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# The structure of the surface compound CrN formed by cosegregation on a Fe–15%Cr–N(100) single crystal surface

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## Abstract

Cosegregation is known to cause the formation of two-dimensional chemical compounds (surface compounds) which can be epitaxed to substrate surfaces of a suitable structure. In the present work the cosegregation-induced formation of the CrN surface compound on nitrided Fe–15%Cr–N(100) single crystal surfaces was studied by means of Auger electron spectroscopy and low-energy electron diffraction. Intensity versus energy spectra ( $I(E)$ ) were measured and analysed fully dynamically to investigate the structural details of the CrN surface compound. It is found that nitrogen is segregated to the surface forming the sample's top layer and substantial amounts of chromium are cosegregated with nitrogen. Nitrogen atoms reside in four-fold symmetric hollow sites about 0.1 Å above the metallic substrate. There is a huge relative expansion of the distance between the first and second metal atom layers ( $\Delta d_{12}/d_0 \approx 26\%$ ), while the distances between deeper layers are almost bulk-like. The small distance between the nitrogen and the top metal layer as well as the huge layer expansion  $\Delta d_{12}/d_0$  are in agreement with results found for N/Cr(100). © 1998 Elsevier Science B.V.

**Keywords:** Auger electron spectroscopy (AES); Chromium; Iron; Low energy electron diffraction (LEED); Nitrides; Nitrogen; Surface compound formation; Surface phase transition; Surface segregation

## 1. Introduction

In ternary or even more complex alloy systems, the cosegregation of two (or more) solutes at surfaces and grain boundaries is possible, and is caused by strong attractive interactions between different solutes [1]. Since the late 1970s the study of cosegregation phenomena has attracted considerable interest, which basically has been driven by the need to understand the influence of cosegregation processes on the temper embrittlement

of steels [2]. Although the possibility of the segregation- and cosegregation-induced formation of two-dimensional compounds was discussed quite early [3], it was only a decade later that the first experimental evidence for this was provided, with the formation of TiC on Fe–6%Al–0.5%Ti–C(100) alloy single crystals [4]. Because such surface-confined and epitaxially stabilized compounds represent a new class of material and promise a broad spectrum of interesting physical properties (e.g. two-dimensional conductivity, superconductivity and magnetism), surface compound formation has been studied in detail for a variety of (bcc) iron-based alloys with different surface orientations. In most of these studies the

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emphasis was on the investigation of epitaxially stabilized two-dimensional surface carbides and nitrides on (100)-oriented alloy surfaces, for example TiC on Fe–6%Al–0.5%Ti–C(100), CrN on Fe–15%Cr–N(100) [5,6] and MoN on Fe–3.5%Mo–N(100).

One of most thoroughly investigated examples is CrN formed upon the cosegregation of the constituents on ferritic Fe–15%Cr–N(100) single crystals. The CrN surface compound was found to be stable over a wide range of temperatures and nitrogen bulk concentrations [5,6]. With further cosegregation to near the surface (which is possible at low temperatures when the nitrogen solubility limit in the Fe–15%Cr bulk is exceeded) the system undergoes a 2D–3D phase transition between the two-dimensional CrN surface compound and a three-dimensional CrN surface precipitate which are both epitaxed to the Fe–15%Cr(100) alloy surface [5,7,8]. Both phases were recently analyzed by means of X-ray photoelectron diffraction (XPD). It was found that the structure of the CrN surface precipitate corresponds to the rocksalt structure (i.e. the structure of the well-known bulk chromium nitride CrN [9]). The thickness of the CrN surface precipitate characterized in that study was estimated from the attenuation of Fe 2p<sub>3/2</sub> photoelectrons to be about 1 nm [10]. The CrN surface compound was reported to consist of a top nitrogen layer and two cosegregated Cr layers below [11]. The nitrogen layer was found to reside in four-fold symmetric hollow sites about 0.6 Å above the uppermost Cr layer. There is a considerably increased distance between the two Cr layers (1.80 Å) corresponding to a 26% expansion with respect to the bcc interlayer spacing. This might indicate the propensity for a transition between the bcc- and fcc-like spacings of the Fe–15%Cr bulk (1.43 Å) and the CrN compound (2.08 Å), respectively [12].

