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# Defect-induced localized lattice distortions in Sn/Ge(111)

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The gradual $(\sqrt{3}\times\sqrt{3})$ to $(3\times3)$ phase transition of the Sn/Ge(111) system nucleates at substitutional Ge defects in the Sn layer, as observed by scanning tunneling microscopy (STM). We offer an interpretation of the STM images in terms of frozen defect-induced localized phonon modes, resulting in local lattice distortions with $(3\times3)$ symmetry. Furthermore, we speculate on the nature of the phase transition.

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The Sn/Ge(111)$(\sqrt{3}\times\sqrt{3})R30°$ phase (see Fig. 1) created by depositing approximately 1/3 of a monolayer of Sn on the Ge(111) $c(2\times8)$ surface undergoes a gradual structural phase transition to a $(3\times3)$ phase upon cooling slightly below room temperature. There seems to be consensus about the structure of the low-temperature phase, with one Sn atom per unit cell displaced outwards and two inwards, as determined by low-energy electron diffraction (LEED) and surface x-ray diffraction (SXRD),[1–3] and photoelectron diffraction.[4] This structure is also supported by scanning tunneling microscopy (STM) images.[5–8] Local density approximation (LDA) calculations find that the one Sn up, two down structure is marginally stable compared to a flat $(\sqrt{3}\times\sqrt{3})$ structure (by 5–9 meV/atom).[9,10] The two-component Sn $4d$ core-level[9,11,12] and the two dispersing surface bands[9,13,14] also support this picture. The precise structure of the room-temperature $(\sqrt{3}\times\sqrt{3})$ phase and the nature of the phase transition are still a matter of some controversy. STM[5–7] and LEED/SXRD[1–3] indicate that all Sn atoms are equivalent, i.e., the surface is flat, whereas electronic spectroscopies[9,11–13] find no significant difference between the $(3\times3)$ and $(\sqrt{3}\times\sqrt{3})$ phases, which cannot be readily explained assuming a flat $(\sqrt{3}\times\sqrt{3})$ phase.

STM is unrivaled in that it offers a unique opportunity to study local (defect-induced) perturbations of a surface, revealing instabilities of the system. STM studies of the role of substitutional Ge defects have demonstrated that they play an important role in the transition.[6,7] The Ge defects create local $(3\times3)$ patches, the sizes of which increase as a function of decreasing temperature. Analysis of the STM results furthermore suggests that in the absence of defects, the phase transition may still take place, at a temperature of approximately 70 K.[6] Since STM images to first order are maps of the surface charge density and because filled-state and empty-state images are complementary, these local modulations have implicitly been assumed to be electronic rather than structural in nature and have been interpreted as Friedel oscillations, that in the low-temperature phase evolved into a charge density wave (CDW).[6] Melechko *et al.*[15] have been able to succesfully model the STM images using a ''charge compensation model'' that contrary to the CDW picture emphasizes nearest-neighbor interactions, and they have shown that this model can be mapped onto a Ginzburg-Landau description of the phase transition.

Recently, in a theoretical paper Pérez *et al.* have proposed that a soft phonon mode is responsible for the phase transition.[16] The soft phonon is located at the $\bar{K}$-point of the $(\sqrt{3}\times\sqrt{3})$ surface Brillouin zone (SBZ) (see Fig. 2), and corresponds to one adatom per $(3\times3)$ unit cell being displaced in one direction, and two in the opposite direction. When the mode is frozen, this corresponds to the $(3\times3)$ phase. In this paper, we demonstrate that the STM images showing local $(3\times3)$ patches developing around substitutional Ge defects can be explained within Pérez and coworkers' simple nearest-neighbor force model as frozen localized phonon modes.

