) is involved in the measurement of tunneling spectra. However, we have presently no simultaneously recorded high-quality topographic images telling on which area we are doing spectroscopy. Since the tunneling tip is very crucial in all STM work, there is also a possibility that the different spectra are due to tip changes, where the tip sometimes favors the VSe_2 state and sometimes the CDW gap.

Our low-temperature STS results must therefore be considered as preliminary, and more work is needed to straighten out the details of this system. In particular, the CDW effects, for example locally induced CDWs, CDW suppressions, onset temperature changes and energy gap changes, should be further investigated.

4 Conclusions

We have studied clean and Na-intercalated $1T$-VSe$_2$ by STM and STS. STM images at room temperature of the clean material showed large and defect-free areas separated by single and multilayer steps. At 60 K the 4×4 CDW was seen together with the atomic lattice. STM images of Na intercalated VSe$_2$ at room temperature showed that the Na is non-uniformly distributed, with areas of intercalated and non-intercalated material, and small holes of locally missing Na in the intercalated areas. Room-temperature STS of the clean material showed a weak VSe$_2$ state 100 mV below E_F. In the intercalated material the state seemed to be shifted towards E_F, to ~ 60 mV. At 60 K the clean material showed a CDW gap $\Delta \approx 80$ mV together with the VSe$_2$ peak. The intercalated material showed two different types of spectra. One type showed a strong and broad VSe$_2$ peak but no CDW gap, while the other type showed a CDW gap, but no VSe$_2$ peak. We cannot decide whether the origin of these two types comes from the non-uniform distribution of Na.

Note added in proof

We now know that the ‘type 2’ spectra are connected to a strong CDW in the intercalated areas, while the ‘type 1’ spectra come from the clean material, that however still exhibits a 4×4 CDW.

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