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Structure determination of Cu(100)-$p(2\times2)$-S using x-ray diffraction

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The role of substrate reconstruction in the Cu(100)-(2×2)-S system has been investigated using x-ray diffraction. It is found that the first-layer Cu atoms are laterally displaced away from the S atoms by 0.03 ± 0.01 Å. This result resolves a recent controversy between a low-energy electron-diffraction study and an angle-resolved-photoemission extended-fine-structure analysis in favor of the electron-diffraction result.

In order to obtain a detailed understanding of the properties of adsorbates on metals, knowledge of the geometric structure at the surface is a prerequisite. This allows one to look at systematic differences between related systems,[1] and also provides model systems against which theoretical calculations can be tested. One system that has received considerable experimental attention is S on Cu(100).[2-6] As a function of S coverage, various phases appear on the surface, one of which is a $p(2\times2)$ overlayer for a S coverage of ~0.25 monolayer. Though various techniques have agreed that in this system the S is adsorbed at a fourfold-hollow site,[3,4,6] there is no such consensus on the question of whether the first-layer Cu substrate atoms also are part of the reconstruction, that is whether these show a lateral displacement.[7,8] In particular, a low-energy electron-diffraction (LEED) analysis[7] arrived at a model in which the top-layer Cu atoms move *away* from the S, whereas an angle-resolved-photoemission extended-fine-structure (ARPEFS) study[4] concluded that the Cu atoms are displaced *towards* the S. A very recent investigation with surface-extended x-ray absorption fine structure (SEXAFS)[6] could not resolve this matter, because, though this technique accurately measures first-neighbor bond lengths, the other structural parameters needed to deduce the reconstruction could not be determined.

Surface x-ray diffraction is a technique particularly well suited to measure lateral displacements with a high accuracy.[9,10] Due to the kinematical nature of the scattering process, the interpretation of the diffracted intensity is straightforward and does not involve complicated model calculations. This is not the case in LEED or ARPEFS, and doubts on the validity of the theoretical approaches used in such model calculations were raised in order to explain the conflicting results obtained by these two techniques.[8] Since with x-ray diffraction the data interpretation is unquestioned, that technique is used in this paper to resolve the controversy between LEED and ARPEFS.

The experiment was performed at the AT&T beam line X16A at the National Synchrotron Light Source (NSLS) at BNL. The x rays from the storage ring are focused by a toroidal mirror and are monochromated by a Si(111) double-crystal monochromator before entering the vacuum chamber where the sample is mounted.[11]

The Cu(100) substrate (12-mm diam) was cleaned by repeated cycles of sputtering (1-keV Ar^+ ions) and annealing (450 °C) until no contamination could be detected using Auger electron spectroscopy. The $p(2\times2)$ overlayer was prepared by exposing the substrate at room temperature to $\mathrm{H_2S}$ at a pressure of 1×10^{-7} Torr. By measuring the peak height and width of the (0.5,0,0.1) reflection, the degree of order of the $p(2\times2)$ overlayer could be monitored. After a total dose of ~80 L (1 L $=10^{-6}$ Torr s) the peak height stopped increasing. A subsequent anneal to 250 °C was found to improve the quality of the overlayer, as displayed in Fig. 1, where the peak height (above background) of the (0.5,0,0.1) reflection is shown as a function of sample temperature. Above 200 °C the peak starts to disappear, but upon cooling it reappears with increased height. There is no measurable change in peak width between the surface before and after the anneal, thus the increase seems not to be due to a higher surface order, but it probably corresponds to a higher fraction of surface atoms contributing to the signal. This could be caused by the desorption of a small excess amount of $\mathrm{H_2S}$ that initially destroyed part of the $p(2\times2)$ order. After the first cycle the temperature dependence is reversible, indicating that no further S is lost (diffused into the bulk or desorbed).