In order to proceed, let us briefly recall what a soft phonon is. Assuming a simple harmonic potential, let the displacement $\mathbf{u_k}(\mathbf{R})$ of an atom from its equilibrium position at lattice site $\mathbf{R}$ be given by

$$\mathbf{u_k}(\mathbf{R})=\mathbf{u}_0\exp\{i[\mathbf{k}\cdot\mathbf{R}-\omega(\mathbf{k})t]\}, \tag{1}$$

where $\omega(\mathbf{k})$ is the phonon dispersion relation. A soft phonon corresponds to a dip in the phonon dispersion, i.e., at a given $\mathbf{k}$-vector the energy of the corresponding lattice vibration is

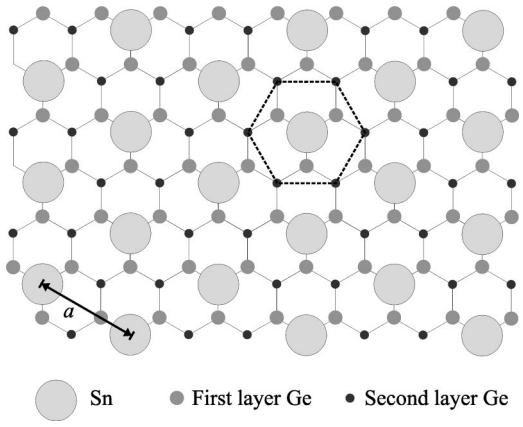


FIG. 1. Ball model of the $(\sqrt{3}\times\sqrt{3})R30°$ phase. The $(\sqrt{3}\times\sqrt{3})$ unit cell is indicated.

 

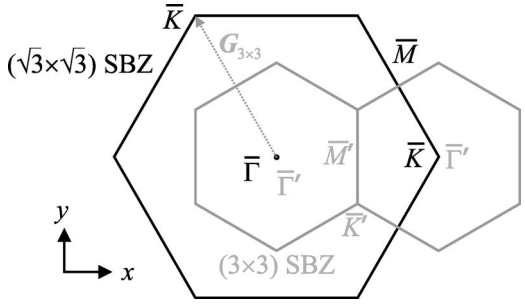


FIG. 2. The surface Brillouin zones of the $(\sqrt{3}\times\sqrt{3})$ (black) and $(3\times3)$ (gray) phases. Notice that the $(3\times3)$ reciprocal lattice vector corresponds to the $\bar{K}$-point of the $(\sqrt{3}\times\sqrt{3})$ SBZ. Also notice that the rotational symmetry is threefold, not sixfold.

very low. If $\omega(\mathbf{k})$ becomes zero, it follows from Eq. (1) that the associated displacement becomes static—the soft phonon is said to be frozen, resulting in a static lattice distortion commensurate with the **k**-vector of the soft phonon. $\omega(\mathbf{k})$ may also be imaginary, indicating that the crystal is unstable towards disturbances with the given wave vector.

With this in mind, we shall find that the soft phonon picture of Pérez *et al.*[16] can be reconciled with the experimental findings. First, Fig. 2 illustrates that the $\bar{K}$-point of the $(\sqrt{3}\times\sqrt{3})$ SBZ corresponds to a $(3\times3)$ reciprocal lattice vector. Thus, at low temperature, a static $(3\times3)$ reconstruction of the surface can be viewed as the result of the freezing of a soft phonon located at the $\bar{K}$-point. This is exactly where Pérez and co-workers find a soft, transverse phonon that is frozen at 0 K [since the LDA ground state is the $(3\times3)$ structure] with one Sn up, two Sn down. As the temperature rises, the phonon dispersion $\omega(\mathbf{k})$ is "renormalized"[16] and the phonon energy at the $\bar{K}$-point is no longer zero, but low compared with other modes. Effectively this means that the Sn atoms (in fact entire tetrahedrons consisting of the Sn atom and the three underlying Ge substrate atoms[16]) easily vibrate perpendicularly to the surface, and the motion is correlated resulting in local $(3\times3)$ symmetry because the phonon mode with the designated **k**-vector is the most populated. This explains why spectroscopies (core-level and valence band) do not see any major difference between the two phases: they operate at a very fast time scale and snapshots of the surface even at room temperature (RT) will have $(3\times3)$ structure because of the soft phonon. STM, on the other hand, sees the average picture: a flat $(\sqrt{3}\times\sqrt{3})$ structure.

