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A Variable Temperature Scanning Tunnelling Microscopy Study of the Electronic Response of the Sn/Si(111) α Surface to Extrinsic Defects

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The α-phase of Sn/Si(111) surface has been studied with variable temperature STM. When temperature is reduced this system undergoes a phase transition from $\sqrt{3} \times \sqrt{3}$ R30° to $2\sqrt{3} \times \sqrt{3}$-like. The low temperature phase is characterised by a one-dimensional electronic perturbation of the $\sqrt{3}$ surface accompanied by a modulation of the density of the substitutional Si defects having the same periodicity, namely a Defect Density Wave. At room temperature, STM shows that Si defects are slightly shifted off the T_4 site. This local break of the C_{3v} symmetry is also characteristic, at larger scale, of the low temperature phase. The two observations must be intimately related.

In the study of low temperature phase transitions, investigation of the local electronic response of a surface to the presence of an extrinsic defect can provide fundamental information [1,2]. Recent discoveries have demonstrated that defects on a purely 2D metallic surface (the 1/3 ML Sn/Ge(111) system) play a pivotal role in driving a symmetry lowering observed when the temperature is reduced [1,2].

There is a system closely related to the one mentioned above, the Sn/Si(111) α surface, whose analogies with Sn/Ge are striking: T_4 Sn adsorption site [3,4], metallic behaviour of the surface [5,6], and similar qualitative response to the presence of defects at very low densities and at low temperatures (2%, 120 K) [7]. In this system, the density of defects can be tuned in a wide range (2% up to 40–45% [7,8], compared to the usual 3–4% in Sn/Ge) thus their influence in mediating or stabilising new surface symmetries at reduced temperature can be more suitably studied.

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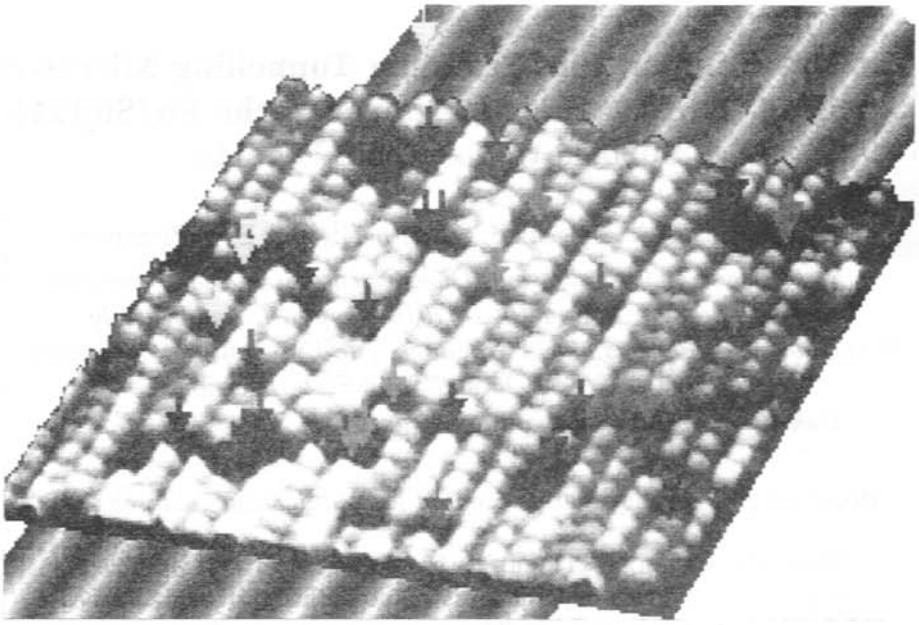

Figure 1. 3D 70 K empty state (+1.5 V, 0.5 nA, 150 × 100 Å^2) STM image of $2\sqrt{3} \times \sqrt{3}$-like low temperature phase of Sn/Si(111). The underlying 1D wave indicates the super-periodic electronic perturbation of the surface which is slightly (7°–8°) off perpendicular to a ⟨112⟩ direction. Arrows with the same colors mark defects placed onto the same periods of the 1D wave.

