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Long-range interaction between adatoms at the Cu(111) surface imaged by scanning tunnelling microscopy

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Abstract. We have used an ultra-high vacuum variable temperature scanning tunnelling microscope to study the Cu(111) surface at temperatures from 90 K to 300 K. After the sample is heated to 900 K, adatoms enriched at the surface. Around these adatoms ring-formed standing-wave features can be seen in the local density of states (LDOS). When more than one of the adatoms were imaged it became evident that the adatoms preferred lateral distances in which they shared LDOS standing-wave maximas. This means that adatoms were positioned at multiples of half the Fermi wavelength (15 Å) from each other. We ascribe the interaction that gave these results to the surface state electrons which form the LDOS standing waves. Furthermore the interaction was long-ranged (at least in the order of 80 Å), oscillatory with the pair distance, and present at high temperatures since the adatoms stick to the surface above room temperature.

Interactions of adatoms at a surface are important as they take part in many processes such as diffusion, cluster formation, and film growth. The interaction between the adatoms can, at close distances, be of different types of direct forces: an overlap between the atoms, which gives an essentially chemical bond, a van der Waals attraction, or a dipole–dipole interaction if the atom–substrate bond is polar. This article will, however, be concerned with adatoms at longer distances where the interaction between adatoms has to be indirect, mediated by the substrate electrons. These long-range interactions at surfaces have been studied since 1967 when Grimley investigated the force between two adatoms mediated by the electrons of the conduction band; these electrons are shared by the adatoms [1]. Grimley found the interaction to be both oscillatory and long range. His results where later refined [2–5] and confirmed by field ion microscopy (FIM) experiments, where adatom pairs were imaged at a FIM tip [6, 7]. A FIM suffers from the drawback of using single-crystal tips instead of flat single-crystal surfaces. However, the same interactions can be investigated by a scanning tunnelling microscope (STM), which is known for its high lateral resolution. The use of a flat sample and an STM has many advantages compared to FIM: larger areas can be imaged, it is easy to obtain clear images of atoms, cluster formations, step edges and dislocations. This makes it possible to investigate interactions between adatoms and all these features. The main drawback of using an STM is that the system studied has to be selected so the adatoms do not move laterally when imaged, this means that they have to stick quite well to the surface.

1 Experimental details

The apparatus used in this study is a variable temperature scanning tunnelling microscope, equipped with sputtering guns and a LEED system (Omicron Vakuumphysik GmbH). The system permits STM imaging from 50 K to 300 K at pressures below 10^{-10} mbar. Tips are electrochemically etched from tungsten wire, and then prepared by Ar ion sputtering (4 kV) and annealing [8], and checked with field emission [9]. The Cu crystal was electropolished [10] before it was clamped with copper plates to the sample holder and inserted into the experimental chamber. The sample was then finally prepared by repeated Ar ion bombardment (1 kV, 2 μA) and annealing. The adsorbed atoms we studied originate from the bulk of the Cu(111) and emerged at the surface when the sample was annealed at temperatures above 800 K. In the experiments reported here the sample, after sputtering, was annealed to 900 K for about 10 min, and then allowed to cool down to or below 300 K. This gave an adatom density of the order of 0.001 relative to the density of Cu atoms in the uppermost substrate layer. The density estimate was obtained from STM images recorded after the crystal had reached 300 K or lower temperatures.

All images presented here are acquired with a low bias voltage in the constant current mode, in which the tip height is varied to keep the tunnelling current constant while the tip is scanned laterally. When STM images are acquired in this manner one probes the local density of states (LDOS) of the electrons on a flat surface [11]. Characteristic of the (111) surface of a noble metal is the existence of an elec-

tronic surface band found in the bulk band gap responsible for the necks of the Fermi surface [12]. The surface band has its minimum 0.4 eV below the Fermi level at the centre of the surface Brillouin zone, and a dispersion corresponding to an effective band mass of 0.4 m_e. This means that the band is occupied by only 0.04 electrons per surface atom, and that the Fermi wavelength is large compared to the interatomic distance (30 Å). In all images shown below lateral oscillations can be seen, which are standing waves formed by the surface state when it scatters against adatoms or steps. This has been studied by Crommie et al. and Avouris et al. [13, 14] who found the wavelength of these oscillations to be half the Fermi wavelength if the surface state was imaged at the Fermi level. Crommie et al. studied Cu(111) with a wavelength of the LDOS oscillations of 15 Å [13].

