Phonon Softening, Chaotic Motion, and Order-Disorder Transition in Sn/Ge(111)

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The phonon dynamics of the Sn/Ge(111) interface is studied using high-resolution helium atom scattering and first-principles calculations. At room temperature we observe a phonon softening at the $\overline{K}$ point in the $(\sqrt{3} \times \sqrt{3})R30°$ phase, associated with the stabilization of a (3×3) phase at low temperature. That phonon band is split into three branches in the (3×3) phase. We analyze the character of these phonons and find out that the low- and room-temperature modes are connected via a chaotic motion of the Sn atoms. The system is shown to present an order-disorder transition.

Low dimensional materials exhibit a wide range of phenomena that cannot be observed in three dimensional systems. The different reconstructions that a crystalline surface may exhibit, and the phase transitions that relate them, are a prominent example [1,2]. These topics are widely investigated because of their implications in many different fields of solid state physics. The α phase of Sn on Ge(111) undergoes a temperature-induced phase transition [3] that has received attention in recent years. The room-temperature (RT) phase has a $(\sqrt{3} \times \sqrt{3})R30°$ structure (in the following $\sqrt{3}$) that becomes (3×3) at low temperature (LT). The (3×3) phase is well understood: out of the three Sn adatoms (on T_4 sites) per (3×3) unit cell, one is displaced outwards and the other two inwards, with a total vertical distortion of ~ 0.3 Å [4–6]. However, in spite of the efforts made, the nature of the RT $\sqrt{3}$ phase, the driving force underlying the phase transition and its character—order-disorder vs displacive—are still open questions [3–12].

Different models have been put forward to explain the structural and electronic properties of the phase transition [3–12]. In the dynamical fluctuations model [4], Sn adatoms fluctuate at RT between "up" and "down" positions, with a correlated motion that keeps locally the (3×3) structure, explaining the apparent contradiction between electronic and structural evidences [3,4,8]. STM studies have shown that Ge defects have a significant influence on the phase transition [9,10], stabilizing (3×3)-ordered regions around them. Recent theoretical work has proposed that a soft phonon may be at the heart of the phase transition [13]. This surface phonon would be associated with the dynamical fluctuations of the Sn atoms, and it may also be responsible for the (3×3) ordering around defects [14]. Therefore, measuring the surface phonons and understanding their behavior seems to be of crucial importance to clarify the driving force behind this controversial phase transition. In this Letter, we report a combined experimental and theoretical study on the phonon dynamics of both the $\sqrt{3}$ and (3×3)

structures. The experiments show that the $\sqrt{3}$ phase exhibits a soft surface phonon at the zone edge. This branch gives rise to three bands in the LT structure, associated with the vertical motion of the Sn adatoms. A molecular dynamics (MD) analysis was used to understand the $\sqrt{3}$ phase and its phonon spectrum. We find that at RT Sn adatoms occupy up positions in a chaotic sequence and that the phase transition is of the order-disorder type.

The experiments were performed in a high-resolution helium atom scattering (HAS) spectrometer previously described [15]. For details on the sample preparation we refer the reader to previous Letters [4,5]. The (3×3) phase was prepared by monitoring the intensity of a $\sqrt{3}$ He-diffraction peak along the Sn deposition at ~ 500 K, which exhibits a maximum at a coverage of $1/3$ ML (monolayer). Because of the low deposition rate used the error in the coverage is ± 0.01 ML. The quality of the reconstruction was judged from the elastic HAS spectra recorded along the $[11\overline{2}]$ direction ($\overline{\Gamma K}$), which exhibited sharp diffraction peaks indicating the formation of a well-ordered and low-corrugated surface structure [16]. In the time-of-flight (TOF) spectra we observed, in addition to several phonon-inelastic signatures, a significant quasielastic peak indicating the presence of defects at the surface, in agreement with previous STM results [9].