In this paper we discuss the important discovery of a quite unexpected behaviour of Sn/Si(111) at 70 K [9], in relation with STM observations reported at room temperature (RT) on the same system. This surface provides the first direct experimental evidence of a phase transition accompanied by a one-dimensional ordering of defects. In particular, we will focus on quantitative details and on the symmetry of the local response of the lattice to defects at RT in comparison with similar features that are typical of the surface at 70 K [9].

The experiments were performed using UHV Omicron Variable Temperature STMs (30–300 K), and LEED. The Si(111) 7×7 reconstructed substrates were prepared by direct resistive heating at 1250°C for 1 min after out-gassing for 12 hours at dark glowing temperature (550°C). The α phase of Sn/Si(111) ($\sqrt{3} \times \sqrt{3}$) was obtained by depositing 1/3 of a mono-layer of Sn at room temperature and then annealing it up to 650°C in front of LEED until the $\sqrt{3} \times \sqrt{3}$ pattern was observed.

In Fig.1 it is shown in 3D a typical STM empty state image of the 1/3 ML Sn/Si(111) surface taken at 70 ± 10 K. The average defect density for this surface is 4%. Clearly the surface is locally composed of alternating *high* and *low* $\langle 112 \rangle$ rows, the surface periodicity is doubled along one direction resulting in a new structure with the symmetry $(2\sqrt{3} \times \sqrt{3})$ R30°. Nonetheless, if one looks carefully there is a significant deviation from a perfect $2\sqrt{3} \times \sqrt{3}$ structure. The apparent height of each ad-atom row is clearly modulated with a half period of 7–8 adatoms so that, according to this super-periodicity, it varies periodically from *high* to *low* along each row. Moreover the adatoms are apparently laterally shifted from ideal T_4 position. It has been demonstrated [9] that this superstructure can be obtained by superposition of the $\sqrt{3}$ unperturbed structure plus a purely one-dimensional wave characterised by $2\sqrt{3}$ periodicity with a **K** wavevector which is slightly rotated (7°–8°) from the perpendicular $\langle 112 \rangle$ direction. As a guide to the eye, in Fig.1 this wave has been artificially reproduced in grey under the STM 3D image, the slight misalignment of the maxima and minima of the 1D wave with respect to the $\langle 112 \rangle$ Sn ad-atom rows is clear. Information from LEED experiments at 70 K [10] leads to reckon that the 1D perturbation of the surface can be regarded as purely electronic, and is not accompanied by a significant structural phase transition.

The most important observation in this low temperature phase concerns the surface arrangement of the substitutional Si ad-atoms, namely the "defects". They are clearly identifiable on the surface as the dark spots and, surprisingly, in Fig.1 are preferentially aligned with the 1D wave perturbing the surface. To highlight this occurrence, each period of the 1D corrugated wave underlying the STM image in Fig.1 has been marked by an arrow with a definite colour. The defects in the STM image placed along the same "row" of the underlying 1D wave have been marked by arrows of the same corresponding colour. According to this labelling, the vast majority (75%) of the defects can be marked with a well defined arrow, as it has been quantitatively demonstrated elsewhere [9]. If the same procedure is used with the direction and wavelength of the underlying wave given by the reciprocal lattice vector associated with the pure $2\sqrt{3} \times \sqrt{3}$ structure, $\sim 50\%$ of the defects cannot be unambiguously assigned to a definite colour. Thus we show that there is clearly a periodic modulation of the defect density along the canted (**K**) direction. Melechko *et al.* have recently shown with direct STM measurements a two dimensional ordering of the Ge substitutional defects at low temperatures (110 K) on the 1/3 ML Sn/Ge(111) system [1,2], but what firstly reported in Ref. [9] is the first direct experimental evidence of a one-dimensional defect density wave (DDW).

