

Comment on "Structure of the Mn-induced Cu(100) $c(2 \times 2)$ surface"

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We have studied the atomic arrangement of Mn upon deposition on Cu(100) at room temperature using low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM). Scanning tunneling microscopy reveals that Mn is already incorporated at very low coverages (~ 0.005 ML Mn). Both LEED and STM show that the surface alloy is characterized by a considerable corrugation where Mn atoms are displaced outside by 0.30 \AA . Our findings are at variance with a recent STM study [Phys. Rev. B **52**, 2735 (1994)] which reports a corrugation of approximately 0.12 \AA and claims Mn incorporation only above a critical Mn coverage which should be larger than 0.06 ML.

In a recent set of scanning tunneling microscopy (STM) measurements on the surface alloy Cu(100) $c(2 \times 2)$ Mn, Noh *et al.* (NHJKPS) (Ref. 1) reported that (i) Mn atoms adsorb as isolated atoms or small clusters at coverages below approximately 0.1 ML on Cu(100), and (ii) that the corrugation of the $c(2 \times 2)$ structure found after deposition of 0.5 -ML Mn is approximately 0.12 \AA . Both findings are clearly at variance with our results obtained by scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) I/V measurements, partly published in Refs. 2 and 3.

In our previous work^{2,3} we presented a structure analysis of the ordered Cu(100) $c(2 \times 2)$ Mn phase formed after deposition of 0.5 -ML Mn on Cu(100). To determine atomic positions the measured energy dependence of the intensity of several LEED beams (I/V curves) was compared with spectra calculated for a large number of different atomic positions. It was shown that the $c(2 \times 2)$ structure corresponds to a surface alloy confined to the topmost layer (Fig. 1), while a $c(2 \times 2)$ Mn overlayer on the substrate could be excluded. Our structure determination revealed a large outwards displacement of the Mn atoms in the surface alloy layer of $0.30 \pm 0.02 \text{ \AA}$. Figure 2 reproduces measured I/V spectra for six different beams and I/V spectra assuming (geometric) corrugations in the surface alloy of 0.30 (our best model) and of 0.12 \AA [as suggested from the STM work of NHJKPS (Ref. 1)]. The fit between experiment and theory is evaluated by the Pendry R factor (R_p).⁴ While the calculated spectra assuming a corrugation of 0.30 \AA describe the measured spectrum sufficiently well ($R_p = 0.30$), this is not the case for a corrugation of 0.12 \AA . The high value of the R factor of 0.88 supports the visual impression of a rather poor agreement between theory and experiment for the small corrugation suggested from the STM work. This is shown in more detail in Fig. 3, where the variation of the R factor with corrugation is depicted. A deep minimum of the R factor is found at a corrugation of 0.30 \AA . From the variance of the R factor, $\text{var}(R_p) = R_p \times \sqrt{8V_i/\Delta E}$, where ΔE is the range of energies where calculated and measured spectra overlap, and V_i is the absorptive potential, we can estimate the error bar in

the structure determination⁴ to be 0.02 \AA . Hence, at this point we want to repeat that the LEED analysis determines the surface layer corrugation to $0.30 \pm 0.02 \text{ \AA}$ and excludes a smaller corrugation of 0.12 \AA . The corrugation of NHJKPS is also at odds with our *ab initio* structure optimization, which leads to an outwards relaxation of 0.25 \AA .² Since these calculations are based on the local-density approximation, both magnetism and outwards relaxation are underestimated in our theory. One would therefore expect that the experimentally observed buckling is larger than our theoretical re-

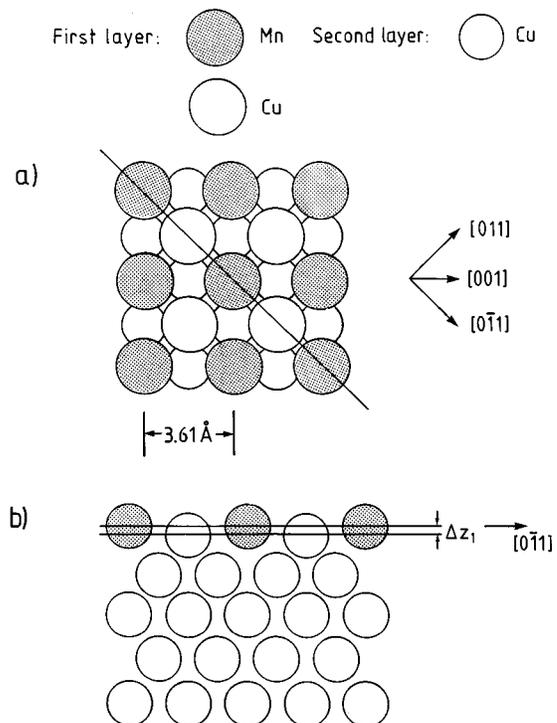


FIG. 1. Atomic model of the Cu(100) $c(2 \times 2)$ Mn surface alloy. (a) Top view. The solid line denotes the direction of the cross section shown in (b), where the side view is depicted. Δz_1 describes the corrugation in the surface alloy layer.

