Direct Evidence for Mesoscopic Relaxations in Cobalt Nanoislands on Cu(001)

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Surface x-ray diffraction in combination with scanning tunneling microscopy and molecular dynamics calculations provide first quantitative evidence for unusually large relaxations in nanometer-sized Co islands deposited on Cu(001) at 170 K. These lead to sharply reduced interatomic Co distances as low as 2.36 Å as compared to bulk Co (2.51 Å) involving low symmetry Co adsorption sites. Our results prove the validity of the concept of mesoscopic mismatch which governs the strain relaxation of nanosized islands in general.

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Since the atomic arrangement in nanoscale objects is decisive for their physical properties the study of nanostructures has become a major subject in solid state physics. With decreasing sample size an increasing fraction of atoms experiences reduced coordination leading to fundamentally different structural, magnetic, optical, and chemical properties as compared to the bulk.

In this context, heteroepitaxial metallic systems are prototypes frequently investigated. However, even at submonolayer coverage the adlayers still represent large objects characterized by island sizes exceeding several nanometers and consisting of hundreds or thousands of atoms. On low-index metal surfaces the adatoms in general occupy high-symmetry adsorption positions such as the threefold- or fourfold-hollow site, and the lattice mismatch between adsorbate and substrate is determined by the difference between the corresponding bulk lattice constants, which usually is referred to as the macroscopic lattice mismatch (m_0).

By contrast, for nanosized islands consisting of several tens of atoms only, dramatic modifications of the atomic arrangement have been theoretically predicted involving giant atomic relaxations not seen experimentally so far [1,2]. Using molecular dynamics (MD) calculations [2] it was shown that in Co islands on Cu(001) consisting of less than about 100 atoms the average interatomic bond length (r_b) is dramatically reduced to values in the 2.40–2.45 Å range as compared to bulk Co (2.51 Å). This scenario is referred to as "mesoscopic lattice mismatch" (m) and is defined as $m = (r_b - r_0)/r_0$, where r_0 is the bond length in bulk Cu.

The mesoscopic lattice mismatch has wide implications on the structure and the physical properties of the nanoislands. At first, in contrast to the common view that Co atoms reside in hollow sites at a distance of $r_0 = 2.56$ Å characteristic for the Cu(001) surface (macroscopic strain $\varepsilon = +2\%$), this implies that a considerable fraction of adatoms are not located in hollow sites but also occupy low symmetry positions off the hollow site.

Furthermore, the mesoscopic misfit has been recently shown to have important consequences on physical properties such as the electronic structure and atomic segregation processes [3–5]. Despite some indirect experimental evidence from stress [6,7] and reflection high-energy electron diffraction [8] experiments that bulk lattice mismatch arguments are inappropriate to describe the adlayer structure in the early stages of heteroepitaxial growth, no direct quantitative experimental proof has been given so far.

This can be attributed to the difficulty to determine the atomic structure of the nanoislands ($\oslash \approx 1$ nm) lacking both long-range order and a well-defined shell structure of interatomic distances. In real space, STM does not provide the required resolution of the order of a few hundredths of an angstrom. On the other hand, k-space structure analysis techniques such as low energy electron diffraction and surface extended x-ray absorption fine structure measurements must surrender in the case of large ensembles of atoms characterized by a distribution of interatomic distances.

In this Letter we follow a different approach by analyzing the local structure of the adatoms relative to the substrate (1×1)-surface unit cell. Surface x-ray diffraction (SXRD) is used to provide first direct evidence for the mesoscopic relaxation in nanoislands. The adatom registry relative to the Cu(001) substrate lattice is analyzed in terms of the width of the static (Gaussian) displacement distribution function of the Co atoms out of the substrate hollow sites. The SXRD results are in agreement with MD calculations.

The experiments were carried out *in situ* under ultrahigh vacuum conditions (base pressure 1×10^{-10} mbar). The Cu(001) sample ($\oslash = 9$ mm) was prepared by several

cycles of ion bombardment (Ar^+, 1 keV) and subsequent annealing at 720 K until the surface showed no contaminants on the basis of Auger electron spectroscopy and terraces several hundred nm wide were observed in STM images. Nanometer-sized Co islands of monoatomic height were prepared by depositing submonolayer (ML) amounts (< 0.5 ML) of Co on a clean Cu(001) surface kept at 170 K to avoid intermixing and island coalescence ($1\ \text{ML} = 1.53 \times 10^{15}\ \text{atoms/cm}^2$).

