Structure and magnetism of ultra-thin chromium layers on W(110)

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Abstract. We have investigated the structural and magnetic properties of ultra-thin Cr films on W(110) by means of low-energy electron diffraction intensity-versus-voltage (LEED IV) data acquired using selected-area diffraction within a low-energy electron microscope (LEEM), spin-polarized scanning tunneling microscopy (SP-STM), and \textit{ab initio} calculations. The interlayer distances as obtained from LEED IV data are compared to \textit{ab initio} calculations. The first-principles calculations predict very different interlayer spacings depending on whether the Cr films are antiferromagnetic or non-magnetic. Only antiferromagnetic spin ordering leads to interlayer spacings similar to the experimental spacings determined by LEED IV. This strongly suggests that films of one, two and three atomic layers of Cr on W(110) have antiferromagnetic short-range order. SP-STM data confirm this finding: the Cr monolayer on W(110) shows characteristic stripes along the [001] direction due to the antiferromagnetic order of nearest-neighbor Cr atoms. Additionally, the SP-STM data of the Cr monolayer reveal a periodically varying magnetic amplitude that peaks every 7.7 ± 0.5 nm. On thick Cr(110) films the signature of an
incommensurate spin density wave, existing in two different orientations, is found. We also compare the LEED IV and \textit{ab initio} relaxations of bare W(110) and bulk-like Cr(110) surfaces.

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1. Introduction

Chromium is a transition metal with a rich variety of magnetic properties that has been the focus of many studies. It is an itinerant antiferromagnet (AFM) in the bulk and presents an incommensurate spin density wave (SDW) [1]. In thin films the coupling with the substrate transforms this AFM SDW from an incommensurate to a commensurate one [2, 3]. Furthermore, the current interest in spintronics [4] has been partially initiated by the discovery of the giant magnetoresistance effect in Fe/Cr multilayers [5]. Further progress in this area depends on atomic level control in the manufacturing of spintronic devices.

Surprisingly, structural and magnetic characterizations of ultra-thin Cr films on W(110), a common substrate for thin metal films because of its resistance to alloying, are scarce [6]. Most studies actually focus on the thick-Cr regime [3], where the surface is assumed to be a proxy of bulk Cr. One open basic question is whether ultra-thin films of Cr on W(110) present magnetic ordering, and if so, what kind? The problem is challenging because few methods are capable of detecting antiferromagnetism in such thin layers. Recent \textit{ab initio} calculations seem to indicate that a monolayer might be magnetic [7]. We note that spin-polarized scanning tunneling microscopy (SP-STM) has shown that a monolayer of Mn on W(110) exhibits local antiferromagnetic order [8]–[10].

Here we present a combined low-energy electron diffraction intensity-versus-voltage (LEED IV), SP-STM, and \textit{ab initio} calculation study with the aim of obtaining a thorough understanding of the atomic and magnetic structure of Cr films a few atomic layers thick on W(110). LEED IV is the classic tool for determining the interlayer spacings between the first few atomic surface layers with errors in the 0.01–0.02 Å range. A satisfactory comparison of LEED with \textit{ab initio} density functional theory (DFT) is also a mature approach and, in general, is considered the gold standard for surface structure determinations. Well-converged
spin-polarized (SP) DFT calculations usually predict surface relaxations in good agreement with experiment even for magnetic materials. In the past, a systematic discrepancy has been reported between experimental and \textit{ab initio} calculations for particular transition metal surfaces \cite{11}. To check for any of the presumed effects that caused those discrepancies \cite{12}, we also include in our LEED IV study the limiting cases of the bare W(110) and bulk-like Cr(110) surfaces. Finally, SP-STM is one of the few techniques able to measure local antiferromagnetic order on surfaces \cite{13}. By depositing a ferromagnetic film on the tunneling tip, images with contrast related to the magnetic structure of the surface can be acquired. The sensitivity of the tip to either in-plane or out-of-plane surface magnetic moments can be tuned by applying magnetic fields.