Figure 1 shows TOF spectra recorded along the $\overline{\Gamma K}$ direction as a function of temperature, but for the same scattering conditions. The temperature range shown spans the $\sqrt{3} \leftrightarrow (3 \times 3)$ phase transition. The largest peak corresponds to the diffuse elastic peak. Right and left of it, we find sharp inelastic features related to the scattering of He atoms by the different phonon modes discussed below. Collecting such data for different scattering conditions and converting them into energy loss spectra permits one to draw the experimental points depicted in Fig. 2. An analysis of these data reveals several phonon branches for the (3×3) phase. From a comparison with the slope of the bulk phonon dispersion curves, we identify the mode at lower energies with $Q = 0.0–0.2$ Å^{-1} as the Rayleigh
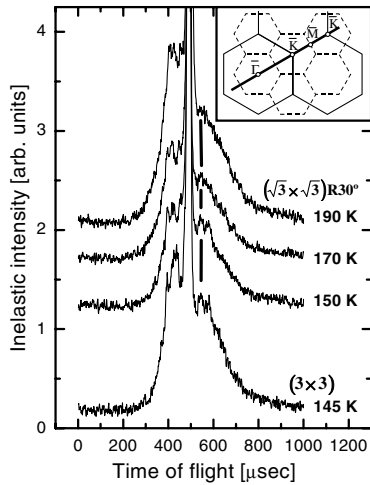
FIG. 1. TOF spectra recorded along $\overline{\Gamma K}$ for different surface temperatures. Diffraction shows a well-ordered (3×3) structure at 145 K, and a $\sqrt{3}$ one at 190 K. Tick marks follow a surface phonon peak related to the (3×3) surface periodicity. The intensity of this peak decreases strongly when crossing the phase transition. Every spectrum has been integrated over 10 h. Inset: surface Brillouin zones of the $\sqrt{3}$ (solid lines) and (3×3) (dashed lines) phases, and $\overline{\Gamma K}$ direction (thick solid lines).

wave. A dashed line is shown as a guide to the view for the Rayleigh wave, folded with (3×3) periodicity in Fig. 2 (left panel). Besides the Rayleigh wave, a branch with low dispersion is detected around 6.5 meV, and two additional modes appear at ~4 and 3 meV [17]. The points found in the Q range 0.4–0.5 Å^{-1} at ~2 meV are due to (3×3) folding of the Rayleigh wave.

In order to understand these results we have performed plane-wave (PW) generalized gradient approximation in the density functional theory calculations [13,19] of the (3×3) $\overline{\Gamma}$-point phonon frequencies [20] associated with the vertical (z) displacements of the Sn atoms *with respect to their positions in the ground state of the (3×3) reconstruction*. An effective way of calculating these three phonon frequencies is to use a modal analysis for the atomic motions: we decompose the three vibrations $\mathbf{z} \equiv (z_1, z_2, z_3)$, associated with the displacement of the topmost Sn atom (z_1) and the lower Sn atoms (z_2, z_3), into

a linear combination of the three normal modes $\mathbf{k}_1 \equiv 1/\sqrt{3}(111)$, $\mathbf{k}_2 \equiv 1/\sqrt{6}(2\overline{1}\overline{1})$, and $\mathbf{k}_3 \equiv 1/\sqrt{2}(01\overline{1})$: $\mathbf{z} = \alpha\mathbf{k}_1 + \beta\mathbf{k}_2 + \gamma\mathbf{k}_3$. Only the $(01\overline{1})$ mode represents a well-defined vibration of the (3×3) reconstruction: the other two vibrations are mixed although we have found this mixing small. Using these modal displacements, we calculate the potential energy of the three modes around the (3×3) ground state geometry: this yields 5.4, 4.0, and 3.7 meV [21]. The lowest energy corresponds to the $(01\overline{1})$ vibration, while the highest one is associated approximately with the (111) mode. We have also obtained these frequencies by fitting an up to second-nearest-neighbor coupling model to the experimental phonon frequencies. This model presents three bands associated with the z displacements of the three Sn atoms and yields the following frequencies at the $\overline{\Gamma}$ point: 6.8, 4.0, and 2.8 meV. The result of the fit is shown as solid lines in Fig. 2 (left panel) [21].