Figure 1(a) shows a STM image ($15 \times 15\ \text{nm}^2$) of 0.3 ML Co. STM images were recorded in the constant current mode at 0.8 V tip bias voltage and 2 nA tunneling current. Co islands represented by the brighter areas are of monoatomic height and cover 28% of the Cu(001) surface (darker areas). Islands are in the 1–2 nm size range and consist of 10–20 atoms, in some cases up to 40 atoms. Figure 1(b) shows as black dots the unrelaxed positions of the Co atoms within the frame of the STM image.

The SXRD experiments were carried out *in situ* at the Advanced Photon Source (Argonne, USA) and at the European Synchrotron Radiation Facility (Grenoble, France). SXRD is based on single scattering theory, greatly facilitating the structure determination. We analyze the intensity distribution along the crystal truncation rods (CTRs) [9], which allows to derive the adsorption sites of adatoms relative to the substrate (1×1)-unit cell due to the interference of the structure factor of the substrate (F_{sub}) with the adsorbate (F_{Ad}): $|F| = |F_{\text{sub}} + F_{\text{Ad}} \exp[i\phi]|$, where the phase factor accounts for the registry [10,11].

Precise calibration of the amount of Co deposited (Θ_{Co}) was achieved by following the intensity oscillations of the (1 0 0.1) reflection versus time (indexing is according to the primitive setting of the surface unit cell). This position is close to the (1 0 0) antiphase condition along the (1 0 ℓ) CTR. We estimate an uncertainty of at most 10–15% for Θ_{Co}. Integrated x-ray intensities were collected by rotating the sample around the surface normal under grazing angle of incidence of the incoming beam. Structure factor amplitudes, $|F_{\text{obs}}|$, were derived by correcting the integrated intensities for geometric factors [12].

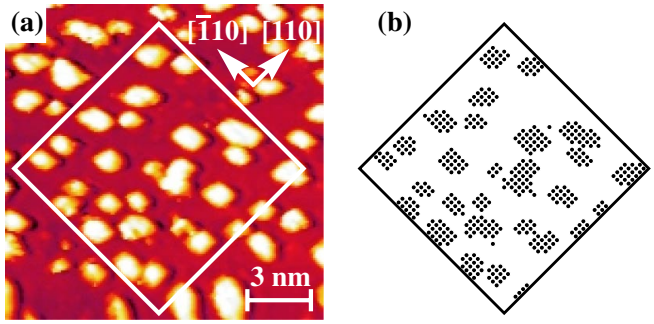

FIG. 1 (color online). (a) $15 \times 15\ \text{nm}^2$ STM image of 0.3 ML Co/Cu(001). (b) Arrangement of Co atoms (black dots) in nanoislands within the frame of the STM image used as starting model for MD calculations.

In total 11 data sets were collected at 170 K after 8 independent preparations. Each data set consists of about 300 reflections along 18 CTRs reducing to 150 independent reflections along 9 CTRs by symmetry equivalence. Because of the high beam intensity the total standard deviation (σ) for $|F_{\text{obs}}|$ is dominated by the reproducibility of symmetry equivalent reflection intensities [10,11], which lies between 4 and 9%.

As an example, Fig. 2 shows the CTRs for 0.3 ML Co. Symbols and error bars represent the measured $|F_{\text{obs}}|$ and the σs, respectively. The solid (red) lines represent the best fit according to the model including disorder as discussed below, while the dotted (black) and dashed (blue) lines correspond to calculated structure factor amplitudes, $|F_{\text{calc}}|$, for uncovered Cu(001) and for 0.3 ML Co placed in hollow sites only.

