

## Tilting, Bending, and Nonterminal Sites in CO/Cu(001)

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Using scanning tunneling microscopy experiments in combination with first-principles calculations we have studied the geometric structure of the compressed  $c(7\sqrt{2} \times \sqrt{2})$  antiphase domain structure of CO on Cu(001). We find direct evidence for structural relaxations involving an inhomogeneous CO environment characterized by molecular tilting, bending, and nonterminal sites. Our analysis solves the long-standing problem of the adsorption structure of the compressed phase and is important for understanding the physical properties of this fundamental adsorption system.

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Carbon monoxide (CO) adsorbed on metals represents an archetype system in surface science. In parallel with the development of modern analytical tools more than 40 years ago, the structural and spectroscopic properties of CO adsorbed on low-index surfaces of metals like Pd, Ni, and Cu [1–4] were investigated and numerous studies have been published since then.

In the case of CO on Cu(001) it is undisputed that the  $(\sqrt{2} \times \sqrt{2})$  structure is characterized by  $\theta = 0.5$  monolayers (MLs) of CO molecules located on top of every other Cu atom with carbon bonded to the metal [5–7] (here, and in the following, we refer to one ML as one molecule per surface atom, i.e.,  $1.53 \times 10^{15}$  molecules/cm<sup>2</sup>). By contrast, the detailed structure of the “compressed phase” (CP) at  $\theta > 0.5$  ML has escaped an unambiguous determination so far.

The CP was first described by Tracy [4] and later identified as a  $c(7\sqrt{2} \times \sqrt{2})$  superstructure [8,9]. Analysis of low energy electron diffraction (LEED) patterns led to the conclusion that the CP is an antiphase domain structure in which  $(\sqrt{2} \times \sqrt{2})$  domains of terminally bonded CO molecules are separated by an ordered array of hard domain walls (DWs) [10]. Despite this consensus, the interpretation of electron energy loss spectroscopy (EELS) studies [5,7] and infrared spectroscopy experiments [9,11,12] arrived at contradictory conclusions and were largely a matter of speculation.

The appearance of spectral features in EELS was suggested as due to tilting of the CO molecules within the CP [7], and also by the partial occupation of bridge-bonded sites [9]. However, a later study challenged these interpretations [11]. A more recent reflection absorption infrared spectroscopy (RAIRS) study indicated distinct changes of frequency, width, and intensity of the absorption maxima going in parallel with the onset of the compression [12]. Broadening of the RAIRS CO-stretch peak was tentatively interpreted as being correlated with the onset of disordering but without providing a conclusive model. In summary, a clear-cut interpretation of the coverage-dependent

spectroscopic features in relation with structural changes remained an open question up to now.

This clearly shows the need for a detailed investigation of the compressed CO/Cu(001) adsorption geometry. During the recent 20 years, surface structure analysis has made considerable progress especially with regard to low- $Z$  molecular adsorbates by using different techniques like scanning tunneling microscopy (STM), LEED, and photoelectron diffraction [13,14]. However, with regard to CO on Cu(001), so far only the quantitative intensity versus energy LEED analysis of the  $(\sqrt{2} \times \sqrt{2})$  structure by Andersson [6] exists, but almost nothing is known about the  $c(7\sqrt{2} \times \sqrt{2})$  CP and its relation to the spectroscopic properties. In part this might be attributed to experimental difficulties to prepare the well-ordered CP which requires sample temperatures below 100 K for stabilization [4].

In this Letter we present a combined experimental and theoretical study which goes far beyond current knowledge. Using STM, LEED, and first-principles density functional (DFT) calculations, we show that the conventional model of the  $c(7\sqrt{2} \times \sqrt{2})$  structure requires substantial revision. This includes strong relaxations of all CO molecules within the unit cell including lateral shifts, tilting, and bending (tilt angle  $77^\circ$  with respect to the surface instead of  $90^\circ$ ) involving nonterminal sites. Consequently, there is a significant structural inhomogeneity, in which each symmetry independent CO molecule is in a different local environment. Our results are important for the interpretation of the spectroscopic results published during the past two decades.