Figure 2 (right panel) shows the experimental points obtained at RT for the $\sqrt{3}$ phase. Significant changes take place upon increasing the temperature. First, the folding induced by the (3×3) long range periodicity is lost, as shown in detail in the T-dependent spectra of Fig. 1. Two phonon branches can be distinguished at RT. Following the analysis of the (3×3) phase, we identify the mode with lower energies close to the $\overline{\Gamma}$ point as the Rayleigh mode (dashed line). The other mode corresponds to a transversal surface resonance. Note the decrease of the phonon frequency of the surface resonance, with a minimum at the $\overline{K}$ point of the $\sqrt{3}$ surface Brillouin zone (the critical wave vector is $Q = 0.60 \pm 0.02$ Å^{-1}). This is precisely the wave vector where the soft phonon associated to the $\sqrt{3} \leftrightarrow (3 \times 3)$ phase transition was predicted [13]. The frequency of the soft phonon does not go to zero at $\overline{K}$: this "renormalization" of the soft phonon frequency is associated with the underlying (3×3) vibrations (see below).

The theoretical analysis of the $\sqrt{3}$ phonon spectrum is a challenging task since, due to the presence of the soft phonon, a complex atomic motion can be expected, and long simulations are required. Performing these simulations with a PW-DFT approach would be too computationally demanding. Therefore, we have used an efficient local-orbital MD-DFT technique [22], which has been
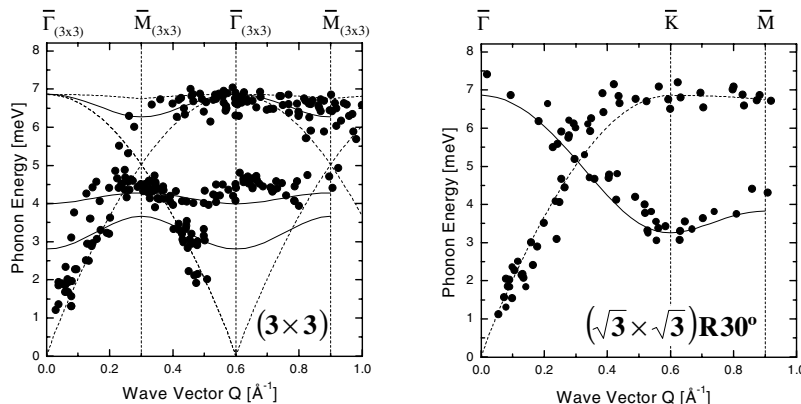

FIG. 2. Surface phonon experimental points for the (3×3) [$T = 145$ K (left panel)] and the $\sqrt{3}$ [$T = 300$ K (right panel)] phases. Rayleigh waves are indicated in both cases by dashed lines. Solid lines correspond to the calculated surface bands (see text).

successfully applied in previous studies of this system [23]. In our MD simulations we start with the (3×3) geometry [6] and calculate the atomic motion of the system for initial velocities obtained from a Maxwellian distribution associated with a given temperature. Figure 3 shows the z displacements of the three Sn atoms in the unit cell as a function of time, for $T = 350$ K. This simulation shows how the $\sqrt{3}$ symmetry appears: initially the system vibrates around the (3×3) structure. However, after 3 ps the Sn atom located in the up position (blue line) exchanges heights with one of the Sn atoms in the down position (red). This process is repeated ~ 40 times during the 54 ps of the MD simulation. Thus a technique, such as STM, that operates in times much longer than the time scale of these dynamical fluctuations, sees in average a $\sqrt{3}$ surface.