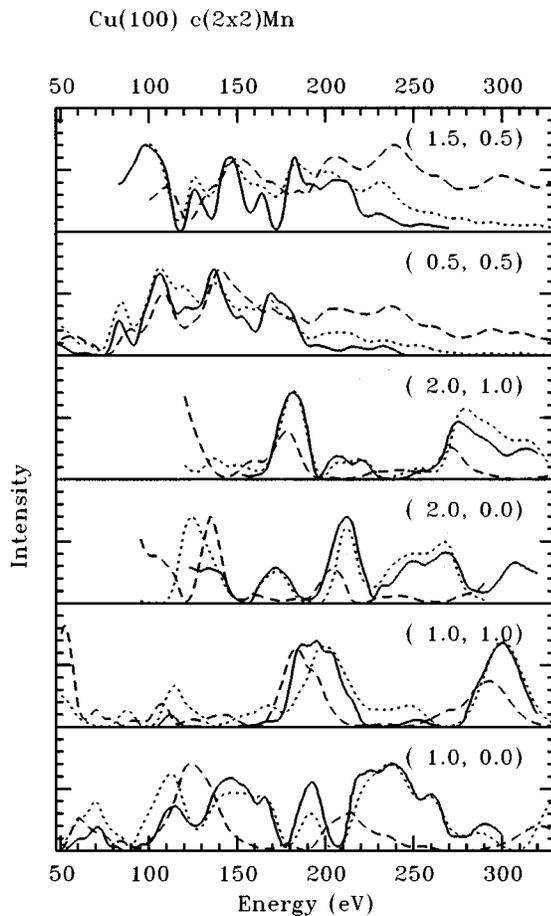


FIG. 2. Experimental spectra (solid line) for the Cu(100) $c(2 \times 2)$ Mn structure compared to the best-fit spectra with a corrugation of 0.30 Å (dashed line), and the corrugation of 0.12 Å as suggested by NHJKPS (broken line).

sult, in agreement with our LEED analysis.

Figure 4 shows an STM image of the Cu(100) $c(2 \times 2)$ Mn structure obtained after deposition of 0.47 ± 0.02 -ML at 300 K. Both islands and a large terrace are atomically resolved. Even though the surface shows quite a few point defects, good long-range order is observed. The [011] direction is denoted by an arrow. Nearest-neighbor Cu atoms in the Cu(100) surface have a distance of 2.55 Å along the [011] and $[0\bar{1}1]$ directions, respectively. The atoms visible in the Cu(100) $c(2 \times 2)$ Mn structure, however, have a larger distance of 3.56 ± 0.07 Å, and are aligned along the [010] and [001] directions, respectively. This implies that only one atomic species of the surface alloy layer is imaged. Similar images have also been obtained by NHJKPS. As these authors acknowledge, a STM measurement of the corrugation need not accurately reflect the heights of nuclear positions, because of tip effects and the measurement of electron density near the Fermi level.^{5,6} Since we have measured almost identical images for a wide range of tunneling parameters, we interpret the STM pictures as a strong indication that the surface alloy layer has a considerable corrugation. Most likely, due to this corrugation only the Mn atoms are imaged. In contrast, for shallow corrugations⁷ it has been possible, at least sometimes, to observe both alloy constituents.⁸ From their STM images, where only one atomic species is visible,

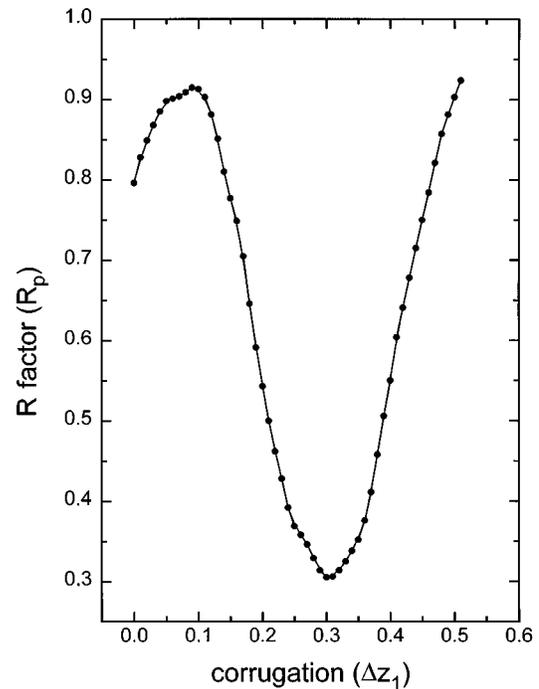


FIG. 3. Influence of the variation of the corrugation on the theory-experiment comparison as estimated from the Pendry R factor for the Cu(100) $c(2 \times 2)$ Mn surface alloy.