It is well known that the introduction of an impurity atom in an otherwise perfect lattice leads to the existence of a localized phonon, i.e., a lattice vibration that is spatially localized around the impurity atom.[17,18] The remaining phonon spectrum is virtually unchanged. In a simple linear chain model with a light impurity, the real part of the wave vector of the localized phonon is found at the zone boundary, and the phonon energy is slightly higher than the top of the acoustic branch.[17,18] The larger the energy difference, the more localized is the impurity phonon mode. Also in the two-dimensional case localized phonons associated with impurity atoms may show up at the zone boundary. To illustrate

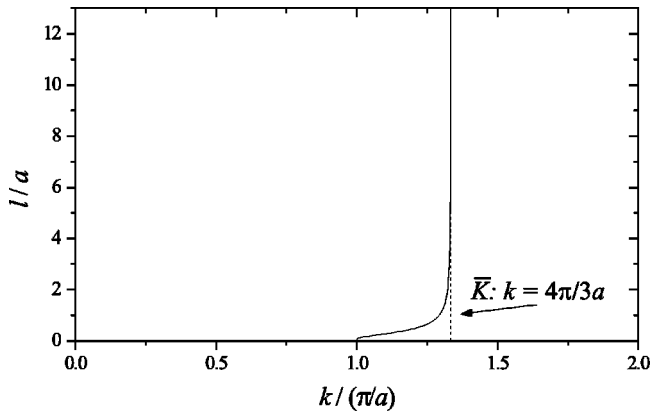


FIG. 3. The decay length, $l$, for a localized phonon, plotted along the $\bar{\Gamma}$-$\bar{K}$ line of the $\sqrt{3}$ SBZ.

this in the present case of Sn/Ge(111), we adopt the simple force constant model presented by Pérez and co-workers. Following Ref. 16, the dispersion of the transverse vertical phonon is given by

$$M\omega^2=\alpha+6\beta-\beta\sum_{j=1}^{6}\cos(i\mathbf{k}\cdot\mathbf{d}_j). \tag{2}$$

Here, the vectors $\mathbf{d}_j, j=1,\ldots,6$, are the six first nearest-neighbor vectors in the two-dimensional hexagonal lattice, $\alpha$ is the spring constant of the spring holding the adatoms to the surface, and $\beta$ is the spring constant of the spring connecting to the nearest neighbors. From their LDA calculations, Pérez *et al.*[16] find $3\beta/\alpha=-1/3$. The negative $\beta$ value corresponds to a repulsive interaction along the surface normal between nearest neighbors. If this dispersion relation is plotted along the $\bar{\Gamma}$-$\bar{K}$ line of the $\sqrt{3}$ SBZ, the result is a soft phonon exactly at the $\bar{K}$-point, as shown in Fig. 3 of Ref. 16 (notice that $\bar{K}'$ of Ref. 16 corresponds to our $\bar{K}$).

Now, in a simple picture of a localized phonon the amplitude should decay exponentially with distance from the impurity, i.e., in our case the displacement should be of the form

$$z_j=u\exp(i[\mathbf{k}\cdot\mathbf{R}_j-\omega t])\exp(-|\mathbf{R}_j-\mathbf{R}_0|/l), \tag{3}$$

where $\mathbf{R}_0$ is the location of the defect. However, with this choice the dispersion relation is not easily derived analytically. Instead, we examine the existence of a phonon that decays in the direction of propagation by means of a complex **k**-vector $\mathbf{k}_R+i\mathbf{k}_I$, where $\mathbf{k}_R\|\mathbf{k}_I$. The dispersion relation is then given by

$$M\omega^2=\alpha+6\beta-\beta\sum_{j=1}^{6}\cos(\mathbf{k}_R\cdot\mathbf{d}_j+i\mathbf{k}_I\cdot\mathbf{d}_j). \tag{4}$$