It should be pointed out that in practice there are in principle six different

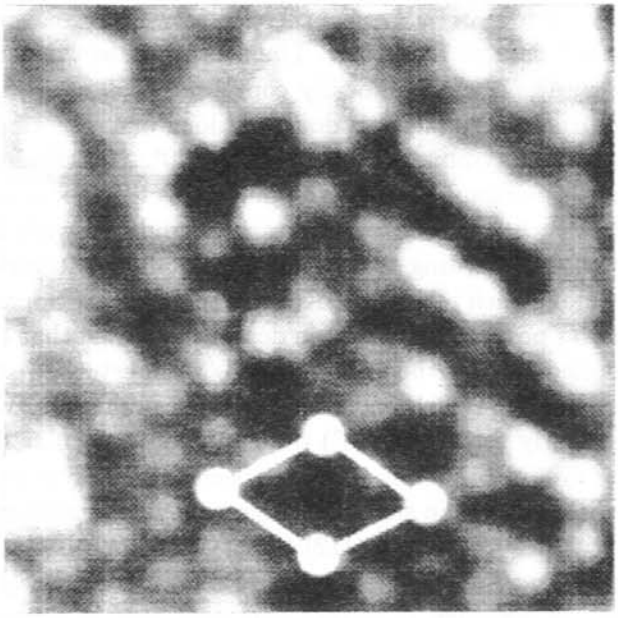

Figure 2. Superposition of two DDWs at 120 K (24% defect density); filled state image (1.5 V, 0.5 nA).

one-dimensional waves possible, two associated with each of the three $\sqrt{3}$ directions. Occasionally, STM images can contain a superposition of 1D waves in at least two directions leading to $2\sqrt{3} \times 2\sqrt{3}$ superstructure. The occurrence of the superposition of multiple waves can be more easily observed at higher defect densities at even significantly higher temperatures. Fig. 2 shows an example of such superposition of two 1D waves. This image has been taken at 120 K on a surface prepared with 24% average defect density. There, the formation of the $2\sqrt{3} \times 2\sqrt{3}$ superstructure is evident and the corresponding unit cell has been marked in the figure. Alignment of defects in this case, as in similar images, takes place obeying to the two 1D waves perturbing the surface, and the preferred occupation site corresponds to the central ad-atom site in the $2\sqrt{3} \times 2\sqrt{3}$ unit cell (see the ad-atom marked with a dark spot in the $2\sqrt{3} \times 2\sqrt{3}$ unit cell of Fig. 2). Noteworthy, as there are four surface atoms per $2\sqrt{3} \times 2\sqrt{3}$ unit cell, at 24% defect density, each defect can be accommodated at the center of a unit cell.

Measurements of the arrangement of defects in a $\sqrt{3} \times \sqrt{3}$ phase at RT (without prior cooling) show a distribution of defects that has been investigated in detail recently [11]. It has been demonstrated that there is indeed still at

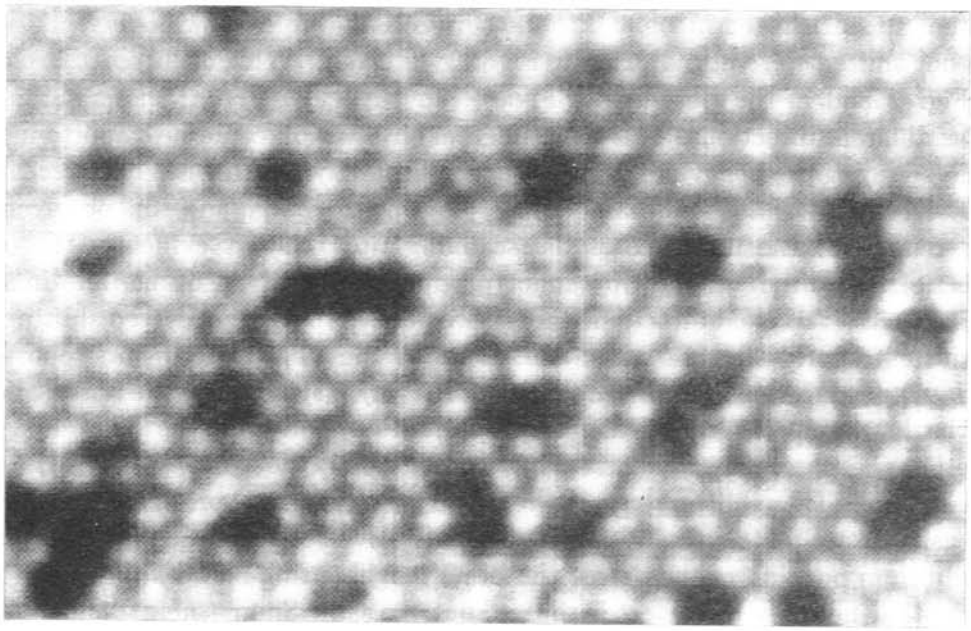

Figure 3. Room temperature empty state STM image (1.2 V, 0.5 nA) of Sn/Si(111). Most defects are clearly shifted from the T_4 site.