In comparison to the uncovered Cu(001) surface, Co adsorption leads to a strong intensity reduction ($\approx 65\%$) at the antiphase condition ($\exp[i\phi] \approx -1$) of the CTRs given by $h + k + \ell = 2n + 1$ (n integer) [13]. However, the straightforward model in which 0.30 ML of Co is placed into the Cu(001) hollow site does not fit the data (dashed blue lines). The $|F_{\text{calc}}|$ for the hollow site model are too low as compared to the $|F_{\text{obs}}|$ in the range between the Bragg positions; i.e., it overestimates the antiphase scattering contribution of the Co atoms. Notably, there is a strong dependence on the momentum transfer, which is most obvious at $\ell \approx 0$ on the left panel of Fig. 2, where the

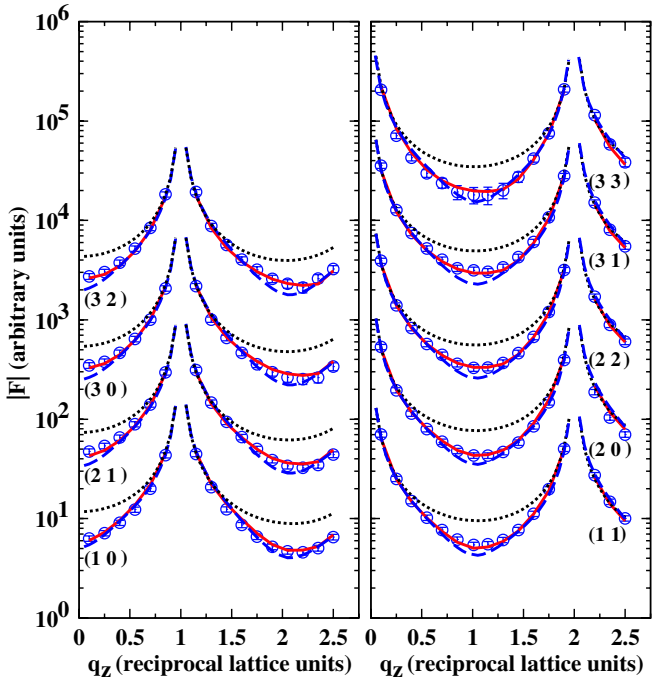

FIG. 2 (color online). Measured (symbols) and calculated (lines) structure factor amplitudes for 0.30 ML Co/Cu(001). Solid lines represent the best fit; dashed and dotted lines correspond to models with Co in hollow sites only and the clean Cu(001), respectively (curves are shifted for clarity).

deviation increases from 15% at the (1 0 0.15) reflection to 35% at the (3 2 0.15) reflection. Qualitatively, this can be explained by the presence of strong structural disorder as described by a Debye–Waller-like damping term as outlined in the following.

Co placed in the hollow site position corresponds to the equilibrium electron density ρ_0. The disordered adlayer structure of the Co atoms, ρ_r, is given by the electron density ρ_0 convoluted with the probability density function, pdf(u), representing the displacement field of the Co atoms out of the hollow site: $\rho_r = \rho_0 * \mathrm{pdf}(u)$, where u represents the displacement amplitude [14].

Correspondingly, the adlayer structure factor amplitude is given by $|F_{\mathrm{Ad}}(q)| = |F_{\mathrm{Co}}(q)T(q)|$; i.e., $T(q)$ represents the damping of the structure factor amplitude of the Co atoms (F_{Co}) due to static structural disorder. In many cases pdf(u) can be approximated reasonably well by a Gaussian distribution function leading to an analytic expression for $T(q)$ as follows [14]: $T(q) = \exp[-Bq^2/4]$, where B is the Debye parameter ($B = 8\pi^2\langle u^2\rangle$) and q the modulus of the scattering vector [15]. The parameter $\langle u^2\rangle$ represents the (isotropic) mean squared displacement amplitude of pdf(u) related to the width of the distribution. The concept applied here for describing the disorder of the Co atoms relative to the substrate is analogous to the conventional approach to treat thermal vibration, where $T(q)$ is commonly referred to as the "temperature factor" [15]. We confine the discussion on the isotropic description of the disorder; a more detailed analysis allowing for anisotropy (in-plane vs out-of-plane) will be presented elsewhere [16].