2. Experimental and theoretical calculation details

2.1. Low-energy electron microscopy and diffraction

A low-energy electron microscope (LEEM) \cite{14} was used both to characterize the growth of Cr on W(110) and to acquire the LEED IV curves \cite{15,16}. While imaging, Cr was evaporated by electron-bombardment at a typical flux of 0.14 AL min\(^{-1}\) for the ultra-thin films and up to 1 AL min\(^{-1}\) for thick films. The background pressure remained in the 10\(^{-10}\) torr range during the experiments. The W(110) crystal was cleaned by exposure to O\(_2\) followed by repeated flashes to 2200 K. Terraces wider than a few microns could be routinely found on the surface.

The first 3 AL of Cr grow layer-by-layer on W(110). As soon as the 4th layer nucleates, the films break up, giving rise to tall three-dimensional (3D) islands surrounded by a monoatomic Cr wetting layer on W(110) \cite{3,6}. For Cr films with thickness below 3 AL the LEED data always showed a 1×1 pattern, indicating in-plane pseudomorphic growth of Cr on W(110) in ultra-thin films. To obtain a film surface with properties equivalent to the (110) surface of bulk Cr, relatively thick Cr films (15–40 AL Cr) were first grown on W(110) with the substrate held at room temperature (RT), and subsequently annealed to 600 °C while observed in LEEM. Thick Cr films also exhibit a 1×1 pattern, but with the in-plane lattice spacing of a bulk-Cr (110) surface.

The IV curves are acquired within the LEEM instrument by changing the power of the lenses in order to image the back-focal plane of the objective lens. The use of LEEM as a LEED diffractometer provides several advantages over a conventional LEED system, among them the ability to acquire the specular beam in normal incidence. The LEED IV data was obtained from 2 µm diameter areas using an illumination aperture to limit the electron beam size on the sample. The sample was cooled to RT before measuring the IV data.

The (00), four symmetry-equivalent (01) and two symmetry-equivalent (11) beams were measured at primary electron energies of 50–350 eV, giving a total energy range \(\Delta E\) of 900 eV, which is more than enough to provide accurate estimates of the last layers’ relaxations \cite{12}. Equivalent beams were averaged. The Pendry factor \(R_P\) between equivalent beams was always lower than 0.10.

Fully dynamical LEED IV curve calculations were performed with a modified version of the Van Hove–Tong package \cite{17}. The surface was modeled by stacking the necessary number of Cr layers over five layers of W bulk, using the renormalized forward scattering (RFS) approach. Relativistic phase-shifts \cite{18} were calculated and subsequently spin-averaged.
explored the parameter space comprised of the topmost three interlayer spacings, \(d_{1-3}\) (up to the 4th layer distance for the 3 AL Cr case) by calculating the IV curves over fine 3D parameter grids. The interlayer spacings were swept over wide ranges.

All simulations were performed for a temperature of 300 K. The experiment–theory agreement was quantified via Pendry’s \(R\)-factor \([19]\), \(R_P\), while the error bars for each parameter were obtained from its variance \([20]\) \(\Delta R_P = R_{P_{\text{min}}} \sqrt{8E_i/\Delta E}\), where \(E_i\) gives the optical (inner) potential. Correlations between the structural parameters were taken into account for the estimation of error limits. We note that all structural parameters derived in this work represent well-defined minima in their respective \(R\)-factor plots. Non-structural parameters such as the muffin-tin radius, the optical potential or the Debye temperatures at the surface planes were also varied.

2.2. Ab initio calculations

Modeling of thin magnetic films on a non-magnetic material within DFT requires a careful choice of approximations and estimates of the overall accuracy. As we will see, especially how the electronic exchange and correlation is treated (local density approximation (LDA) or generalized gradient approximation (GGA)) crucially affects the interplay between heteroepitaxial stress, relaxation and magnetic structure. We calculate the ideal bulk W and Cr lattice parameters using both LDA and the Perdew–Burke–Ernzerhof (PBE) GGA \([21]\), using the Vienna VASP code \([22]\). The clean slab calculations are performed using eight-layer slabs for W(110) and nine for Cr(110), at the ideal in-plane lattice constants. Nine layers is the minimum number of Cr layers required to obtain in-plane antiferromagnetic coupling with magnetic moments like in bulk Cr in the center of the slab. Only GGA finds an antiferromagnetic ground state for Cr \((m = 1.08 \mu_B \text{ atom}^{-1})\). The LDA result is always non-magnetic, a well-know issue with LDA.