We can analyze these fluctuations using displacement patterns $\mathbf{k}_1'$, $\mathbf{k}_2'$, $\mathbf{k}_3'$, $\mathbf{z}' = \alpha \mathbf{k}_1' + \beta \mathbf{k}_2' + \gamma \mathbf{k}_3'$, analogous to the ones described in the (3×3) case, but with (z_1', z_2', z_3') displacements referred to an ideal, flat $\sqrt{3}$ surface. The first normal mode $(\mathbf{k}_1')$ is associated with the $\overline{\Gamma}$ point of the $\sqrt{3}$ Brillouin zone, while the other two modes are associated with two $\overline{K}$ points, where the soft mode develops. The $\overline{\Gamma}$ vibration, namely, $\alpha(t) = 1/\sqrt{3}[z_1'(t) + z_2'(t) + z_3'(t)]$, shows a very regular pattern (not shown) in its time evolution, similar to a weakly coupled harmonic oscillator. The other two components, $\beta(t) = 1/\sqrt{6}[2z_1'(t) - z_2'(t) - z_3'(t)]$ and $\gamma(t) = 1/\sqrt{2}[z_2'(t) - z_3'(t)]$, present a rather irregular pattern showing that the two modes are strongly *anharmonically* mixed. Figure 4 shows $\gamma(t)$ vs $\beta(t)$, for three temperatures, $T = 350$, 170, and 50 K. Our simulation for $T = 350$ K shows how, at high T, the system evolves following a chaotic trajectory that jumps among the three equivalent (3×3) ground state geometries (black dots in Fig. 4). Notice that Sn atoms do not oscillate around the ideal $\sqrt{3}$ structure [coordinates $(\beta = 0, \gamma = 0)$ in Fig. 4]. When the temperature is lowered the system becomes more and more localized around

one particular (3×3) reconstruction. At $T = 170$ K the system needs around 20 ps in order to jump out of the initial (3×3) configuration, while at $T = 50$ K the surface already presents the (3×3) reconstruction.

The chaotic motion shown in Fig. 4 (350 K) suggests how to obtain the phonon frequencies for the $\sqrt{3}$ phase. The $\overline{\Gamma}$ frequency should be close to the one obtained for the (111) mode of the (3×3) reconstruction. The $\overline{K}$ frequency should be an average of the two frequencies, 4.0 and 2.8 meV, associated with the $(2\overline{1}\overline{1})$ and $(01\overline{1})$ modes. The phonon dispersion curve for the $\sqrt{3}$ phase obtained with this information [13] is in good agreement with the HAS measurements, as shown in Fig. 2. Thus, we see the microscopic origin of the soft-mode frequency renormalization: the soft phonon at the $\overline{K}$ point provides the physical mechanism leading to the (3×3) reconstruction, which is the stable structure at LT. At RT, however, the system displays an atomic motion where different (3×3) configurations are visited in a chaotic way (see Fig. 4, 350 K), with Sn atoms basically oscillating around (3×3) atomic positions. Thus, the $\sqrt{3}$ phonon frequency at this $\overline{K}$ point is derived from the $(2\overline{1}\overline{1})$ and $(01\overline{1})$ (3×3) vibrations. These vibrations, on the other hand, present low frequencies because they are reminiscent of the soft mode at the $\overline{K}$ point.

We have found that a soft phonon explains the instability of the ideal, flat $\sqrt{3}$ structure with respect to the (3×3) phase. Although soft phonons are usually associated with displacive phase transitions, our results indicate that at RT the surface is better described as a mixture of configurations. This is typical of order-disorder transitions, where atoms reside in one of several displaced sites. As shown in Fig. 4 (350 K), the system is most of the time localized around a (3×3) configuration, jumping between different alternatives. In a displacive phase transition, the system would evolve in a different way, residing most of the time around the origin of Fig. 4, namely, around the ideal $\sqrt{3}$ geometry. Thus, the actual $\sqrt{3}$ phase
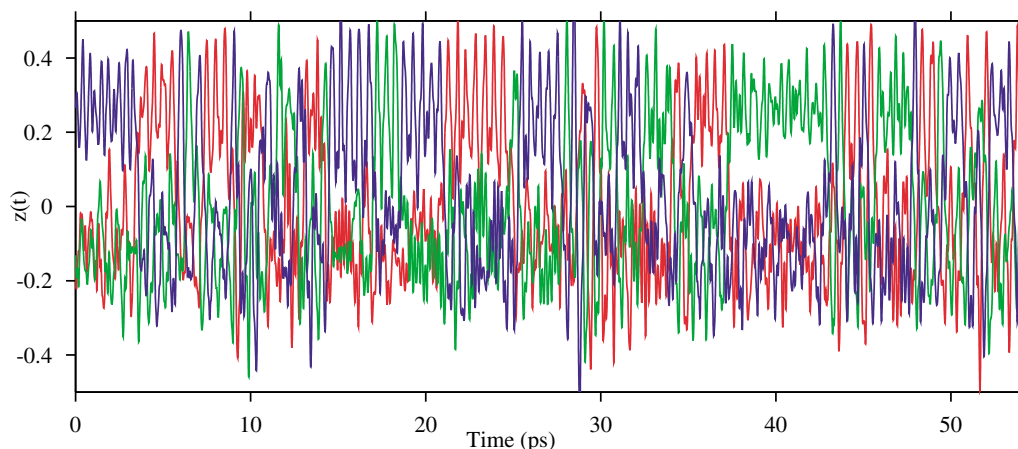