The experiments were carried out in an ultrahigh-vacuum system equipped with a variable temperature STM. The copper surface was cleaned by standard methods until no traces of contaminants were detected by Auger electron spectroscopy. CO was deposited by dosing at a partial pressure of  $p(\text{CO}) = 10^{-7}$  mbar while the sample was kept at a temperature of 25 K. In agreement with previous studies [4] the  $(\sqrt{2} \times \sqrt{2})$  structure is formed after dosing of 1.5 Langmuirs (1 L =  $10^{-6}$  Torr s). Prolonged dosing up

to 4.5 L leads to the formation of the  $c(7\sqrt{2} \times \sqrt{2})$  superstructure, whose long-range ordering is improved by short annealing up to 75 K. The  $c(7\sqrt{2} \times \sqrt{2})$  structure is the most densely packed phase of CO on Cu(001) with  $\theta = 4/7 = 0.57$  ML. At lower coverage several less dense locally ordered structures of type  $c(n\sqrt{2} \times \sqrt{2})$  with  $n = 9, 11, 13, 15,$  and  $17$  were also observed by STM.

Figure 1(a) shows a  $1000 \times 500 \text{ \AA}^2$  constant current STM image of the CP taken at 25 K ( $U = -1.7$  V sample bias,  $I = 40$  pA). Bright lines correspond to antiphase DWs running along both equivalent  $\langle 100 \rangle$  directions. DWs are regularly spaced at a distance of  $12.6 \text{ \AA}$ . In Figs. 1(b) and 1(c) the Fourier transform (FT) of the STM image and the LEED pattern ( $E = 30$  eV) are shown, respectively. In both images the characteristic arrangement of four spots around the half order  $(1/2, 1/2)$  position is clearly visible. It is in agreement with previous studies (see, e.g., Ref. [9]). In combination with positions of other spots, this proves the formation of the long-range-ordered CP. In the following we first provide a geometric interpretation of the STM image.

Figure 2(a) shows the idealized model of the  $c(7\sqrt{2} \times \sqrt{2})$  superstructure in top view. The solid rectangle represents one unit cell ( $25.27 \times 3.61 \text{ \AA}^2$ ), whose plane group symmetry is  $c2mm$ . Red and bright (small) balls represent oxygen and copper atoms, respectively (carbon atoms are hidden below the oxygen atoms). Molecules are labeled by 1–4. Atoms labeled by primed numbers represent symmetrically related molecules. DWs are separated by  $12.64 \text{ \AA}$  as observed in Fig. 1(a). Within the locally ordered ( $\sqrt{2} \times \sqrt{2}$ ) domains labeled by “D” (composed of

molecules 1, 2, 3, and 4), the spacing between the molecular rows is equal to  $3.61 \text{ \AA}$ , but it equals only  $1.81 \text{ \AA}$  at the antiphase DWs (molecules 4', 1).

For comparison, Fig. 2(b) shows a high resolution STM image in which the bright dots are interpreted as corresponding to the positions of the terminating oxygen atoms. The STM image directly reveals that the distance distribution between the oxygen atoms deviates considerably from that in the (idealized) model structure shown in Fig. 2(a).

Depending on the tip condition, CO molecules appear as protrusions or depressions [15,16]. In experiments carried out by us at very low CO coverage, single molecules were imaged as depressions, but in the case of a fully covered surface they are imaged as protrusions. We conclude that in the latter case the tip has always picked up a CO molecule as discussed in Ref. [16].

For the quantitative analysis of the distances, we used the length of the unit cell ( $25.3 \text{ \AA}$ ) as a reference. For the distances between the rows, we find an average value of  $3.2 \text{ \AA} \pm 0.1 \text{ \AA}$ . Minima ( $2.8$  and  $2.9 \text{ \AA}$ ) are found between those rows within the center of the domain (molecules 2 and 3) and their symmetrically equivalent ones (molecules 2' and 3'). We attribute this to the tilting of molecules 1 and