However, when comparing this structure to that for the segregation of N on a Cr(100) single crystal surface, whereby the adatoms arrange into a (1×1) arrangement occupying all four-fold symmetric hollow sites, there is a considerable discrepancy with respect to the distance of the nitrogen layer to the first metal layer  $d_{12}$ . According to quantitative low-energy electron diffraction

(LEED) nitrogen atoms segregated on top of Cr(100) reside in hollow sites 0.16–0.22 Å above the substrate [13–15], i.e. considerably lower than that found for the the CrN surface compound (0.6 Å [12]). This is in spite of a very similar expansion determined by LEED for the distance between the top two chromium layers (23–28% [13–15]).

We therefore decided to apply a quantitative LEED structure determination to the surface compound, as this method is known to be very sensitive (and therefore accurate) with respect to vertical-layer distances. It also ensures full methodological comparability to the results for the N/Cr(100) adsorption system. In addition we provide one of the rare examples where both XPD and LEED are applied to the same surface structure. Besides the crystallographic information aimed for, the present paper also monitors the transition from the CrN surface compound to the three-dimensional CrN surface precipitate via the development of LEED intensities.

## 2. Sample preparation and experimental details

The ferritic Fe–15%Cr–N single crystal studied in this work was produced applying the Bridgman crystal growth technique. The nitrogen content of the untreated crystal (cylindrical rod of  $l=60$  mm length and  $\phi=20$  mm diameter) was determined by chemical bulk analysis according to  $c_N=15$  wt-ppm. The other (unwanted) surface-active impurities of the crystal are sulphur (10 wt-ppm), phosphorous (5 wt-ppm) and carbon (<5 wt-ppm). The specimen was spark-eroded to 1.5 mm thick slices with the (100) orientation ( $\pm 1^\circ$ ) and cut into 8 mm × 8 mm × 1 mm samples using a diamond saw. The sample studied in the present work was doped for 48 h at 1200°C in a flowing N<sub>2</sub>–H<sub>2</sub> gas mixture. This ex-situ nitriding procedure, which has been shown to be a fully reproducible procedure [16] and is accompanied by desulphurization, dephosphorization and decarburization of the sample, led to a final nitrogen bulk concentration of  $c_N=190 \pm 10$  wt-ppm. The sample was ground and polished mechanically

until a mirror-like finish was obtained. After introducing into the UHV system, up to 10 cycles of  $\text{Ar}^+$  ion sputtering ( $E_{\text{Ar}^+} = 3 \text{ keV}$ ) and annealing to  $700\text{--}900^\circ\text{C}$  were performed in order to obtain an atomically clean alloy surface. After the final sputtering process, mild annealing to  $400^\circ\text{C}$  for several hours was applied to annihilate lattice defects as far as possible and to generate a geometrically well-ordered alloy surface. Indeed the sample preparation described resulted in a sharp and low-background ( $1 \times 1$ ) LEED pattern according to the symmetry of a bcc (100) surface.

Experiments were carried out in a stainless-steel UHV chamber with a base pressure of  $4 \times 10^{-11}$  mbar. It was equipped with a spherical electron spectrometer for Auger electron spectroscopy (AES) and a four-grid back-view LEED optics. LEED intensity versus energy spectra ( $I(E)$ ) were recorded using a computer-controlled video-based data acquisition system. As described in detail elsewhere [17–19], this technique allows us to take intensity data from the luminescent screen via a TV camera from outside the UHV almost automatically and at high speed (fastest: 20 ms for a single intensity measurement) and under simultaneous background subtraction. All intensity data were taken at temperatures of about 120 K by contact of the sample holder with a liquid-air reservoir. Normal incidence of the primary electron beam was adjusted by comparison of symmetrically equivalent beams using the Pendry  $R$ -factor [20] as a quantitative measure of agreement. The spectra were taken in steps of 0.5 eV between 40 and 500 eV, whereby repeated measurement of all beams was applied to improve the signal-to-noise ratio. Eventually, the spectra of symmetrically equivalent beams were averaged to reduce the influence of residual sample misalignment and/or inhomogeneities of the luminescent screen.