room temperature a short-range interaction among defects. This short-range interaction is responsible eventually, at the highest defect density reported for this system, for the local $2\sqrt{3} \times 2\sqrt{3}$ order observed in the so-called "mosaic" phase [8]. Nonetheless the defect arrangement at room temperature does not give rise to any observable long-range DDW. STM filled state images of this system at RT have been reported by several authors [7,8,10]. Here we present an empty state image the same size as the one shown in Fig.1 obtained at 70 K. The choice of an empty state image is deliberate for better comparison with the 70 K data, where the DDW and its accompanying 1D electronic perturbation is only evident in the empty state regime [9]. In consistency with the absence of any one-dimensional defect density modulation, there is no sign of any 1D electronic wave perturbing the $\sqrt{3}$ symmetry of the RT surface. The vast majority of the Sn ad-atoms show the same apparent height, and there is no lateral deviation from their expected T_4 position. Nonetheless, if one looks carefully, the local response of the lattice to Si defects shows remarkable short-range similarities with the low temperature phase. It is already known that substitutional atoms on the 1/3 ML Sn(Pb)/Si(Ge)(111) surfaces are visible in empty state images, as those adatoms which appear dimmer with respect to the others [8]. Most interesting is the fact that, differently from the other similar surfaces, Si defects in the Sn/Si

system appear shifted in general from their ideal T_4 position, while defects that are not shifted were also observed (Fig. 4, left panel). This occurrence is clear in Fig. 3 and in the close-ups of Fig. 4. In particular Fig. 3 shows shifts in three different directions. This experimental observation could be important for understanding the behavior of this surface. Effectively, shifting has been recently observed by other authors mainly along just one direction, and this occurrence was related to the influence of the scanning tip [12], but evidently the one directional scanning of the tip cannot produce, as observed by us, an "image artifact" in a threefold direction. Indeed we believe that the observed shifting is intrinsic property of this surface and, as far as the STM experiments reported to date are concerned, it is a peculiarity of the Sn/Si system like the observation of the low temperature DDW phase. It is not clear from the STM images whether the observed shifting is structural or purely electronic. Anyway, as a consequence of the shifting, among the six Sn ad-atom neighbors of a defect there are usually two preferentially closer. A quantitative determination of the lateral equilibrium position of the defect and of its neighbouring Sn ad-atoms (Fig. 4) shows that not only the defect is shifted, but the same Sn first neighbours closer to the shifted defect are significantly shifted off their T_4 site (approximately 15%) toward the defect. Namely, there is a local pairing of adjacent $\langle 112 \rangle$ rows. Similarly, the ad-atoms in the 70 K superstructure are visibly shifted from ideal T_4 position so that the bright and dark rows are paired, and in average the apparent deviation of Sn-Sn distance from ideal can be estimated as large as 15%. In the low temperature STM data the vertical rippling between adjacent bright and dark rows is 0.2 Å. This value is, within experimental error, identical to the apparent indentation measured between perturbed (first neighbours of a defect) and unperturbed (second neighbours) Sn adatoms at RT. Finally, let us consider the type of symmetry lowering due to the presence of a defect and to its shifting. Evidently, a defect breaks the translational symmetry of the lattice but, provided that the defect stays in the T_4 site, the response of the surface must by identical at the six first neighbours and at least the C_{3v} symmetry is preserved around it. If a defect is shifted, this lower symmetry is also broken. It is a matter of fact that the same type of broken C_{3v} symmetry can be observed locally at RT (around a defect) and on the overall surface at 70 K.