NHJKPS performed a line scan in [001] direction (Fig. 3 of Ref. 1) to determine the atomic corrugation of the Cu(100) $c(2 \times 2)$ Mn phase. This scan direction cuts through two adjacent Mn atoms, but does not pass over a Cu atom in

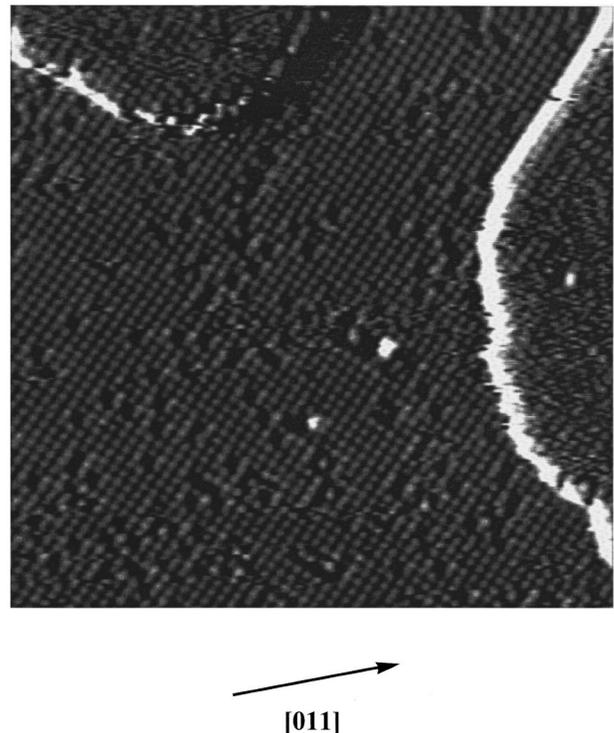


FIG. 4. STM image of the Cu(100) $c(2 \times 2)$ Mn structure taken after deposition of 0.47-ML Mn at 300 K, scan width 180×180 Å².

between. A comparison with Fig. 1 shows that this is the wrong direction to determine the corrugation. If one wants to determine the outwards displacement of the Mn atoms, one should rather perform the line scan in $[011]$ direction. Even for this direction, the inability to image Cu atoms in the surface alloy layer and the strong dependence of STM images on the surface local density of states at the Fermi level^{5,6} rather than atomic positions in our opinion exclude a precise determination of the geometric corrugation of the ordered Cu(100) $c(2\times 2)$ Mn surface alloy with the STM. We believe, however, that STM images obtained at low-Mn coverages can be used to determine the corrugation more precisely.

The determination of the outwards displacement of the Mn atoms at low coverage offers two major advantages. First of all, both Mn and Cu are imaged simultaneously, which is a necessary prerequisite to measure the corrugation. Then the Mn atoms are much further apart at low coverages. This results in a less pronounced reduction of the electronic corrugation as compared with the $c(2\times 2)$ superstructure at 0.5 Mn, where adjacent Mn atoms are so close that the local density of states has much less (electronic) corrugation.^{9,5} Therefore, the Cu(100) $c(2\times 2)$ Mn structure could only be atomically resolved with very sharp tips, while imaging of incorporated Mn atoms, even though with larger size, was also possible with less sharp tips. In a recent LEED investigation¹⁰ we could show that Mn incorporation is observed at least at a coverage of 0.2-ML Mn. Furthermore, the local atomic arrangement around the Mn atoms is independent of coverage in the range of 0.2–0.5-ML Mn. This means that the Mn atoms are displaced outwards by 0.3 Å in the entire coverage range mentioned above. Below 0.2-ML Mn the signal measured in the diffuse LEED experiment is too low to allow a structure determination. With STM images, for coverages between 0.005- and 0.3-ML Mn, we observe a qualitatively similar behavior. A typical example is shown in Fig. 5, which has been obtained after deposition of 0.020 ± 0.008 -ML Mn. Visible are both a monoatomic step¹¹ and a number of protrusions.