### 3. CrN formation

In good agreement with the literature [5,7,8], we found the cosegregation-induced formation of the two-dimensional CrN surface compound on

Fe–15%Cr–N(100) crystals with  $c_{\text{N}} = 190 \pm 10$  wtppm to occur in a wide range of temperatures (i.e. between  $\sim 650$  and  $\sim 850^\circ\text{C}$ ). Fig. 1 shows a representative Auger spectrum after annealing to  $650^\circ\text{C}$  for several minutes. The Cr and N signals are substantially increased with respect to the sputter-cleaned alloy surface, indicating the cosegregation of both solutes. The ratios of the Auger peak-to-peak intensities  $r_{\text{Cr/Fe}} = I_{\text{Cr}}(529 \text{ eV})/I_{\text{Fe}}(651 \text{ eV}) \approx 1$  and  $r_{\text{N/Fe}} = I_{\text{N}}(379 \text{ eV})/I_{\text{Fe}}(651 \text{ eV}) \approx 1$  are found to be largely independent of the annealing time and the precise temperature chosen. Even after extended annealing to  $800^\circ\text{C}$ , no further increases in the Cr and N signals are observed, indicating the completion of the segregation process. The saturation of the signals indicates that only a limited amount of both Cr and N are accommodated at the very surface (i.e. the formation of CrN must be confined to near the surface). This was also shown previously by means of sputter depth profiles [5,6]. Annealing at lower temperatures ( $< 650^\circ\text{C}$ ), however, causes both  $r_{\text{Cr/Fe}}$  and  $r_{\text{N/Fe}}$  to increase nearly linearly with time, whereby values larger than 5 can be measured. This indicates the surface precipitation of three-dimensional CrN films probably growing from the surface edge into the bulk. If this phase is annealed for extended periods at temperatures of  $\sim 700^\circ\text{C}$ , the Auger ratios fall

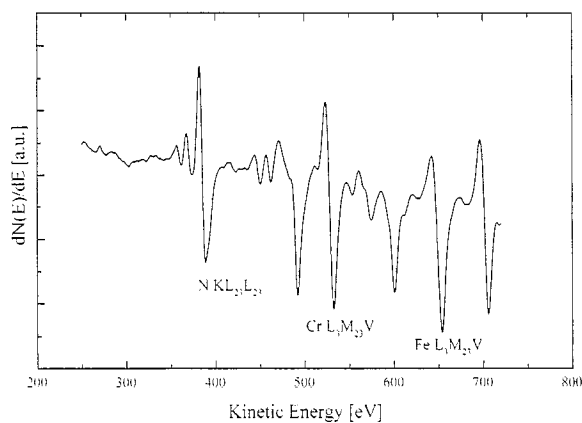


Fig. 1. AES spectrum of the Fe–15%Cr–N(100) surface after formation of the two-dimensional CrN surface compound at  $600^\circ\text{C}$ .

again to  $r_{\text{Cr}/\text{Fe}} \approx r_{\text{N}/\text{Fe}} \approx 1$  (i.e. to the value representative of the surface-confined CrN). This is in agreement with earlier reports, according to which, at these elevated temperatures nitrogen desorbs from the surface, as found by means of residual gas mass spectrometry, and chromium atoms diffuse back to the bulk [2,3,21]. We also note that annealing the sample for at least 2 h to temperatures in excess of 800°C makes the nitrogen bulk concentration of the Fe-15%Cr-N(100) crystal fall from an initial value of  $c_{\text{N}} = 190 \pm 10$  wt-ppm to values below  $\sim 10$  wt-ppm. However, even at such a low nitrogen bulk concentration, cosegregation is possible and causes the formation of the two-dimensional CrN surface compound. However, under such circumstances the surface precipitation of three-dimensional CrN is not observed in practice, even at temperatures around 400°C, although in principle the precipitation should take place as the nitrogen solubility limit is exceeded.