As it turns out, the condition $\omega^2\in\Re$ and requiring $\mathbf{k}_R$ to be on the $\bar{\Gamma}$-$\bar{K}$ line of the $(\sqrt{3}\times\sqrt{3})$ SBZ leads to

$$l=\frac{a}{2}\left\{\ln\left[\frac{-1}{2\cos k_{Rx}a/2}+\sqrt{\frac{1}{4\cos^2 k_{Rx}a/2}-1}\right]\right\}^{-1}, \tag{5}$$

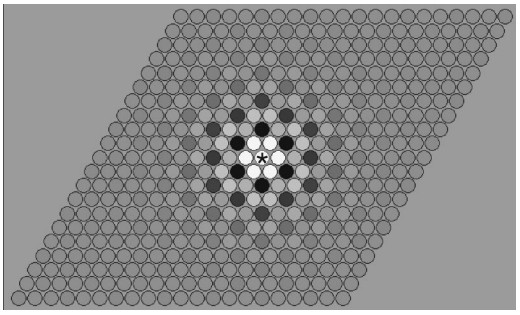

FIG. 4. Solution with periodic boundary conditions and $\alpha_{\text{impurity}}=0.85\alpha$. The height scale is black (low) to white (high), and the defect is marked with an asterisk.

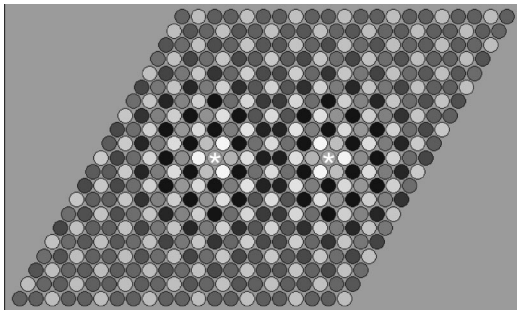

FIG. 5. Solution with periodic boundary conditions and $\alpha_{\text{impurity}}=0.89\alpha$ for the two impurities, resulting in a larger decay length than in Fig. 4. The height scale is black (low) to white (high), and the defects are marked with asterisks.

where $l=1/k_I$, and $a$ is the Sn–Sn distance in the $(\sqrt{3}\times\sqrt{3})$ phase. Figure 3 shows a plot of $l$ as a function of $k_{Rx}$. Evidently, for most decay lengths, a localized phonon can only exist for $k_R=4\pi/3a$, which is exactly the $\bar{K}$-point. With parameters corresponding to a soft $(3\times3)$ phonon that is not yet frozen, this localized phonon splits off the bottom of the phonon band at the $\bar{K}$-point, becoming the mode with the lowest energy in this part of $k$-space. No bulk modes with similar energy exist at the $\bar{K}$-point. This is indeed very suggestive of the existence of a phonon mode spatially localized around substitutional defects, with the correct $(3\times3)$ symmetry. Solving the linearly coupled force equations leading to Eq. (2), requiring harmonic motion of the atoms and assuming a lower mass as well as a different spring constant $\alpha$ of the impurity atom, confirms this. An example is shown in Fig. 4. The fact that the localized phonon has lower energy than the rest of the phonon band indicates that it may freeze and become a static, localized lattice distortion at higher temperatures than the surface as a whole. Such a local distortion has also been suggested in the case of a vacancy on Si(111).[19]

Thus, it seems clear how to interpret the STM images that reveal that substitutional Ge defects act as nucleation centers for local $(3\times3)$ patches.[6,7] The ''amplitude'' of the $(3\times3)$ patch around a given defect decays exponentially with distance from the defect, and the decay length increases with decreasing temperature.[6,7] With the above comments in mind, *the patches are identified as localized phonon modes that are frozen and have become static defect-induced lattice distortions, allowing the STM to detect them.* As the phonon band is ''renormalized'' as a function of temperature, the energy difference between the localized phonon and the rest of the phonon band varies with temperature, and consequently so does the decay length.