The number density of the protrusions increases with coverage, which allows us to identify them as either Mn atoms or Mn clusters. A line scan through two protrusions and the step enables a determination of their height. The result is 0.32 ± 0.06 Å. From this number we can clearly exclude Mn atoms or clusters on the surface. The height of the protrusions shows that Mn atoms or clusters must rather be incorporated into the surface layer. NHJKPS have observed similar protrusions, but have interpreted them as Mn clusters on the surface, even though in their images the height of the protrusions is considerably smaller than a monolayer step. This is inconsistent with an interpretation as a Mn cluster on the surface. We have employed a large range of tunneling conditions and coverages between 0.005 and 0.3-ML Mn to determine the apparent height and size of the protrusions. While their height always was close to 0.3 Å, their apparent size varied considerably between one and four atoms. However, the most pronounced effect was not due to tunneling parameters but the tip condition itself. The sharper the tips, the smaller were the resulting protrusions. Since the size of the best resolved images corresponds to a single atom, we identify the protrusions as single, isolated Mn atoms.

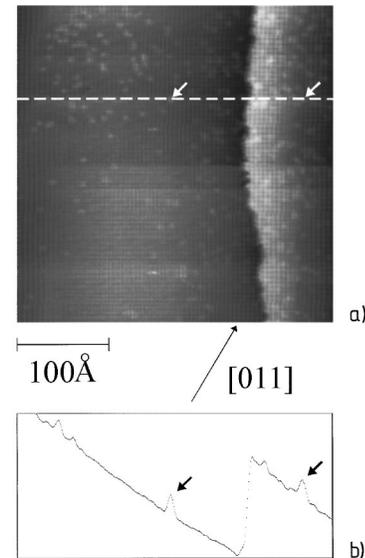


FIG. 5. STM image taken after deposition of 0.02-ML Mn at 300 K, scan width 90×90 Å². Below, a line scan is shown which is performed along the dashed line depicted in the STM image above. The white arrows in the image denote the positions of incorporated atoms that lie on the line scan.

NHJKPS comment that the density of protrusions they observe is smaller than the amount of Mn deposited on the surface. From this finding they conclude that the protrusions must consist of several Mn atoms.¹ We have determined the Mn coverage by counting the protrusions and by measuring the area covered by islands. Our determination of the coverage assumes that the concentration of Mn in the adatom lattice gas is negligible, as we have shown by separate measurements. For the STM image in Fig. 4, the determination of the Mn coverage from counting incorporated Mn atoms gives 0.45-ML Mn. The islands consist of both Mn and Cu atoms, but each Cu atom has been brought into the islands upon Mn incorporation in the lower terrace. Hence the area covered by the islands corresponds to the Mn coverage. Counting this coverage for STM images with larger scan areas gives a value of 0.49-ML Mn. We thus specify the coverage as 0.47 ± 0.02 -ML Mn. For smaller coverages the determination of island sizes is more difficult, since the size of these considerably smaller islands is easily overestimated by the STM. We believe that this can account for the difference in the coverage for small amounts of Mn deposition, such as the one in Fig. 5(a), where the coverage determination from island sizes gives 0.027-ML Mn, but counting incorporated Mn only gives 0.012-ML Mn. Presumably the coverage determination from counting island sizes overestimates the actual coverage considerably, since the islands are rather small at this coverage. Therefore we do not think that there is convincing evidence that the protrusions consist of a cluster of several Mn atoms, as suggested by NHJKPS.

Before ending this paper we would like to reiterate one point, namely that the formation of the huge local Mn moment and not the ferromagnetic order of the Mn atoms is responsible for the buckling relaxation of Mn. The formation of the large local moments lowers the total energy per Mn atom about 1.4 eV, and the large Mn corrugation reduces the

energy further by 0.1 eV.² Conversely, the long-range magnetic order contributes not more than 80 meV to the total energy, and is hence negligible.¹² Therefore, the buckling of Mn also exists above the magnetic Curie temperature when long-range magnetic order disappears, but the local moments still exist. This view is confirmed by O'Brien and Tonner,¹³ who used soft-x-ray-absorption measurements to detect Mn being in a high-spin state, and used at the same time magnetic circular dichroism to show the lack of long-range magnetic order for Cu(100) $c(2 \times 2)$ Mn at room temperature.

In conclusion, we have shown that Mn is incorporated into the Cu(100) surface layer already at coverages considerably below 0.02-ML Mn. The Mn atoms in the surface

alloy layer are displaced outside by 0.30 Å, a finding that is in excellent agreement with the results of the LEED structure determination for coverages between 0.2- and 0.5-ML Mn. There is increasing experimental evidence that this outwards relaxation is accompanied by a large magnetic moment, as suggested by our *ab initio* total-energy calculation.

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