The drop in peak height around 200 °C is much faster

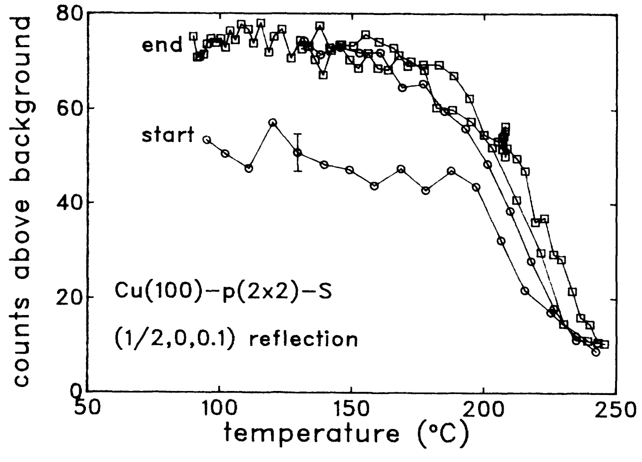

FIG. 1. The peak intensity above background of the (0.5,0,0.1) reflection during thermal cycling of the sample. Circles denote measurements while heating, whereas squares denote cooling.

than can be explained by the Debye-Waller effect, indicating that at this temperature a phase transition occurs. There is some indication that the peak broadens during the transition. Because of the large background in the data, no attempt was made to investigate carefully whether the integrated peak intensity was constant during the phase transition. This would have indicated whether the transition is of the order-disorder type.[12] From the final low-temperature peak width a correlation length of ~100 Å is derived, corresponding to an average reconstructed domain length of ~20 unit cells.

Over 400 different reflections were measured, corresponding to 84 nonequivalent ones, which belonged to 16 fractional-order and 4 integer-order rods. All scans were done with the rods aligned in the horizontal plane (along the instrumental resolution function), by rotating the entire setup to the corresponding angle.[13] This eliminates a number of corrections related to changes in resolution function.[14]

The high background levels and broad low peaks of the data required careful data analysis, especially of the weaker reflections. Therefore the data were fitted using, as a working approximation, a Lorentzian peak shape with a linear background. This fitted background was then used in a numerical peak integration. After area and polarization-factor corrections,[9,10] and taking the square root, the experimental structure factor was obtained. Even after using this procedure, more elaborate than usual,[9] the average agreement between equivalent reflections was 14%, to be compared with typical values of (5–10)%. The error in the data was estimated by combining the average agreement with the statistical error.[9]

In the analysis the experimentally derived structure factors F_{hkl} are fitted to the ones calculated for a model structure

$$F_{hkl}=\sum_{j}^{\text{unit cell}} f_j\exp[-B_jQ^2/(16\pi^2)]\times\exp[2\pi i(hx_j+ky_j+lz_j)]\,, \tag{1}$$

with x_j, y_j, and z_j the position of atom j in the unit cell in reduced coordinates, f_j the atomic scattering factor, B_j the isotropic Debye-Waller parameter, and Q the momentum transfer. The generally accepted structure model with S at a fourfold hollow site (see Fig. 2) was used as a start in fitting the data. The parameters that were allowed to vary were an overall scale factor, the distance d_{SI} of the S atom to the first-layer Cu atoms, a lateral displacement Δ of the top-layer Cu atoms, and isotropic Debye-Waller parameters B for S and Cu. The optimum parameters were $d_{\mathrm{SI}}=1.19\pm0.14$ Å, $\Delta=0.03\pm0.01$ Å, $B_{\mathrm{S}}=3.5\pm1$ Å^2, and $B_{\mathrm{Cu}}=2.0\pm0.5$ Å^2, giving a reduced χ^2 of 0.75. The low value of χ^2 is probably related to the conservative estimate of the errors in the data.

The data are particularly sensitive to the lateral displacements of the Cu atoms. This can be illustrated by comparing some typical rod profiles (Fig. 3) with calculated ones. The solid curves in Fig. 3 are calculated using the optimum fit parameters. If the Cu atoms were not reconstructed, they would not contribute to the fractional-order structure factor and the only l dependence in the rod profiles would be due to the atomic scattering factor of S [see Eq. (1)]. The computed rod profiles for this case are shown as the dashed curves in Fig. 3. Clearly the data show more structure than these monotonically decreasing profiles, implying that the Cu atoms must be reconstructed. Fitting the data without allowing the Cu to reconstruct gives a χ^2 of 1.6, more than twice the minimum value. The sign of the Cu displacement can be inferred by noting that only a displacement away from the S gives rod profiles with the correct increase or decrease as a function of l for adjacent reflections. This is particu-