The scenario described above is also consistently reflected by LEED intensity spectra. For the phase prepared at high temperatures ( $> 650^\circ\text{C}$ ) rather sharp spots develop, for which  $I(E)$  spectra can be measured in a routine way. This is in contrast to the phases prepared at low temperatures ( $< 650^\circ\text{C}$ ), for which rather diffuse spots accompanied by considerable background are characteristic. This indicates that for these phases, long-range order is far from perfect and many defects exist in the surface. Accordingly, spectra of the respective spots were difficult to measure and are, in our experience, not suitable for a quantitative structural analysis. Nevertheless, Fig. 2 shows a sequence of  $I(E)$  spectra in the range 100–360 eV for a representative beam ((1,1) beam) as a function of  $r_{\text{Cr}/\text{Fe}}$ . The bottom spectrum corresponds to the surface compound prepared by high annealing temperatures. Consistent with the above findings, and as shown in Fig. 3, it is largely independent of the annealing time and the precise annealing temperature above 700°C. The spectra displayed for increasing values of  $r_{\text{Cr}/\text{Fe}}$  in Fig. 2 resulted from annealing at 625°C for different times. They change gradually but significantly, in that the top spectrum is completely different from the bottom curve. According to the AES results,

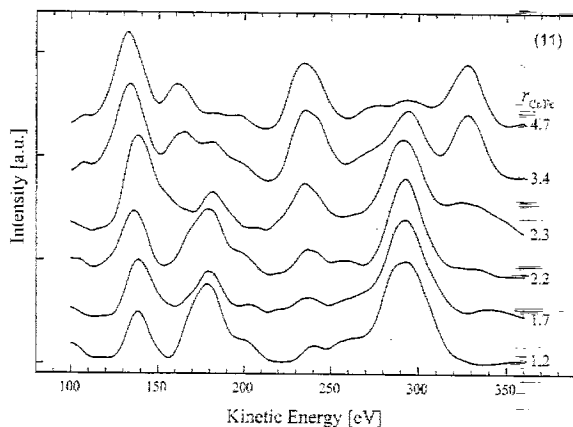


Fig. 2. LEED intensity spectra for the (1,1) beam from the Fe-15%Cr-N(100) surface for various stages of CrN formation extending increasingly into the bulk (the figures given in each case correspond to the respective Auger ratio  $r_{\text{Cr}/\text{Fe}}$ ). The bottom curve corresponds to the two-dimensional CrN surface compound formed after 2 h annealing at 600°C.

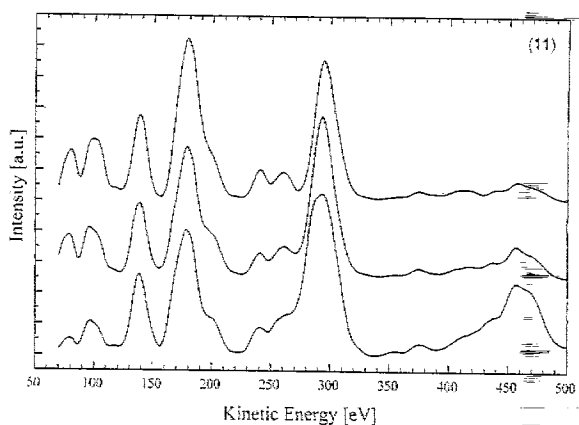


Fig. 3. Compilation of experimentally determined LEED spectra for the (1,1) beam of the Fe-15%Cr-N(100) substrate surface after formation of the two-dimensional CrN surface compound. Three different preparation procedures have been used (from top to bottom): (a) heating to 600°C for 2 h, (b) heating to 850°C for 5 min and (c) heating to 800°C for 2 min.

we interpret this upper curve as characteristic of the three-dimensional CrN precipitate extending to the bulk by at least the electron attenuation length. Consistently, the middle spectrum ( $r_{\text{Cr}/\text{Fe}} = 2.3$ ) should be representative of nitride extending roughly half that way below the surface.