The lattice constants determined by SP GGA-PBE reproduce the experimental numbers better than LDA. Still, the calculated lattice mismatch between W and Cr is 9.9%, compared to 8.8% for literature bulk values. The larger mismatch should lower the tendency for pseudomorphic wetting in SP-GGA-PBE and even more so for non-magnetic GGA and LDA.

The different strain-energy cost is reflected in the calculations of bulk Cr strained to the W(110) in-plane lattice constant. In non-magnetic LDA the energy cost is 0.290 eV per Cr atom with the \(z\)-layer (out-of-plane) spacing compressed by 23.3%. In non-magnetic GGA these values reduce to 0.259 eV and 21.8%, respectively. In SP-GGA, finally, they are 0.218 eV and 15.3%. To estimate the effect of the exaggeration of the W–Cr lattice mismatch in W–Cr pseudomorphic slabs, the latter calculation was repeated for an in-plane strain corresponding to only 8.8%, instead of a 9.9%, mismatch. Now the strain costs only 0.180 eV per Cr atom. Therefore, the calculations of pseudomorphic Cr layers on W(110) are expected to be 0.038 eV too high in energy.

Finally we note that all the slab calculations for W(110) and films of Cr on W(110) are done at the fixed, theoretical W in-plane lattice constant. All other geometry parameters, which include the separation between layers, are allowed to relax. The layer relaxation is reported relative to the theoretical bulk layer separation.

2.3. SP-STM

The SP-STM measurements were performed at the University of Hamburg in a five chamber ultra-high vacuum (UHV) system with separate chambers for sample and tip preparation,
thin-film deposition, conventional surface analysis (LEED, Auger electron spectroscopy, etc), and low-temperature STM using a home-built instrument [23]. During the STM measurements the tip and the sample were held at a temperature $T = 13 \pm 1$ K. Tips were prepared by electrochemically etching a polycrystalline W wire. Upon introduction of the tip into the UHV system via a load lock, the tip was briefly heated at a temperature $T \geq 2200$ K to remove tungsten oxides. For spin-sensitive experiments the tips were coated by a thin Fe film. The substrate is cleaned by cycles of oxidation at $T = 1500$ K and subsequent high-temperature flashing ($T \geq 2200$ K) [24]. Cr films were grown by thermal evaporation from a W crucible at a pressure $p \leq 3 \times 10^{-10}$ mbar. All STM data presented here were recorded in the constant current mode.

3. Results and discussion

3.1. Growth of Cr on W(110)

At temperatures between 200 and 360°C the growth of Cr on W(110) takes place layer by layer, but only for the first three monolayers [3]. Figure 1 shows a growth series taken by LEEM at 360°C. Within the field of view of the images shown (7 µm, although 20 µm images were also acquired), all the growth proceeds by step flow. But before the third layer is completed, four-layer thick islands appear in the film, and a dewetting process takes place by...
which further growth removes the second and third layers and produces tall 3D islands in the
Stranski–Kranstanov growth mode (see figure 7(a)). The LEED pattern of the films between one
and three monolayers is the same as that of the substrate indicating a common in-plane lattice
parameter. This pattern indicates a relaxed spacing [6]. A similar behavior has been observed
on Cr/Mo(110) by STM [25].

As the interlayer distance between the surface layer and the first sub-surface layer, \(d_{1-2}\), of unreconstructed transition metals has been the subject of a lively debate [11], we first
focus on the bare W(110) and bulk-like Cr(110) surfaces to check our agreement between
theory and experiment. A systematic discrepancy between LEED experiments and \textit{ab initio}
calculations was reported for transition-metal surfaces: in most available cases, the first layer
DFT contractions were larger than the experimental ones. This disagreement is—given the
simplicity of the problem—surprising and prompted suggestions that the smaller experimental
relaxation could be related to contamination, for example by hydrogen absorption [26].
Currently, many of the previous discrepancies have been resolved, including W(110), Rh(100)
and Ti(0001) [12] as well as for Ru(0001) [15].