FIG. 3 (color).　MD-simulation time evolution of the z coordinate of the three Sn atoms (blue, red, and green lines) in the (3×3) unit cell at 350 K. Atoms exchange heights ~ 40 times during the simulation.
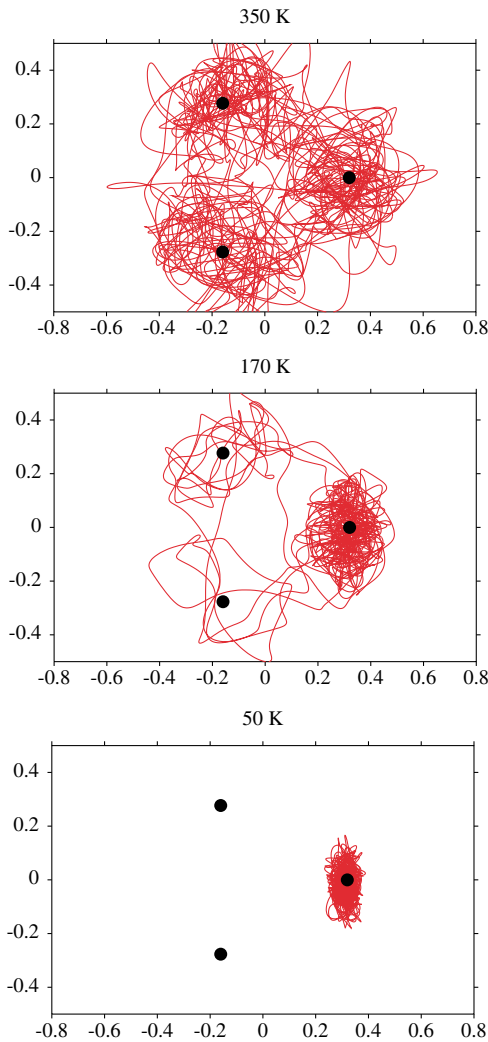
FIG. 4 (color). $\gamma(t)$ vs $\beta(t)$ for temperatures, $T = 350\,170\,50$ K. The black dots indicate the equivalent (3×3) ground states, $\mathbf{z}' = (0.26, -0.13, -0.13)$, $(-0.13, 0.26, -0.13)$, and $(-0.13, -0.13, 0.26)$ (in Å) [6] which, defined in (β, γ) coordinates correspond to $0.32(1,0)$, $0.32(-1/2, \sqrt{3}/2)$, and $0.32(-1/2, -\sqrt{3}/2)$ (also Å). The system starts at $0.32(1,0)$ and evolves during ~ 50 ps.

is described for a broad temperature range as a mixture of configurations sequentially occupied on a local scale, in agreement also with other findings [24]. This connection between soft phonons, chaotic motion, and phase transitions might also help to elucidate other surface systems.

In conclusion, using high-resolution HAS we have measured the surface phonons of both the (3×3) and the $\sqrt{3}$-Sn/Ge(111) phases. The (3×3) reconstruction shows a phonon structure in agreement with PW-DFT calculations. We have detected a soft phonon in the $\sqrt{3}$ phase related to the (3×3) periodicity. Our theoretical analysis shows how the system develops at high T a chaotic motion, jumping between configurations associated with equivalent (3×3) geometries. Using this dynamical process, we have also calculated the phonon

frequencies of the $\sqrt{3}$ phase and have found good agreement with the HAS measurements. Our results indicate that at RT the surface is better described as a mixture of configurations typical of an order-disorder transition.

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