Interestingly, one can reproduce all the spectra (for any value of  $r_{\text{Cr,Fe}}$ ) as a linear combination of the bottom, middle ( $r_{\text{Cr,Fe}}=2.3$ ) and top ( $r_{\text{Cr,Fe}}=4.7$ ) spectra with a high accuracy (Pendry  $R$ -factors  $\leq 0.1$ ). This may be a hint for the simultaneous presence of different phases on the surface during the process of three-dimensional compound formation.

#### 4. Structure determination of the CrN surface compound

The LEED spectra measured for the high-temperature phase (i.e. the surface-confined CrN compound) were subjected to a full dynamical intensity analysis in order to determine its structure quantitatively. Data in the energy range 100–400 eV were used, providing a total database of 1465 eV. A first rough fit was made using conventional full dynamical programs [22] and, as shown in Fig. 4, assuming a full nitrogen layer on top of the surface followed by alloy layers with bulk stoichiometry. The height  $d_{01}$  of nitrogen atoms residing in four-fold symmetric hollow sites of the top alloy layer was varied, as well as the next two interlayer distances in the alloy ( $d_{12}$  and  $d_{23}$ ). The resulting best-fit structure was then used as a reference structure for a more detailed fit by tensor LEED [23,24], including powerful extensions to determine the layer stoichiometry (chemical tensor LEED [19,25–27]) and thermal atomic vibrations

(thermal tensor LEED [19,27,28]). In this structural search a total of 11 parameters were varied for the surface model displayed in Fig. 4, i.e. the interlayer distances  $d_{01}$ ,  $d_{12}$ ,  $d_{23}$  and  $d_{34}$ , the nitrogen concentration  $c_{\text{N}}$  in the top layer and the chromium concentrations  $c_1$ ,  $c_2$  and  $c_3$  in the first three alloy layers as well as the (isotropic) vibrational amplitudes of nitrogen ( $\Delta r_{\text{N}}$ ) and iron ( $\Delta r_{\text{Fe}}$ ) or chromium ( $\Delta r_{\text{Cr}}$ ) in the top alloy layer (amplitudes of atoms in deeper layers were considered by a single Debye temperature of 467 K). The concentrations in the alloy layers were simulated by a weighted average scatterer with a scattering matrix  $t_i^{\text{av}} = c_i t_{\text{Cr}} + (1 - c_i) \times t_{\text{Fe}}$  ( $i=1, 2, 3$ ). Submonolayer concentrations of nitrogen in the top layer were simulated by averaging the nitrogen  $t$ -matrix with that of vacancies (zero  $t$ -matrix), i.e.  $t_{\text{N,av}} = c_{\text{N}} t_{\text{N}}$ . A directed automatic structural search procedure guided by the Pendry  $R$ -factor was used, as described in detail recently [29]. The variance of the  $R$ -factor [20] was used to estimate the error limits of the parameters determined.

The best-fit (Pendry  $R$ -factor  $R=0.14$ ,  $\text{var}(R)=0.024$ ) results for a full nitrogen layer ( $c_{\text{N}}=100\%$ ) with nitrogen atoms residing in hollow sites at a height of  $d_{01}=0.09 \pm 0.03 \text{ \AA}$  above the topmost metal layer. The distances between the metal layers was found to be  $d_{12}=1.82 \pm 0.02 \text{ \AA}$ ,  $d_{23}=1.39 \pm 0.02 \text{ \AA}$  and  $d_{34}=1.46 \pm 0.02 \text{ \AA}$ . Compared to the bulk value of  $d_0=1.43 \text{ \AA}$ , this corresponds to a huge expansion of the top metal layer distance of  $\Delta d_{12}/d_0 = +27 \pm 2\%$ , while the relaxation values of deeper layer distances are in the usual range found at surfaces ( $\Delta d_{23}/d_0 = -3 \pm 2\%$ ,  $\Delta d_{34}/d_0 = +2 \pm 2\%$ ). Also, the vibrational amplitude of nitrogen atoms ( $0.12 \pm 0.04 \text{ \AA}$ ) and metal atoms in the first metal layer ( $0.10 \pm 0.03 \text{ \AA}$ ) are in agreement with expected values. Unfortunately, because of the very similar scattering characteristics of iron and chromium, the error limits for the composition in the first three alloy layers are rather large, i.e. of the order of 60–70%. This makes our best-fit values (chromium concentrations of  $c_1=20\%$ ,  $c_2=100\%$  and  $c_3=30\%$ ) rather uncertain. Indeed, if we enforce chromium concentrations of  $c_1=c_2=100\%$  in the first two metal layers, as found by the chemically much more sensitive XPD