3.2. The bare W(110) surface

Given its role as a model system, W(110) has been the subject of recent detailed STM [24]
and LEED studies [27, 28]. To test for the effect of surface roughness, which is not included in
the multiple scattering programs currently in use, flat [27] and stepped substrates [28] have
been investigated. All the more recent experimental studies agree in a contraction of \(d_{1-2}\)
of \(\approx 3\%\), which is also in agreement with surface x-ray diffraction studies [29]. Our results
shown in figure 2 are in the same range. Our best fit (shown in figure 2(b)) to \(d_{1-2}\) results
in a contraction of \((-2.8 \pm 1.2\%)\), with a \(R_p = 0.13\). We note that roughness cannot play a
role in our results as we employ selected-area diffraction with at most two atomic steps in the
surface area 2 \(\mu\)m in diameter where the LEED IV data were acquired. Our comparison with
the \textit{ab initio} calculations \((-3.8\%)\) is actually within the error bars of our experimental data.
Nevertheless, the difference follows the same trend that other studies have observed on W(110):
the experimental contractions tend to be at least 1\% smaller than the theoretical predictions. The
theory/experiment discrepancy seems to be particular to the case of the W(110) surface [29],
and does not extend to other transition-metal surfaces.

3.3. The Cr(110) surface

The Cr(110) surface was obtained by growing thick films of Cr on W(110) (between 15–40 AL
in the LEEM experiments, and close to 100 AL for the SP-STM experiments). As thick-film

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7 In a minority of local regions containing 2 and 3 AL of Cr examined by selected area diffraction the (00),
and first-order spots were weakly split (‘streaked’) along the [001] direction. These streaks disappeared with mild
annealing (well below the growth temperature). In addition, the 3 AL regions contained linear defects visible in the
LEEM images. These observations suggest that 3 AL of Cr can exist in a metastable, non-pseudomorphic
structure, which is likely a precursor to the moiré structure of thicker films. We emphasize, however, that our
LEED IV analysis was performed on pseudomorphic regions.

8 Most of the resolved discrepancies have been attributed so far to experimental problems rather than \textit{ab initio}
calculation issues. Either hydrogen contamination or a dataset of insufficient energy range have been singled out
as responsible in selected cases.
Figure 2. (a) LEED pattern of W(110). (b) LEED IV curves of clean W(110). (c) LEEM image of a 15 AL Cr film on W(110) after annealing to 633°C. The field of view is 20 µm. The dark features are trenches extending down to the 1 AL Cr wetting layer (one is marked by an arrow), which formed during annealing. The circle shows the area where the diffraction data was obtained. (d) LEED IV curves of the thick Cr(110) film.

growth at elevated temperatures produces 3D islands, the growth was performed at RT. After the growth of a few atomic layers, the backscattered electron intensity decreases greatly, until nothing can be seen in LEEM images. Even the diffraction pattern was featureless. To obtain a smooth surface, annealing of the RT-grown film was performed. In agreement with previous reports \[3\] we found that the backscattered electron intensity increased greatly close to 600°C. Annealing at this temperature yielded a locally flat film conformal to the substrate, i.e. the atomic surface steps of the Cr film are mainly located over the substrate steps. However, the film also started to scarify in the same temperature range, with deep trenches extending down to the one-layer-thick wetting layer. By means of the LEEM apparatus we could measure easily the diffraction pattern of the Cr film by performing selected-area diffraction, as shown in figure 2(c).

Caution should be applied, however, when using spatially averaging diffraction techniques since this (rather typical) procedure to obtain a flat Cr film as a proxy of a Cr(110) bulk terminated surface can produce trenches that extend down up to the Cr/W(110) wetting layer.