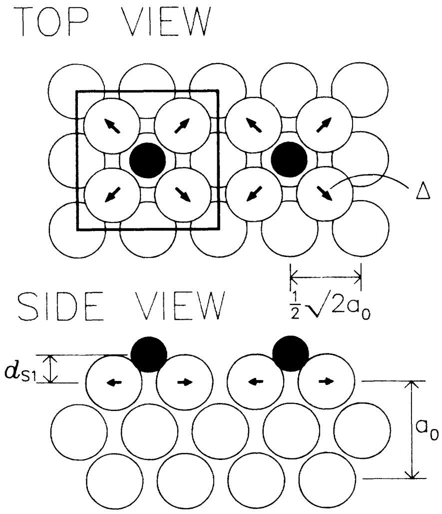

FIG. 2. The model for Cu(100)-$p(2\times2)$-S. The direction of the in-plane relaxation in the substrate is indicated by the arrows.

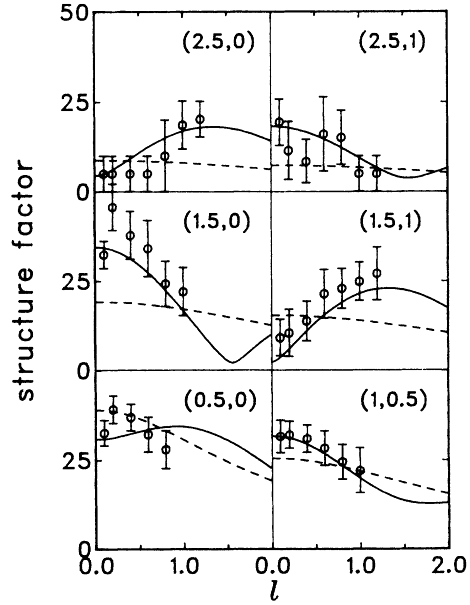

FIG. 3. A series of scans as a function of the perpendicular momentum transfer l (rod scans). The circles are the data points, the solid curves are the best fit, and the dashed curves represent the calculated rod profiles for a model in which there is no reconstruction of the top-layer Cu atoms.

larly clear for the (1.5,0) and the (1.5,1) rods: in the first case the intensity *decreases* for l going from 0 to 1, whereas in the second case the intensity *increases* over the same l range. A displacement towards the S would reverse this behavior, in contradiction with the data.

In Table I the structural parameters as found here are compared with the results of LEED (Ref. 7) and ARPEFS.[4] It is clear that the x-ray results compare well with the LEED, but not with the ARPEFS. The table only shows the two structural parameters Δ and d_{S1} that were optimized in our analysis, but it should be noted that in the LEED and ARPEFS analyses perpendicular relaxations in the second Cu layer were also considered. Due to the limited range of perpendicular momentum transfer, the x-ray data are not sensitive to these small relaxations, and therefore they have been ignored in the analysis. For the same reason, the error bar on d_{S1} is rather large. The table also shows the χ^2 values obtained by comparing the model derived from LEED and ARPEFS (including second Cu-layer relaxations) against the x-ray data. A scale factor and Debye-Waller parameters were allowed to vary. Again the LEED gives a satisfactory fit, but the ARPEFS does not. In addition an electron-energy-loss spectroscopy study[15] measured a value for d_{S1} of 1.30 ± 0.05 Å, consistent with the LEED and x-ray diffraction results, but not with ARPEFS.

Despite the differences, the LEED and ARPEFS results do give the same Cu-S bond length of 2.26 Å, which is in good agreement with a recent SEXAFS measurement that gave 2.27 ± 0.01 Å.[6] The fact that ARPEFS does give the correct bond length is not surprising, because this technique is particularly sensitive to bond length, in a manner that is similar to SEXAFS.[2] The bond-length value also falls within the large error bar of the x-ray result.

Because our results agree well with the LEED analysis, we do not share the objections that were raised against the LEED data interpretation.[8] On the contrary, our work indicates that it is ARPEFS which requires some further development of the theoretical analysis underlying the model calculations.[4,16] Since the present Cu(100)-$p(2\times2)$-S surface appears to be an example where the ARPEFS analysis did not give the correct answer, this could be used as a model system to further improve the ARPEFS technique.