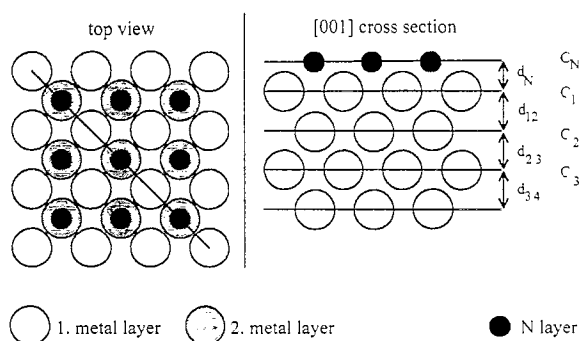


Fig. 4. Structure model of the two-dimensional CrN surface compound epitaxied on the Fe-15%Cr-N(100) alloy surface.

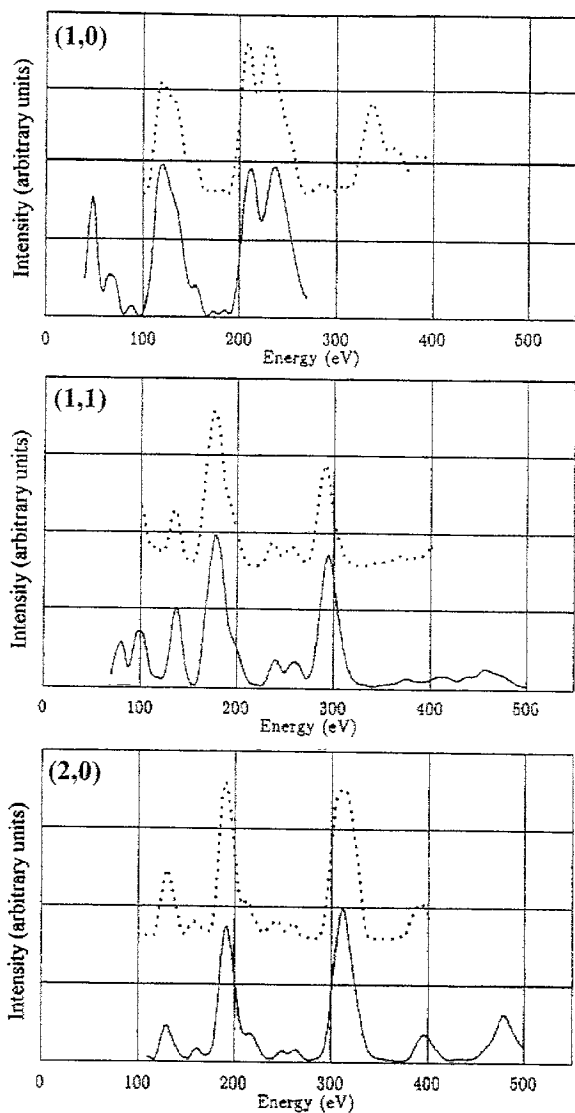


Fig. 5. Comparison of experimental and best-fit spectra for a selection of beams for the two-dimensional CrN surface compound.

interlayer distances, which change slightly to  $d_{01} = 0.12 \pm 0.03 \text{ \AA}$  and  $d_{12} = 1.80 \pm 0.02 \text{ \AA}$  ( $\Delta d_{12}/d_0 = +26 \pm 2\%$ ), the structural and vibrational parameters determined remain the same. A visual impression of the excellent agreement between experimental and best-fit spectra can be taken from Fig. 5 for a selection of beams.