The LEED IV data acquired from the surface of the thick Cr(110) is shown in figure 2(d). From the multiple-scattering fit to the data (\(R_p = 0.10\)) we obtained a last-layer relaxation of \(-2.2 \pm 1.4\%\) relative to the bulk Cr(110) interlayer spacing (see table 1), to be compared to the SP-GGA prediction of \(-2.1\%\). The second layer is also observed to contract in the LEED best fit, although the \textit{ab initio} result indicates a very small expansion.
We have also investigated the surface of thick Cr(110) films on W(110) by means of STM. Figure 3(a) shows an STM image of a $\approx 100$ AL thick flat Cr film grown on W(110). At the measurement temperature of the SP-STM experiments, $T = 13 \pm 1$ K, this film thickness results in an incommensurable SDW [3]. Although we cannot exclude that the film showed annealing-induced trenches on a meso- or macroscopic scale, it was homogeneous on a lateral scale of microns with some very wide atomically flat terraces. For example, figure 3(b) shows an image ($250$ nm $\times$ $250$ nm) taken from such a terrace. In general, two surface patterns can be recognized, which have been identified as different domains of the charge-density wave (CDW) in an earlier spin-averaged STM study employing non-magnetic probe tips [30]. The first pattern, labeled A in the lower part of figure 3(b), is less common. It is characterized by stripes along the $[1\bar{1}0]$ direction with a periodicity $P$ of about 30 Å. The vast majority of the sample surface exhibits another pattern (B,C) with stripes along the $[001]$ direction and a periodicity of about 42 Å. In [30] these patterns were interpreted as the manifestation of CDWs with wave fronts propagating in different directions. Our data fully agree with this interpretation. In the bulk all three $\{100\}$ directions are degenerate and equally probable. At the surface, however, the CDW with the wave vector $\vec{Q} \parallel [001]$ is strongly damped and less frequent. Since it propagates within the sample surface, its apparent periodicity is consistent with the periodicity of the CDW, i.e. 30 Å. The surface is dominated by the CDWs that are propagating along the other two $\{100\}$ directions, which are tilted by $45^\circ$ with respect to the surface plane. Therefore, the apparent periodicity of these CDWs (B,C) is $\sqrt{2} \times 30$ Å $\approx 42$ Å, corresponding to 10–11 times the lattice constant. Both domains can be recognized as spots in the Fourier-transformed image (figure 3(c)).

As stated in [30] ‘a fascinating, however challenging, goal to achieve is the direct observation of the SDW with the help of ferromagnetic STM tips’. In this spirit we have performed spin-resolved STM measurements with Fe-coated probe tips. Figure 4(a) shows

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**Table 1.** Changes in the interplanar spacings as determined from experimental LEED studies and *ab initio* simulations, both spin-polarized (sp) and non-spin-polarized (np), given in percent relative to the W(110) bulk interlayer spacing. Results for the Cr(110) surface are given relative to the Cr(110) bulk spacing.

| Surface       | Method  | $d_{1-2}$   | $d_{2-3}$   | $d_{3-4}$   | $d_{4-5}$   |
|---------------|---------|-------------|-------------|-------------|-------------|
| W(110)        | LEED    | $-2.8 \pm 1.2$ | $+0.2 \pm 1.0$ | $-0.7 \pm 2.2$ |             |
|               | GGA     | $-3.8$      | $0.0$       |             |             |
| Cr(110)       | LEED    | $-2.2 \pm 1.4$ | $-1.3 \pm 1.3$ |             |             |
|               | GGA-sp  | $-2.1$      | $0.24$      |             |             |
| 1 AL Cr/W(110)| LEED    | $-8.0 \pm 0.7$ | $+0.3 \pm 1.4$ |             |             |
|               | GGA-sp  | $-8.55$     | $0.04$      |             |             |
|               | GGA-np  | $-15.4$     | $1.46$      |             |             |
| 2 AL Cr/W(110)| LEED    | $-17.0 \pm 0.7$ | $-7.4 \pm 1.3$ | $+0.4 \pm 1.4$ |             |
|               | GGA-sp  | $-18.3$     | $-6.82$     | $-0.16$     |             |
|               | GGA-np  | $30.1$      | $-6.28$     | $-0.27$     |             |
| 3 AL Cr/W(110)| LEED    | $-16.0 \pm 1.3$ | $-13.6 \pm 1.4$ | $-7.0 \pm 3.6$ | $-1.9 \pm 4.4$ |
|               | GGA-sp  | $-18.1$     | $-15.6$     | $-7.37$     | $-0.16$     |
|               | GGA-np  | $-30.6$     | $-16.9$     | $-10.2$     | $-0.07$     |
Figure 3. (a) Large-scale STM image of an approximately 100 AL thick Cr film on W(110). Wide atomically flat terraces and single atomic step edges are clearly resolved. (b) Atomically flat terraces of a Cr(110) film on W(110) taken with a non-magnetic W tip ($U = -10$ mV and $I = 0.3$ nA). Similar to previous studies that were performed on the surface of bulk Cr(110) \cite{30}, two different regions can be distinguished: wherever the wave vector $\vec{Q}$ of the charge-density wave (CDW) is within the film plane along the [001] direction, stripes along the [1$\bar{1}$0] direction with a periodicity $P = 30$ Å and a relatively small corrugation can be recognized (see region A). If, however, $\vec{Q}$ is along the \{100\} directions, which are not within the surface plane, the periodicity amounts to $P = 42$ Å and the corrugation is larger (region B, C). (c) These domains give rise to discrete spots in the Fourier-transformed image.