The quantitative analysis was carried out by least squares refinement of the $|F_{\mathrm{calc}}|$ to the observed ones. The refinement benefits from the high symmetry of the structure (plane group $p4mm$) on a macroscopic scale given by the footprint size of the beam on the sample. Apart from an overall scale factor only the z positions and B factors of the top Co layer, the upper two Cu layers, and of bulk Cu were taken into account. This sums up to eight parameters only. Correlations between the parameters were below 0.7, most of them in the 0.2–0.4 range, ensuring rapid convergence.

Open circles in Fig. 3 represent the Debye parameter for Co (B_{Co}) plotted versus Θ_{Co}. Giant values in the range between 1.5 and 3.2 Å^2 are found. The average value equals to about 2.5 Å^2 equivalent to a root mean squared (rms) displacement of 0.18 Å. Error bars of the order of ± 0.5 Å^2 are due to the uncertainty of the coverage and correlations with other parameters. B factors of this magnitude can only be attributed to static displacements, since thermal vibrations involve B factors in the range well below 1 Å^2. We do not think that the apparent slight increase of the B factor with Θ_{Co} is significant.

For the (thermal) Debye parameters of the top two Cu layers we derive $B_{\mathrm{Cu1}} = 0.81 \pm 0.31$ Å^2 and $B_{\mathrm{Cu2}} = 0.47 \pm 0.28$ Å^2, where the error bars represent the standard deviation (1σ level) obtained from the scatter of the 11 data sets. In addition two independent data sets were collected for the uncovered sample also; for B_{Cu1} we find 0.64 ± 0.07 Å^2 and 0.78 ± 0.20 Å^2 (see open squares at $\Theta_{\mathrm{Co}} = 0.$ in Fig. 3.

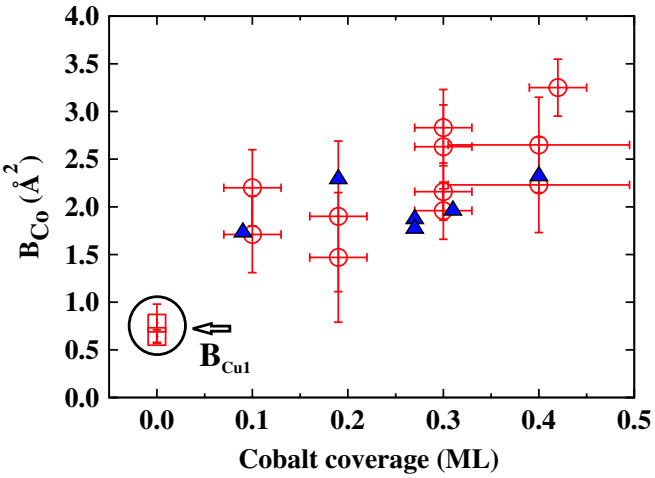

FIG. 3 (color online). Experimentally derived Debye parameters of Co (open circles) versus Co coverage. Triangles represent simulated data based on MD calculations. Experimental Debye parameters for first layer Cu atoms for uncovered Cu(001) are plotted as squares at zero coverage (see label B_{Cu1}).

These values nicely compare with experiment [$B_{\mathrm{Cu1}} = 0.88$ Å^2] [17] and theory [$B_{\mathrm{Cu1}} = 0.55$ Å^2, $B_{\mathrm{Cu2}} = 0.39$ Å^2] [18] for the uncovered Cu(001) surface. Similarly for Cu bulk (beginning with the 3rd layer) we find $B_{\mathrm{bulk}} = 0.37 \pm 0.24$ Å^2 in comparison with $B_{\mathrm{bulk}} = 0.27$ Å^2 (Ref. [18]) and $B_{\mathrm{bulk}} = 0.32$ Å^2 (Ref. [17]).

For the average Co adsorption height above the first Cu layer (d_{Co}) and the first Cu interlayer spacing (d_{12}) we find 1.79 ± 0.03 Å and 1.78 ± 0.02 Å, respectively, also in good agreement with low-energy electron diffraction experiments in Ref. [19]: $d_{\mathrm{Co}} = 1.76 \pm 0.02$ Å, $d_{12} = 1.78 \pm 0.03$ Å.