TABLE I. A comparison between the results obtained with x-ray diffraction, LEED, and ARPEFS. Δ is the lateral displacement of the first-layer Cu atoms, with a positive value meaning a displacement away from the S. d_{S1} is the height of the S above the substrate. $d_{\mathrm{Cu-S}}$ is the Cu−S bond length. The error bars are given in parentheses; for the LEED analysis, no error bars were given. The χ^2 values are obtained by fitting the structural models to the x-ray diffraction data.

	X-ray diffraction[a]	LEED[b]	ARPEFS[c]
Δ	0.03(1)	0.04	−0.05(2)
d_{S1}	1.19(4)	1.29	1.42(2)
$d_{\mathrm{Cu-S}}$	2.19(14)	2.26	2.26(1)
χ^2	0.75	0.89	6.46

[a] This work.

[b] Reference 7.

[c] Reference 4.

The only *ab initio* calculations available of an adsorbate-induced reconstruction of a fcc crystal are for isolated S atoms on Al(100).[17] For that system, it was found that the first-layer Al atoms are displaced away from the S atoms by ~0.03 Å. That the reconstruction for Al(100) has the same sign and order of magnitude as in the Cu(100)-$p(2\times2)$-S system is encouraging, and such calculations for the Cu(100) system are awaited with interest.

In conclusion, we have established the occurrence of a S-induced reconstruction in the Cu substrate. First-layer Cu atoms are displaced 0.03 ± 0.01 Å away from the S atoms. This reconstruction may give rise to an energy barrier which inhibits further H_2S adsorption at room temperature, and therefore prevents the subsequent formation of a $c(2\times2)$ reconstruction.[18]

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[1] F. Sette, T. Hashizume, F. Comin, A. A. MacDowell, and P. H. Citrin, Phys. Rev. Lett. **61**, 1384 (1988).

[2] J. J. Barton, C. C. Bahr, Z. Hussain, S. W. Robey, J. G. Tobin, L. E. Klebanoff, and D. A. Shirley, Phys. Rev. Lett. **51**, 272 (1983).

[3] H. C. Zeng, R. N. S. Sodhi, and K. A. R. Mitchell, Surf. Sci. **177**, 329 (1986).

[4] C. C. Bahr, J. J. Barton, Z. Hussain, S. W. Robey, J. G. Tobin, and D. A. Shirley, Phys. Rev. B **35**, 3773 (1987).

[5] J. C. Boulliard and M. P. Sotto, Surf. Sci. **195**, 255 (1988).

[6] R. McGrath, A. A. MacDowell, T. Hashizume, F. Sette, and P. H. Citrin (unpublished).

[7] H. C. Zeng, R. A. McFarlane, and K. A. R. Mitchell, Phys. Rev. B **39**, 8000 (1989).

[8] D. A. Shirley, L. J. Terminello, and C. C. Bahr, Phys. Rev. B **39**, 8003 (1989).

[9] I. K. Robinson, in *Handbook on Synchrotron Radiation,* edited by D. E. Moncton and G. S. Brown (North-Holland, Amsterdam, 1989), Vol. 3.

[10] R. Feidenhans'l, Surf. Sci. Rep. **10**, 105 (1989).

[11] P. H. Fuoss and I. K. Robinson, Nucl. Instrum. Methods Phys. Res. **222**, 171 (1984).

[12] I. K. Robinson, A. A. MacDowell, M. S. Altman, P. J. Estrup, K. Evans-Lutterodt, J. D. Brock, and R. J. Birgeneau, Phys. Rev. Lett. **62**, 1294 (1989).

[13] E. Vlieg, J. F. van der Veen, J. E. Macdonald, and M. Miller, J. Appl. Cryst. **20**, 330 (1987).

[14] I. K. Robinson, Aust. J. Phys. **41**, 359 (1988).

[15] Z. Q. Wu, M. L. Xu, Y. Chen, S. Y. Tong, M. H. Mohamed, and L. L. Kesmodel, Phys. Rev. B **36**, 9329 (1987).

[16] E. L. Bullock, C. S. Fadley, and P. J. Orders, Phys. Rev. B **28**, 4867 (1983).

[17] P. J. Feibelman, Phys. Rev. Lett. **63**, 2488 (1989).

[18] R. McGrath, A. A. MacDowell, T. Hashizume, F. Sette, and P. H. Citrin, Phys. Rev. Lett. **64**, 575 (1990).