A constant-current SP-STM image as measured on a thick Cr(110) film on W(110) being very similar to the one presented in figure 3. Figure 4(b) displays the same image but fully differentiated along the fast scan direction. The measurements were taken at a bias voltage $U = -2$ mV, i.e. essentially at the Fermi level. While the contrast observed in the constant-current SP-STM image of figure 4(a) is clearly dominated by the CDW, the existence of a weak additional short-range modulation with wave fronts parallel to the CDW (arrows) becomes clearly visible in the differentiated image of figure 4(b). This additional modulation is caused by SP tunneling between the ferromagnetic Fe tip and the antiferromagnetic surface with maxima and minima of the lines representing atomic rows of spins being oriented parallel or antiparallel with respect to the tip magnetization direction, respectively. From earlier investigations on
Figure 4. (a) Constant-current SP-STM image of a thick Cr(110) film on W(110) measured with a magnetic Fe-coated probe tip ($U = -2$ mV and $I = 40$ nA). The image contrast is dominated by the CDW state exhibiting a period of about 42 Å. (b) Differentiated image of (a) making the SP contribution to the tunneling current visible. The observed small-scale periodicity corresponds to an antiferromagnetically ordered state about 0.1 times the period of the CDW. (c) Fourier-transformation of (a) shows satellites (arrows), which are characteristic for the incommensurate SDW of Cr. The inset shows a magnification of the central region with small reciprocal lattice vectors.

Cr(001) [31] we know that the spin-flip transition between a transverse (T) and a longitudinal-SDW (L-SDW), which in the bulk occurs when cooling below $T_{sf} = 123$ K, is suppressed at the surface, probably due to a strong in-plane surface anisotropy. We expect a similar behavior for the Cr(110) surface. Furthermore, the Fe-coated probe tips used here are known to be in-plane sensitive [32]. Therefore, we believe that the atomic scale magnetic contrast in figure 4(b) represents the in-plane component of magnetization. As already mentioned in the introduction, Cr exhibits an incommensurate SDW that gives rise to characteristic satellites in neutron diffraction experiments [1]. The Fourier transform of figure 4(a) is shown in figure 4(c). We can recognize a set of spots close to the central region of figure 4(c), representing the CDW (between arrows on inner circle) and a pair of satellites at much larger reciprocal lattice vectors (outer arrows). The latter are arranged around the positions where the atomic lattice peaks in a non-spin-resolved measurement are to be expected (outer circle). Thus the satellite peaks are caused by the incommensurate SDW and only visible in spin-resolved measurements. Detailed analysis reveals the relative distances are in full agreement with the expected periodicities of the CDW and SDW at low temperatures, i.e. 10–11 lattice constants for the CDW and 20–22 lattice constants for the SDW [2]. Interestingly, the maximal SDW contrast is observed where the CDW exhibits a minimum charge density at the Fermi level.

3.4. Thin Cr films on W

LEED IV data (see figure 5) were acquired in perfect 1 and 2 AL films on W(110) (grown, respectively, at 200 and 360 °C) from single terrace areas. The structures that best fit the LEED IV data have an $R_p$ of 0.10 and 0.08, respectively. The ab initio calculations (see table 1)
have been obtained both without and with spin polarization\(^9\). There is a large difference in the predicted relaxations depending on whether the spin polarization is included or not. In fact the differences are much larger than the error bars of the LEED fits. As seen in table 1, the experimental results are only compatible with the calculations that include spin-polarization, i.e. the calculations of an antiferromagnetic unit cell. Based on this strong effect of magnetism on the structure of the films, we predict that films of one and two atomic layers of Cr on W(110) are antiferromagnetic\(^10\).