2 Results

A striking feature in images acquired between 85 K and 300 K with several adatoms present, is the correlation between the interatomic distances and the wavelength of the standing-wave patterns observed close to zero bias. Plots of the distribution of interatomic distances of nearest neighbours are shown in Fig. 1. They are obtained from a number of images like the one shown in Fig. 2. If all distance measurements are included we find the distribution of distances as shown in Fig. 1a. One can distinguish several peaks in the distribution: three main peaks at 21 Å, 36 Å, and 65 Å, which correspond to the cases in which the two adatoms actually share LDOS maxima, and two small peaks at 52 Å and 70 Å. As it is a very complex task to analyse this structure of different cluster-like combinations we choose to concentrate on the pair interactions, which have been studied before with FIM [6, 7]. To investigate pair interactions we selected pairs of atoms that were not in closed cluster formations, i.e. the adatoms that only had the other adatom forming the pair as next neighbour in that direction. In total, 41 such distances were measured between 58 different adatoms from a total of 18 images to obtain Fig. 1b. This distance distribution show peaks at 21 ± 3 Å, 36 ± 4 Å, and at 66 ± 7 Å (see Fig. 1b). In images like Fig. 2 these distances can be clearly seen from the number of LDOS wavelengths of 15 Å that are dividing the two adatoms of the more isolated pairs. The first peak then comes from when the inner rings are touching each other, since the inner LDOS oscillations rings have a radius of 10 Å, the resulting distance between the adatoms is 20 Å. The second peak at 36 Å then corresponds to the case when the two adatoms are separated by one LDOS oscillation, whereas the third peak at 66 Å corresponds to a separation of three LDOS oscillations, which is the case shown in Fig. 3. For the distance measurements, the period of the standing-wave pattern is used to obtain a common length scale for images that are distorted by drift. This correction is typically in the order of 20%. It is also noticeable that the low electron density close to the adatoms in all pictures suggests that the adatoms are electronegative in nature [14].

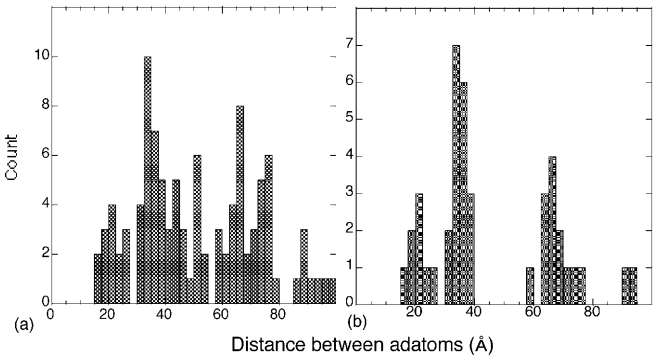

Fig. 1. a A histogram that shows the distribution of different interatomic distances for adatoms. The distances were obtained by using images acquired at temperatures ranging from 85 K to 300 K. **b** Data from histogram **a** has been selected so that only pair interactions are accounted for

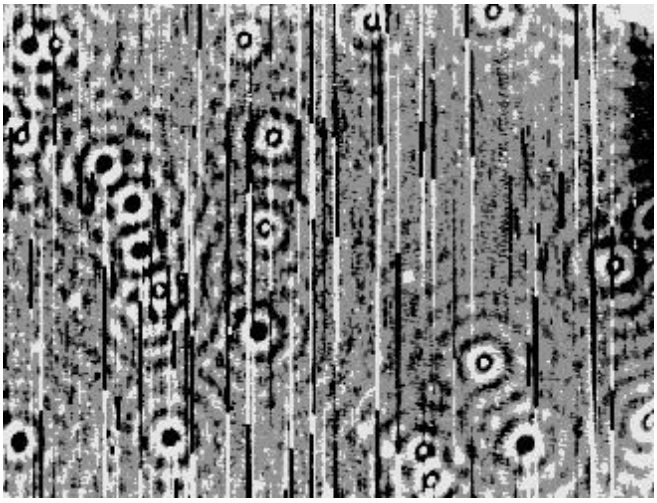

Fig. 2. A typical image used to measure interatomic distances, showing many adsorbed atoms interacting ($V = 0.02$ V to tip, $I = 0.486$ nA, $T = 145$ K, image size: 400 Å × 600 Å)

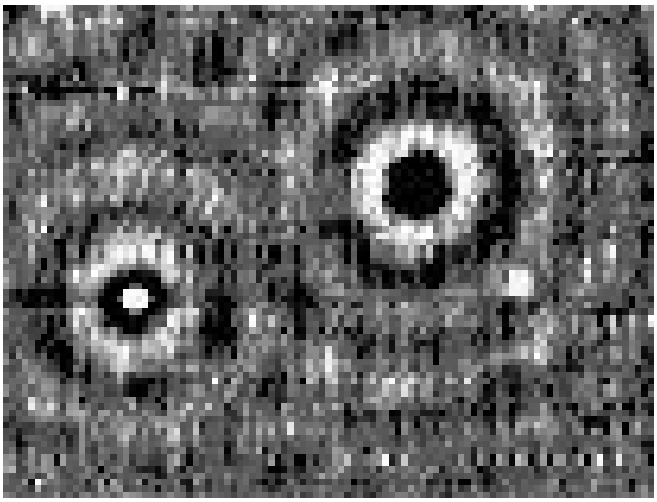

Fig. 3. A close-up of two adatoms at a distance of about 64 Å from each other; note that the atoms seem to share local density of states oscillations with each other ($V = 0.02$ V to tip, $I = 0.131$ nA, $T = 165$ K)