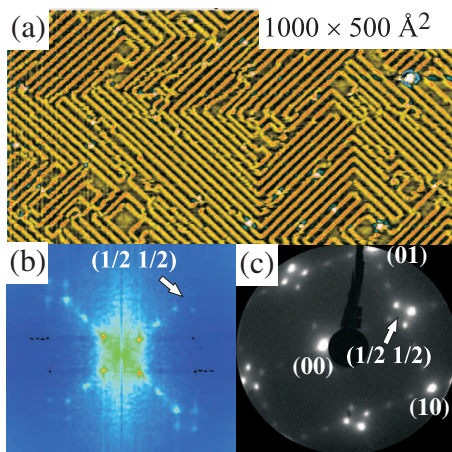


FIG. 1 (color). (a) Constant current topography STM image of the compressed CO/Cu(001) structure ( $U = -1.7$  V,  $I = 40$  pA). Bright lines correspond to antiphase domain walls. The corrugation equals to  $0.22 \text{ \AA}$ . (b) Fourier transform (FT) of STM image. Spot intensities are shown in arbitrary units on a linear scale using spectroscopic color coding. (c)  $c(7\sqrt{2} \times \sqrt{2})$  LEED pattern (30 eV). Reflections are indicated. Note that in the STM FT, (integer order) substrate reflections are absent.

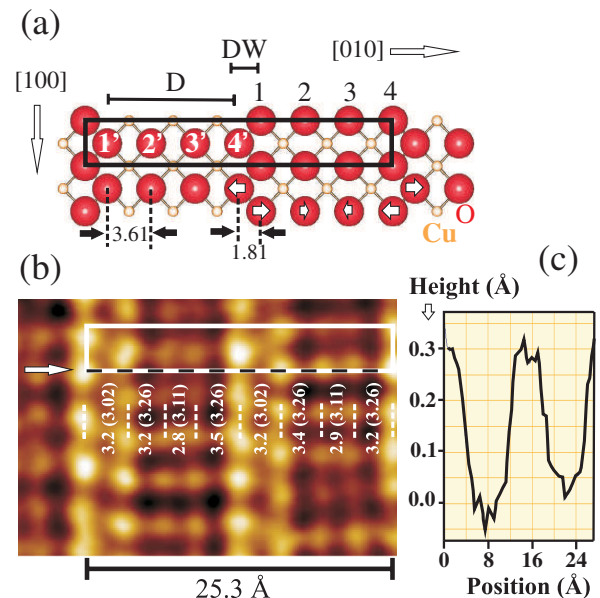


FIG. 2 (color). (a) Idealized model of the  $c(7\sqrt{2} \times \sqrt{2})$  structure in top view. Red balls correspond to oxygen atoms, bright (small) balls to copper atoms as labeled. Carbon atoms are hidden below oxygen. Domains ( $D$ ) are separated by domain walls (DW). Molecules are labeled by 1–4 (numbers with primes indicate symmetrically equivalent atoms). Arrows schematically indicate atomic relaxations. (b) Corresponding STM image. Bright dots correspond to CO molecules. The solid rectangle indicates one unit cell. Distances between molecular rows are given in  $\text{\AA}$ , values in brackets are from DFT calculations. (c) STM height profile along the dashed line indicated by the arrow in (b).

4 which in turn induces a (smaller) tilt of the neighboring molecules 2 and 3 leading to the compression of the distance between the oxygen atoms as seen in the STM image. In Fig. 2(a) the shifts of the oxygen atoms are schematically indicated by the arrows preserving the  $c2mm$  symmetry of the unit cell. The STM image thus reveals a complex structure with a relaxation pattern involving all CO molecules.

Apart from the pure geometric interpretation, we can go one step further by investigating the STM contrast: dots corresponding to the position of those CO molecules belonging to the DW appear brighter than those away from the wall, i.e., within the  $(\sqrt{2} \times \sqrt{2})$  domains. The line profile along the long unit cell axis shown in Fig. 2(c) indicates a maximum corrugation of about 0.3 Å. Assuming top site adsorption for all molecules this would correspond to a tilting of  $48^\circ$  relative to the surface plane, which clearly can be ruled out. Therefore, the corrugation is attributed to an increased density of oxygen and carbon  $p_z$  states induced by the tilting of the molecules.

This interpretation is supported by first-principles calculations of the structural and electronic properties of CO/Cu(001) using the VASP code, well known for its precise determination of energetics and forces. [17] To model the structure within a slab geometry, we used the 5-monolayer-thick Cu supercell covered by CO. A 2 nm vacuum layer separates the slabs along [001]. The positions of the C and O and atomic positions of the two upper Cu MLs were relaxed. The ionic relaxation was performed until the forces were less than  $8 \times 10^{-3}$  eV/Å.