The analogy with what is observed in Sn/Ge(111) [1,2] can help us in deriving a model picture to interpret our data. There, at RT the local break of symmetry around a Ge defect preserves the C_{3v} symmetry (i.e. no shifted defects are observed and the deviation from ideal Sn-Sn distance is less than 5%). Accordingly the defect induced responses of the lattice are nicely described by 3×3 damped density waves, and, due to their coherent superposition, after oc-

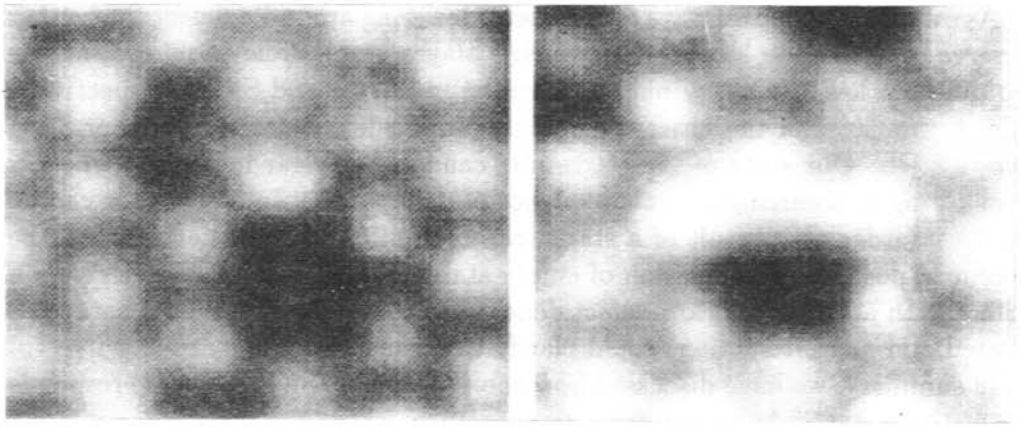

Figure 4. Close-ups of Fig.3 at defect sites. Left: image of a shifted defect close to one in exact T_4 position. Right: detail of the typical local response to a shifted defect.

currence of defect motion below 110 K [2], the overall surface at low temperature shows a similar symmetry lowering with no C_{3v} breaking. Similarly, in this case we can think that:

i) each defect introduces an intrinsic surface damped density wave that, because of shifting, must be preferentially one dimensional;

ii) the effective length of these damped waves increases with decreasing temperature and interaction between defects occurs through these density waves;

iii) eventually, when the average defect spacing equals the effective perturbation length (below a critical temperature, which is likely to be defect density dependent as in Ref. [2]) defects move to accommodate these density waves and, as a consequence of this motion, defect induced density waves become a coherent perturbation at large scale that dictates the low symmetry of the system.

It is worth recalling that in the case of Sn/Si recent theoretical calculations [6,13] indicate that the ground state of the defect-free Sn/Si(111) α surface is the $\sqrt{3} \times \sqrt{3}$ one. So, it is very likely that the observed low symmetry phase is stabilised by the presence of the observed DDW. In other words, shifted defects act as nucleation sites of the observed phase transition, and the local break of symmetry around a shifted defect dictates the type of symmetry observed at large scale after the phase transition has occurred.

As evidenced, the two ways of symmetry lowering around a defect that either preserve or break the local C_{3v} symmetry play a crucial role in nucleating the two different low symmetry phases observed in Sn/Ge and Sn/Si, respectively. Indeed, the cause of the observed shifting of a Si defect deserves further STM investigation. Our state of the art results cannot give clear indication whether this shifting is occurring as a consequence of defect-defect interaction or can be simply regarded as a result of a statistical fluctuation of the defect around the T_4 central position. Observation of empty states images of isolated defects on a surface with a sufficiently low defect density (so that defects can be regarded as isolated and non-interacting) could clarify this issue.

In summary, we have discussed how the 1/3 ML Sn/Si(111) lattice responds to substitutional Si defects at room temperature, where the $\sqrt{3}$ surface symmetry holds, and at 70 K where one dimensional ordering of defects takes place accompanied by a one-dimensional purely electronic perturbation. Our observations lead us to conjecture that the 70 K phase is the result of the coherent superposition of the local responses of the lattice to defects. This coherence and the observation of ordered defects at 70 K imply the occurrence of defect motion when the temperature is reduced from RT.

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