3 Discussion

The Cu(111) surface has a lattice constant of 3.61 Å, which is much smaller than the periodic distance of 15 Å measured

above, this means that it is very unlikely that the surface lattice mediates the interaction that give the distributions above. The surface lattice does, however, play an important part in the imaging process as the adatoms snap to the lattice grid at the temperatures at which we have investigated the system. We have not been able to detect any reconstruction of the surface (Fig. 4) when atoms and oscillations are imaged at the same time. This and the periodical spacing of the pair-interacting atoms, which is connected with the surface-state Fermi wavelength, together with long-ranged periodical behaviour, leads us to deduce that the interaction is mediated by the surface state of the Cu(111) surface.

The interaction between two adsorbed atoms has been estimated theoretically [1–5, 15]. A common result is that there is an oscillatory substrate mediated Friedel-type interaction,

$$\Delta E_{\text{int}} = \frac{\cos(2k_{\text{F}}R+\varphi)}{R^n} \tag{1}$$

where R is the distance between the adsorbed atoms, k_{F} the Fermi wavenumber, and n a constant. The lateral range of the force, given by n, depends on the states providing the screening of the adatom. The theoretical result of current interest is that the interaction is particularly long range when the interaction is mediated by a partially filled surface band of electrons. For a half-filled surface band Lau and Kohn found that $n = 2$, but for a bulk band $n = 5$ [4]. In the case of $n = 2$ Lau and Kohn found an indirect interaction energy of the order of -100 meV for the first minima; this figure should be multiplied with 0.4 in our case to take into account the effective band mass ($0.4\,\text{m}_\text{e}$) of the surface-state electrons. In the theoretical investigation performed by Le Bosse et al. [3] of monovalent adatoms at a metal surface, another oscillating term occurs so that the interaction energy takes the form:

$$\Delta E_{\text{int}} = C_1\frac{\cos(2k_{\text{F}}R+\varphi)}{R^3} + C_2\frac{\cos(k_{\text{F}}R+\varphi)}{R^2} \tag{2}$$

where for electronegative atoms $C_1 > C_2$. These authors primarily investigated the case of electropositive Na on the Cu surface. However, they also estimated the interaction energy (the first term in (2)) to be of the order of 100 meV for O on a Cu surface, and one expects a similar energy in our case [3]. For our system (2) means that for small distances the first term of the interaction energy will dominate with a length period of 15 Å for the interaction energy, whereas for large distances the second term will dominate with a period length of 30 Å. This could give an explanation for the transition to the double period length for distances greater than 40 Å. However, the missing third peak could also be a product of the cluster formation; if the cluster formation process is favourable at distances of about 50 Å, none of the adatoms in that distance range would be counted. We do not have enough data to be able to say if any of the theories can quantitatively describe our system, but the general trends of long-range and periodic behaviour fit our data.

Repeated imaging at 300 K and 95 K showed that adatoms have stable positions, this indicates that the positioning of the atoms occurs above room temperature and that the atomic lattice of the Cu(111) locks the adatoms in position after heating to 900 K. This is in line with the investigations performed by Tsong et al. at the W(110)/Re system. They heated a W(110) field ion microscopy tip with adatoms adsorbed on it to 320 K and recorded the positions of the adatoms after heating. Tsong et al. could then estimate the pair-interaction energy for the W(110)/Re system and the variance of the pair interaction with distance. They reported an interaction energy of the order of 100 meV and the range of the interaction was at least about 50 Å [6, 7], which indicates that the interaction energy can be relatively strong as well as long ranged.

In the few images where adatoms are located close to steps of the Cu(111) surface we note that they are positioned so that their LDOS oscillations are shared with those due to the step (Fig. 5). This can be compared with recent results for the Cu(111)/benzene system studied by Stranick et al. [16, 17]. They ascribe the formation of benzene islands close to steps to the interaction between benzene molecules and the modulated LDOS close to the step.