For the calculation we used the surface unit cell shown in Fig. 2(a) containing two symmetry independent CO molecules labeled by 1 and 2. The vertical and lateral positions of the CO molecules as well as the upper two copper layers were allowed to relax. The relaxed geometric structure is sketched in Fig. 3, which shows the charge density contour plot in top [3(a)] and side view [3(b)] in the vicinity of the DW. Distances are indicated in Å [see also values in brackets in Fig. 2(b)]. Several results of the calculation can be summarized as follows.

(i) Distances between molecular rows (as measured between the terminal oxygen atoms) lie in the range between 3.02 and 3.26 Å. Small distances are found between the molecules forming the DW and between those at the center of the domains (3.02 and 3.11 Å) in correspondence with the STM image. A larger distance is determined at the boundary between the DW and the  $\sqrt{2} \times \sqrt{2}$  domains (molecules 1, 2 and symmetric equivalent ones), where we find 3.26 Å (theory) and about 3.4 Å (experiment). Also, the calculated C–Cu and C–O distances of 1.85 and 1.16 Å are in close agreement with the LEED analysis of Andersson ( $1.90 \pm 0.10$  and  $1.15 \pm 0.10$  Å) [6]

(ii) Cu atoms beneath the CO molecules experience a vertical shift of 0.1 Å towards the vacuum. This shift is roughly the same for all Cu atoms beneath CO irrespective

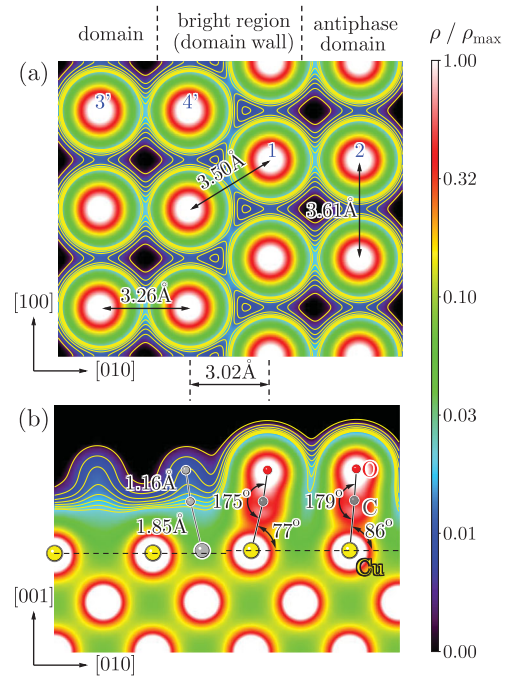


FIG. 3 (color). Calculated charge density contour plot of the CO/Cu(001) CP in top (a) and side view (b). Distances are given in Å.

of their positions within the unit cell. The reason for these vertical relaxations is the electrostatic interaction as a result of the charge transfer from the molecule to the substrate.

(iii) All molecules are tilted. Tilting as well as molecular bending is most pronounced for the (symmetry related) molecules 1 and 4' forming the DW. The angle between the Cu–C bond and the surface plane is equal to  $77^\circ$ , while the angle between the Cu–C and the C–O bond equals to  $175^\circ$ . This configuration involves a nonterminal adsorption site for the DW forming CO molecules. The origin of this effect is electrostatic interaction and symmetry breaking at the domain boundaries. Tilting also affects the first row of CO molecules within the  $\sqrt{2} \times \sqrt{2}$  domain (molecule 2) for which we determine  $86^\circ$  between the Cu–C bond and the surface plane and  $179^\circ$  between the Cu–C and the C–O bond. The origin of the deviation from the idealized structure is of steric nature (Pauli repulsion between the oxygen atoms). Our calculations show that tilting already sets in at an intermolecular distance of  $r = 3.61$  Å.