The simple force constant model does not predict the ''phase'' of the localized lattice distortion, i.e., it does not predict whether the $(3\times3)$ phase has one Sn up, two down or vice versa. From experiments[2–4] it is known that the ground state in the presence of defects is one Sn up, two down, and LDA calculations[9,10] for the clean surface also find this to be the ground state. For the case of localized lattice distortions, STM images are best modeled if substitutional Ge atoms create two Sn up, one down patches.[6] This might seem to contradict that the fully developed $(3\times3)$ phase has one Sn up, two down. However, since the $(3\times3)$ phase has three Sn atoms per unit cell, there are three different positions that a substitutional Ge defect can occupy, and if two Ge atoms are on different subsites, the resulting pattern is in fact one Sn up, two down, as illustrated in Fig. 5 and previously discussed in Refs. 6, 7, and 15. The alternating height pattern of the six nearest neighbors around a defect that is clearly seen in Fig. 5 is also found in the experimental STM images.

The defects interact with each other via these localized phonon modes, giving a hint to the forces responsible for the observed defect-density wave at 105 K:[7] if the defects are constrained to be on two out of the three positions in the $(3\times3)$ unit cell, the resulting pattern corresponds to the ground state with one Sn up, two down.

A detailed description of the phase transition in terms of the interacting defects has been given by Melechko *et al.*,[15] using what is called a charge compensation model. The basic feature of the model is that the charge of a Sn atom depends on the charge of its six nearest neighbors, with a negative coupling: the more positive charge on the neighbors, the more negative charge on the atom in question and vice versa. This obviously corresponds to a repulsive nearest-neighbor interaction as assumed in the simple force constant model discussed above. As also mentioned in Ref. 15, in the charge compensation model one may interpret ''charge'' as ''vertical position,'' and hence the description of the phase transition given by Melechko *et al.* is also applicable to the localized phonon picture. The main difference between the charge compensation model and the localized phonon model is the underlying mechanism, although the resulting phenomena are similar.

It would seem that we have a consistent interpretation of the available data using the soft phonon picture. Recent unpublished LDA calculations[20] do not seem to contradict this view. However, a few problems remain. Although structural techniques such as SXRD find the average position of the RT phase to correspond to a flat $(\sqrt{3}\times\sqrt{3})$ phase, one also gets information about the vibrational amplitudes. On the basis of their SXRD data, Bunk *et al.*[3] could rule out the large RT vibrations predicted by the soft phonon model. Their model

did not consider the effects of substitutional Ge defects and thus assumed a homogeneous $(\sqrt{3}\times\sqrt{3})$ phase. From new unpublished SXRD data with access to a larger part of the crystal truncation rods, Avila and co-workers[21] conclude that a structural model incorporating large vibrations gives the best fit to their data. Also, Kidd and co-workers[14] have observed three surface bands in the $(\sqrt{3}\times\sqrt{3})$ phase.

Finally, we briefly discuss the soft phonon idea in relation to the characterization of the phase transition. Soft modes are generally associated with displacive phase transitions,[22] and recent He scattering data are interpreted to be in favor of an order-disorder transition.[23] However, it is important to realize that the distinction between the two types is not necessarily clear,[22] and in large temperature regimes a displacive phase transition may give rise to order-disorder-like dynamics.[22] An example of this was found in a similar phase transition controversy over the $c(2\times2)$ reconstruction of W(001).[24] It seems clear that an important experiment to do is measuring the surface phonons of Sn/Ge(111) as a function of temperature to verify or disprove the existence of a soft phonon. Notwithstanding, for defects to create local disturbances with a symmetry corresponding to the low-temperature phase at temperatures above the critical temperature of the pure system is a known phenomenon in systems with a ''displacive'' phase transition.[22,25] One may speculate that the inevitable presence of defects, stabilizing local patches of $(3\times3)$ phase, make the transition look more order-disorder-like in the case of spectroscopic measurements as compared to an imaginary pure system.

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