Our UHV system lacks the possibility of chemical analysis, but it is well known that sulphur residues segregates from the bulk when Cu is heated to 900 K [18, 19]. Hinch et al. [18] also showed that S atoms are highly mobile at 820 K, with a diffusion coefficient of $2.9\times10^{-5}\,\text{cm}^2\,\text{s}^{-1}$ which indicates that they are free to take their equilibrium position before the cooling makes them stick to the Cu(111) atomic lattice. For S adatoms one also expects a net negative charge of the adsorbed atom, which fits well with the small LDOS close to the atom [14]. In some pictures the protrusion that marks the centre of the atom seems absent. We can, however, if we investigate the hollow by taking a cross section

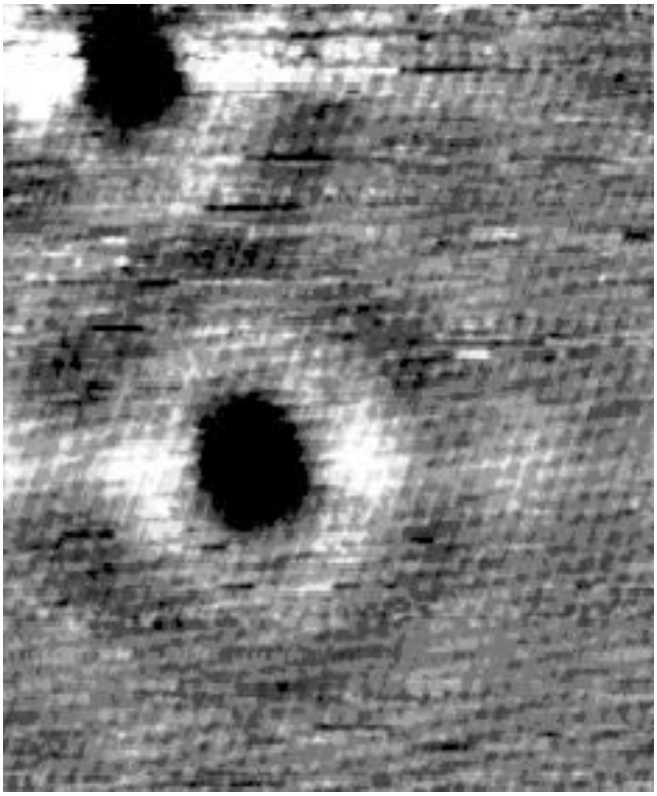

Fig. 4. Adatoms imaged at room temperature. The local density of states oscillations are visible, together with the atomic lattice of the Cu(111) surface ($V = -0,02$ V to tip, $I = 3.793$ nA, $T = 300$ K, image size about: 60 Å × 75 Å)

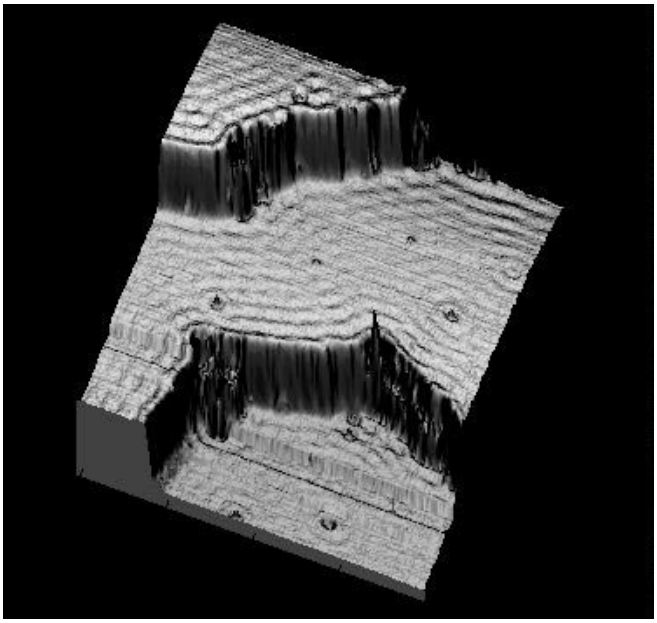

Fig. 5. An image of a double step that shows adatoms that seem to be located at the maxima of the local electron density maxima at the step. ($V = 0.02$ V to tip, $I = 0.131$ nA, $T = 165$ K, image size: 400 Å $\times$ 400 Å)

through it, always find a protrusion in the hollow that we ascribe to the localised electronic charge of the atom. We can give no solid description of why the atoms are imaged differently, but the lateral normalisation of the gray scale, the tip, and the actual positions of the atoms at the surface are factors that might effect the appearance of the atoms. The similarity in appearance of the LDOS oscillations does, however, tell us that all adsorbates have the same phase shift, which means that they are at least chemically indifferent to the surface state.

4 Conclusion

We have imaged adatoms, probably sulphur from the Cu bulk, at a Cu(111) surface. The atoms prefer to be separated by distances given by multiples of half the Fermi wavelength (15 Å). The interaction is long ranged and important for distances up to 80 Å. The long range as well as the spatial period suggests that the interaction between adsorbates is mediated by the Cu(111) surface state.

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