## 5. Conclusion

We are now in a position to compare the findings of the present work with those of earlier studies, notably the XPD study for the same alloy system [12] and the quantitative LEED study for nitrogen adsorbed on Cr(100) [13-15]. We remind the reader that both the metal and the alloy have a bcc lattice and the bulk interlayer distances are almost the same. All three studies agree almost quantitatively in reporting a considerable and unusually large expansion of the first interlayer distance in the metal (i.e.  $\Delta d_{12}/d_0 = 26\%$ ). The same quality of agreement holds for the second metal layer distance, for which the LEED investigations yield  $\Delta d_{23}/d_0 = -3 \pm 2\%$  (in the XPD study,  $d_{23}$  was not determined).

However, considerable differences show up with respect to the height  $d_{01}$  of nitrogen atoms above the top metal layer, in particular when the value of the present LEED study ( $d_{01} = 0.12 \pm 0.03 \text{ \AA}$ ) is compared to the result of the XPD study ( $d_{01} = 0.6 \text{ \AA}$ ). This is in spite of the fact that both studies apply to the same substrate for the nitrogen layer formed by cosegregation in the CrN/Fe-15%Cr-N(100) system. The discrepancy is clearly outside the error. At present we have no explanation for these discrepancies between LEED and XPD. For the adsorption height found for  $(1 \times 1)\text{N}/\text{Cr}(100)$  by LEED, two values are reported ( $0.16 \text{ \AA}$  [14] and  $0.22 \text{ \AA}$  [15]), which are quite near to the value determined in the present study. As a consequence, good agreement also holds for the bond lengths between nitrogen and first- and second-layer chromium atoms. In the present case they amount to  $L_{\text{N-Cr}}^1 = 1.98 \text{ \AA}$  and  $L_{\text{N-Cr}}^2 = 1.91 \text{ \AA}$ , respectively. For  $(1 \times 1)\text{N}/\text{Cr}(100)$

investigations cited above [12], the best-fit Pendry  $R$ -factor is  $R = 0.16$  and so still lies within the variance limits of the absolute minimum. We therefore are inclined to accept the 100% segregation of chromium in the first two metal layers, in particular, because our best-fit composition also corresponds to 100% chromium in the second metal layer. Except the values of the first two

the values vary, depending on the exact value of  $d_{01}$ , resulting in  $L_{N-Cr}^1 = 2.04$  or  $2.05$  Å and  $L_{N-Cr}^2 = 1.98$  or  $2.04$  Å. The slightly lower value found in our study could be due to the different stoichiometry in the third alloy layer, which consists mainly of iron. Also, we cannot exclude that there is some iron in the top metal layer, which might influence the adsorption height.

It is interesting to note that both the interlayer relaxation and the nitrogen layer distance seem to depend strongly on nitrogen coverage. According to a very recent LEED structure determination of  $c(2 \times 2)N/Cr(100)$ , i.e. for only half a monolayer of nitrogen, the distance between the first two metal layers is expanded by only 7.5% [30]. Also, for this system the nitrogen adsorption height is  $d_{01} = 0.36$  Å. This is consistent with some mutual repulsion between nitrogen atoms, which in the submonolayer regime leads to ordered superstructures, i.e.  $c(2 \times 2)N/Cr(100)$  at a coverage of 1/2 and  $c(3\sqrt{2} \times \sqrt{2})$  at a coverage of 2/3 [30]. With increasing coverage the nitrogen atoms go deeper into the surface, profiting from shielding metallic neighbours, which reduce the N–N repulsion. Due to some buckling in the second chromium layer the nitrogen–chromium bond length to the second chromium layer is comparable to the above value (i.e.  $L_{N-Cr}^2 = 1.97$  Å.)

Taking all the results into consideration, we conclude that the segregation of nitrogen on Cr(100) as well as the cosegregation of chromium and nitrogen on Fe–15%Cr(100) leads essentially to the same structure of the surface. This holds down to the third layer with nitrogen as the top layer followed by two chromium layers. The similarity applies in particular and quantitatively to a huge expansion of the top interlayer spacing in the metal, but also the other interlayer distances agree again nearly quantitatively with each other. The findings could indicate that in both cases the same two-dimensional CrN surface compound is formed. However, it is quite clear that structural data alone cannot provide a complete characterization of two-dimensional chemical compounds. It is hoped that detailed electronic structure information on such compounds will become available soon.

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