This result is in agreement with the SP-STM data shown in figure 6. The data were measured on a sample with an average coverage of 1.05 AL Cr grown on W(110) at slightly elevated temperature. The overview of figure 6(a) shows that only a small fraction of the W(110) substrate, mainly on the upper terrace around atomic step edges, remains visible. Large areas of the three visible atomically flat terraces exhibit monolayer coverage (1 AL). On the right side of the image a stripe with a local coverage of two atomic layers (2 AL) can be recognized. As we zoom on to a terrace covered by a Cr monolayer, stripes running along the [001] direction become visible (figure 6(b)). These stripes, being visible with magnetic probe tips only, are characteristic of row-wise antiferromagnetic order [8]. The same local magnetic superstructure was observed for 2 AL Cr/W(110) (not shown). In the high-resolution SP-STM image of the Cr monolayer on W(110) shown in figure 6(c), the inter-stripe distance was determined to be 4.6 ± 0.2 Å, in agreement with the nominal periodicity along the [110] direction of 4.48 Å and the antiferromagnetic order found on the basis of the LEED and \textit{ab initio} calculations mentioned above. Closer examination of figure 6(b) reveals, however, that the magnetic corrugation of the stripes along the [001] direction is not constant but exhibits a weak modulation resulting in areas of blurred contrast every 7.7 ± 0.5 nm. The observed structure resembles recent SP-STM data measured on the pseudomorphic Mn monolayer on W(110), where the magnetic order was not perfectly antiferromagnetic but slightly canted, resulting in a spiral spin structure with a period of about 12 nm [10, 37]. However, in this case the modulation is along a different crystallographic direction, i.e. along the [110] direction (Cr) instead of the [001] direction (Mn).

\(^9\) In the SP \textit{ab initio} calculation, the lowest energy structure was the one shown in the inset of figure 6.

\(^{10}\) Besides using SP STM, we also tried to detect signatures of the magnetic ordering of the surface using LEED. Observations of this type, predicted by theory [33, 34] have been reported for surfaces of bulk AFMs, such as NiO [35], as well as for thin films [36]. We find indeed weak half order spots, however, they correlate with increasing contamination, and annealing temperature. For the cleanest Cr film at low temperature these spots disappear completely. We thus conclude that they are not of magnetic origin.
Figure 6. SP-STM images of 1.05 AL Cr/W(110) taken with a Fe-coated probe tip. (a) The overview shows that a small fraction of the substrate is still visible. The local Cr coverage is indicated. (b) Zooming on to an atomically flat terrace reveals stripes running along the [001] direction. A weak modulation of the magnetic signal with a periodicity of \(7.7 \pm 0.5\) nm can be recognized (gray arrows). (c) High-resolution SP-STM image of the Cr monolayer on W(110). The inter-stripe distance amounts to \(4.6 \pm 0.2\) Å, which is in reasonable agreement with the nominal periodicity of 4.48 Å. (d) Interpretation of the SP-STM in terms of the expected surface antiferromagnetic order from the \textit{ab initio} calculation (the \(p(2 \times 1)\) AFM unit cell is marked). The W atoms are shaded pink or green depending on their spin alignment.

Although we are not yet able to propose a particular spin configuration that is in agreement with the modulation observed in figure 6(b), the Cr monolayer on W(110) may exhibit a similar deviation from perfect antiferromagnetic order. We would like to emphasize, however, that this result does not invalidate the finding of local antiferromagnetic order as deduced from the comparison of LEED IV and \textit{ab initio} calculations because the deviation from perfect antiferromagnetic order is expected to be small.