(iv) Tilting is directly reflected by the increased brightness of the molecules forming the DW as observed in the STM images. Figure 4 shows the calculated  $z$ -projected density of  $p$  states of oxygen [4(a)] and carbon [4(b)] atoms belonging to molecules within the domain ( $D$ ) (black line) and within the DW (red dashed line). In the regime between  $U = -1.5$  and  $-2.5$  eV there is a pronounced enhancement of the  $p_z$  derived density of states (DOS) for oxygen and carbon as indicated by the blue line and the hatched area representing the difference  $\Delta = p_z^{\text{DW}} - p_z^D$ . A similar enhancement is observed for



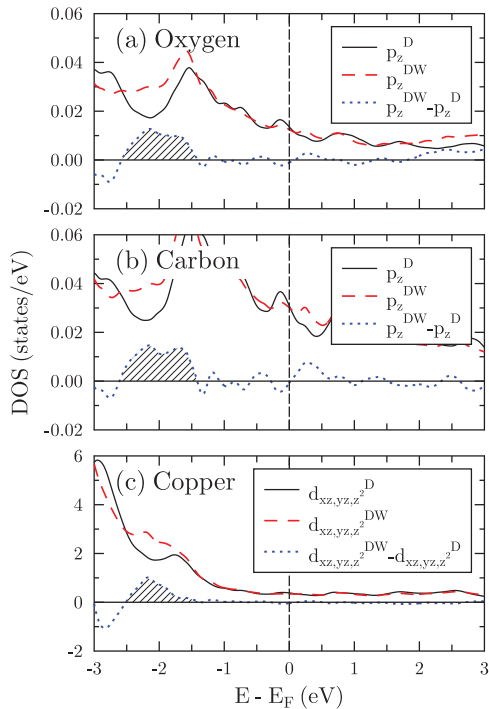


FIG. 4 (color). Calculated DOS of  $p_z$  [oxygen (a), carbon (b)] and  $d$  states [copper (c)]. Black and red lines are related to the DOS of atoms within the domain ( $D$ ) and the domain wall ( $DW$ ), respectively. The blue lines represent the difference. A significant enhancement of the DOS (hatched area) in the range between  $-1.5$  and  $2.5$  eV is observed for atoms located within the  $DW$ .

the  $d$  states of copper [Fig. 4(c)]. According to the Tersoff-Hamann model [18], the tunneling current ( $I_c$ ) is proportional to the local density of states of the surface at the tip position. Here, mainly  $p_z$  electrons of oxygen and carbon contribute to  $I_c$ . Between  $U = -1.5$  and  $-2.5$  eV the states of the tilted molecules are stronger hybridized with  $d_{z^2}$ ,  $d_{xz}$ , and  $d_{yz}$  states of copper. This stronger hybridization leads to a significant enhancement of  $I_c$  as observed in our experiment. In agreement with theory, stable tunneling conditions were found for  $U = -1.7$  eV tip bias voltage (i.e., probing the occupied states) where molecular rows appear brighter.

(v) Our calculations reproduce the line broadening in the RAIRS spectra. We found that the energy for the C–O stretch vibration ( $\nu_1$ ) depends on the local environment (see supplementary information [19]). Values for  $\nu_1$  vary between 245.0 and 255.4 meV. Our simulations demonstrate a continuous increase of  $\nu_1$  with increasing CO coverage. This is in quantitative agreement with experiment [12], where an increase of  $\nu_1$  is observed upon formation of the CP. However, at the  $DW$  the frequencies are smaller by 4 meV than in the ideal  $c(7\sqrt{2} \times \sqrt{2})$  lattice, since the CO bonds in these molecules are longer than elsewhere.

In summary, we have presented a thorough analysis of the long-standing problem of the adsorption geometry of the “compressed”  $c(7\sqrt{2} \times \sqrt{2})$  CO phase on Cu(001). Our combined STM and theoretical DFT analysis reveals a complex structure with a significant inhomogeneity where each CO molecule is in a different local environment. Molecular tilting and bending leads to a relaxed structure with off-terminal sites. Our results considerably contrast with simplified models tentatively assuming “disorder” of the molecular structure. Our study also resolves the so far unresolved problem to explain coverage-dependent changes in RAIRS spectra reported previously [7,11,12]. The observed line broadening can be attributed to “inhomogeneous” broadening due to the uneven distribution of the dipole-dipole coupling. After more than 30 years of investigations, the real nature of the “compressed” CO/Cu(001) phase has been revealed.

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