Very high quality fits were achieved in all cases, such as shown by the solid (red) lines in Fig. 2. The fit quality is expressed by the residual (R_w) and by the goodness of fit parameter (GOF) [20]. While the first measures the average relative deviation between observed and calculated $|F|$s, the latter also takes into account the relation between number of data points and fitting parameters. In general, for R_w and GOF, excellent values in the range of 0.04–0.06 and 0.9–1.0 were achieved, respectively.

The SXRD analysis provides compelling evidence that Co atoms deposited on Cu(001) forming nanosized islands experience unusually large disorder. It is characterized by an rms displacement of 0.18 Å which is attributed to static displacements out of the hollow site position.

We went one step further to compare the SXRD results with MD calculations. Parameters of the potentials [21]

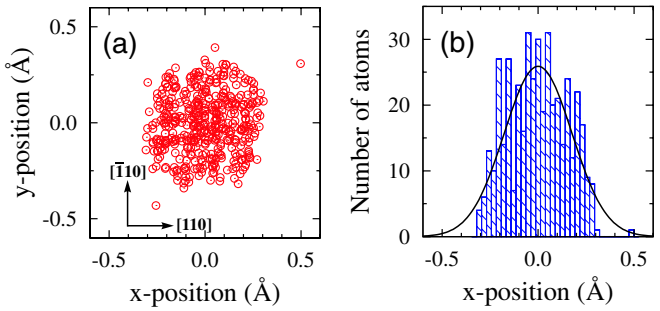

FIG. 4 (color online). MD calculation for 0.3 ML Co/Cu(001). (a) Positions of Co atoms within Cu(001)-surface unit cell. (b) Distribution projected to a axis together with Gaussian fit (solid line).

were fitted to accurate first principle results for Co islands on Cu(001) and the interatomic potentials are formulated in the second moment approximation of the tight binding theory.

MD calculations were carried out using STM images as starting model for the morphology of the islands. This was achieved by placing an atomic grid with unit cell size of 2.56×2.56 Å^2 over the STM image to generate a starting model using the unrelaxed hollow site adatom positions as shown in Fig. 1(b) by the black dots. The system for the calculation consists of nine Cu layers containing 1521 atoms each and of 431 Co adatoms.

The fully relaxed positions of the Co atoms within the (1×1)-unit cell are shown as open circles in Fig. 4(a). The individual positions of all Co atoms are projected into one single unit cell, where the center position corresponds to the hollow site. Figure 4(b) shows the distribution of the Co positions in a projection along the $[\bar{1}10]$ direction. The solid line represents a Gaussian fit with a half width at half maximum of 0.069 lattice units equivalent to the rms displacement amplitude of $\sqrt{\langle u^2 \rangle} = 0.18$ Å equivalent to $B = 2.56$ Å^2, in remarkable agreement with the experimental results. For this model structure a mesoscopic misfit value of $m = -5.25\%$ is derived, which is related to an average interatomic Co distance of $r_b = 2.42$ Å and a minimum distance of 2.36 Å.

Several MD calculations were carried out for different Co coverages. Using the MD-derived coordinates including relaxations of the upper two Cu layers "simulated" structure factor amplitudes, $|F_{\mathrm{sim}}|$ were calculated, which in turn were refined in the same way as the experimental ones. The values of B_{Co} obtained in this way are shown in Fig. 3 by triangles. There is excellent agreement of the Debye parameters derived from the MD calculations with the experimental ones. This proves that the enhanced B factor observed for the Co atoms is directly related to the mesoscopic relaxations. It also shows that the Gaussian approximation is a valid description of the displacement distribution pdf(u). Some scatter observed for the simulated B factors comes from the different sizes and shapes of the individual islands used as starting models. The difference between the $|F|$ calculated from the Gaussian and from the exact MD-derived pdf(u) distribution never exceeds 5%, being in most cases below 3%; i.e., it is within the experimental accuracy.

In summary, our combined SXRD and MD study has provided evidence that Co atoms in nanosized islands on Cu(001) exhibit structural disorder linked to a distribution of adsorption positions off the hollow site. It represents a direct proof for the theoretically predicted concept of mesoscopic misfit, which is decisive for understanding structure and physical properties of nanoislands in general.

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