Three-monolayer-thick films could not be grown as a complete film. As shown in the LEEM image of figure 7(a), our best attempt had \(\approx 75\%\) of the surface covered with 3 AL, while the remaining area had 2 AL Cr, and a few well-separated 4 AL islands. IV data were acquired in an area free of Cr coverages above 3 AL indicated by a circle in figure 7(a). Fitting the IV data to a combination of 3 and 2 AL with the relative ratio as a free parameter gave a relative coverage of \(80\% \pm 18\%\) \((R_P = 0.13)\), in close agreement with the morphology shown by

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Figure 7. (a) LEEM image, 7 µm wide, of an incomplete 3 AL Cr film. (b) LEED IV curves of the area marked by a circle in (a).

Table 2. Calculated magnetic moments of Cr films (all in units of µB/atom).

| Film          | Top W | 1st Cr | 2nd Cr | 3rd Cr | 4th Cr |
|---------------|-------|--------|--------|--------|--------|
| 8 AL W + 1 AL Cr | 0.31  | 2.68   |        |        |        |
| 8 AL W + 2 AL Cr | 0.26  | 1.76   | 2.84   |        |        |
| 8 AL W + 3 AL Cr | 0.25  | 1.64   | 1.95   | 2.89   |        |
| 8 AL W + 4 AL Cr | 0.24  | 1.56   | 1.88   | 2.05   | 2.91   |

LEEM. The theory/experiment comparison (table 1) follows the same trend as the 1 and 2 AL films: only the SP calculations are in reasonable agreement with the experimental structure.

We have no measurement of the Néel temperature of ultra-thin Cr films on W(110). Our direct observations of the antiferromagnetic order in the SP-STM experiments were performed at 13 K. The Néel temperature of bulk Cr is 308 K. In theory, at constant magnetic coupling strength $J$, a thin Cr film should have a reduced or at best unchanged Néel temperature [38]. This could be counteracted if $J$ increases. The Néel temperature, like the Curie temperature, is proportional to $J$, which in turn is proportional to the magnetic moment per atom [38, 39]. Table 2 lists the calculated magnetic moments (GGA-sp) of each layer of the different ultra-thin Cr films. For comparison, the calculated magnetic moment of a Cr atom in bulk bcc-Cr is 1.08 µB. If the bulk Cr is strained in-plane by 9.9% to match the W(110) substrate, the increase in the effective volume per atom results in a magnetic moment of 1.99 µB. For the ultra-thin Cr films we find an even higher value of 2.7–2.9 µB for the top Cr layer. While intermediate Cr layers are close to the strained bulk value, the magnetic moment of the Cr layer at the Cr/W(110) interface is reduced to 1.7 µB. The top W layer picks up about 0.3 µB from contact with Cr. The enhanced moments of the surface Cr compared to bulk can again be explained by the increased effective volume per atom in that case [39].

4. Summary

We have followed the growth of ultra-thin films of Cr on W(110) by LEEM. The growth is layer-by-layer over a wide range of temperature until the fourth layer starts to nucleate. Then 3D islands grow, and the third and second layers are removed.
By means of selected-area diffraction, we have measured the LEED IV curves on both clean surfaces of W(110) and Cr(110) and films of one, two and three atomic layers of Cr/W. For the W(110) and Cr(110) surfaces the experimentally determined last-layer contractions are in good agreement with the \textit{ab initio} calculations of the same surfaces by GGA-PBE. For the Cr films, the \textit{ab initio} calculations are quite different depending on whether the calculation is SP with antiferromagnetic ordering or not, with last-layer out-of-plane relaxations that are twice as large for the non-SP calculations. Our experimental results are in good agreement with the \textit{ab initio} predictions with spin polarization implying that Cr ultra-thin films are antiferromagnetically ordered.

By SP-STM we proved that the 1 and 2 AL films are indeed antiferromagnetically ordered on a short range: using a Fe-coated tip we detect in-plane magnetic contrast that alternates every atomic row in the [1\textbar\bar 10] directions. This agreement validates the proposed method of detecting magnetism in thin films by the effect of the magnetic structure on the interlayer relaxation. Furthermore, on 1 AL Cr films we have detected a long-range modulation along [001] with $7.7 \pm 0.5$ nm periodicity. We also presented the first real-space observations of the SDW of the Cr(110) surface by means of SP-STM experiments. The periodicity of the SDW is consistent with the CDWs observed on the same surface.

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