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 has been studied using high-resolution helium atom scattering and first-principles calculations. At room temperature we observe a phonon softening at the $\overline{\mathrm{K}}$-point in the $(\sqrt{3}\times\sqrt{3})R30^\circ$ 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.

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INTRODUCTION

The α phase of Sn on Ge(111) undergoes a temperature-induced phase transition [1] that has received much attention in recent years. The room-temperature (RT) phase has a $(\sqrt{3}\times\sqrt{3})R30^\circ$ 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[2, 3]. 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 [1, 3, 4]. Different models have been put forward to explain the structural and electronic properties of the phase transition [1, 3, 4]. In the dynamical fluctuations model [2], 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 the electronic and structural evidence [1]. Recent theoretical work has proposed that a soft phonon may be at the heart of the phase transition [5]. 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 [4]. 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.

Here, we report a combined experimental and theoretical study on the phonon dynamics of both the $\sqrt{3}$ and (3×3) structures [6]. 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.

RESULTS

The experiments were performed using a high-resolution helium atom scattering (HAS) spectrometer. The (3×3) phase was prepared by monitoring the intensity of a $\sqrt{3}$ He-diffraction peak along the Sn deposition at ~ 500 K, that exhibits a maximum at a coverage of 1/3 ML. Due to the low deposition rate used the error in the coverage is ±0.01 ML.

Experimental phonon dispersion curves of both the LT and the RT structures are shown in Fig. 1. At LT we see, besides the Rayleigh wave, a branch with low dispersion around 6.5 meV, and two additional modes at ~ 4 meV and 3 meV. 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. Significant changes take place upon increasing the temperature. First, the folding induced by the (3×3) long range periodicity is lost. 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 $\overline{\mathrm{K}}$ point of the $\sqrt{3}$ SBZ (the critical wave vector is $\mathrm{Q} = 0.60 \pm 0.02$ Å^{-1}). This is precisely the wave vector where the soft phonon associated to the $\sqrt{3} \leftrightarrow (3\times3)$ phase transition was predicted [5]. The frequency of the soft phonon does not go to zero at $\overline{\mathrm{K}}$: this 'renormalization' of the soft phonon frequency is associated with the underlying (3×3) vibrations.

In order to understand these results we have performed plane-wave (PW) GGA-DFT calculations [5] of the (3×3) $\overline{\Gamma}$-point phonon frequencies associated with the vertical (z) displacements of the Sn atoms. Using these modal

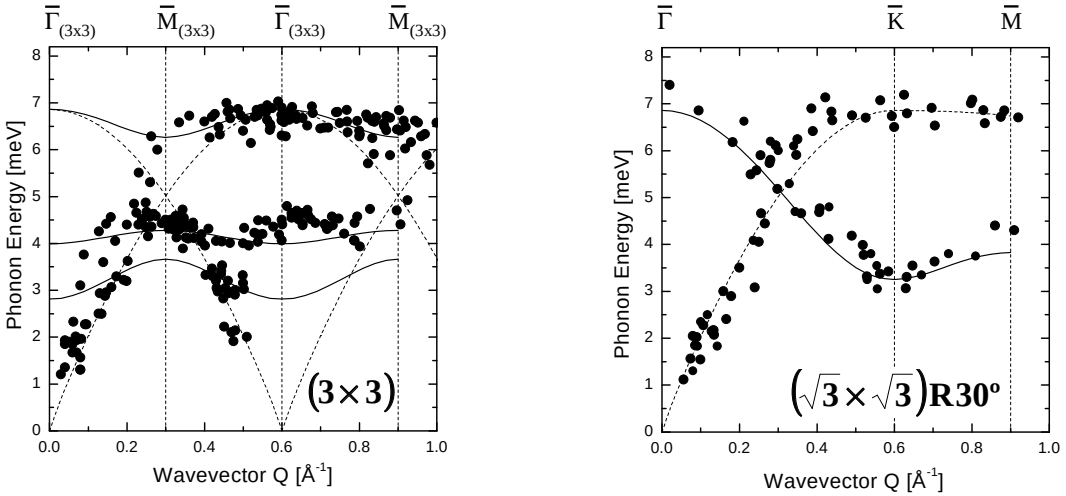

FIG. 1: Surface phonon experimental points for the (3×3) (T= 145 K, left) and the $\sqrt{3}$ (T= 300 K, right) phases. Rayleigh waves are indicated in both cases by dashed lines. Solid lines correspond to the calculated surface bands.

displacements, we calculate the potential energy of the three modes around the (3×3) ground state geometry: this yields 5.4 meV, 4.0 meV and 3.7 meV. 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. Therefore, we have used an efficient local-orbital MD-DFT technique [7], which has been successfully applied in previous studies of this system [8]. In our MD simulations we start with the (3×3) geometry [3] and calculate the atomic motion of the system for initial velocities obtained from a maxwellian distribution associated with a given temperature. Our simulations show 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 exchanges heights with one of the Sn-atoms in the down position. This process is repeated ~ 40 times during the 54 ps of the MD-simulation. 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. 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.

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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[1] J.M. Carpinelli *et al*, Phys. Rev. Lett. **79**, 2859 (1997).
[2] J. Avila *et al*, Phys. Rev. Lett. **82**, 442 (1999).
[3] J. Ortega *et al*, J. Phys.: Condens. Matter **12**, L21 (2000).
[4] L. Petersen, Ismail, and E.W. Plummer, Prog. Surf. Sci. **71**, 1 (2002).
[5] R. Pérez *et al*, Phys. Rev. Lett. **86**, 4891 (2001).
[6] D. Farías *et al*, Phys. Rev. Lett. **91**, 016103 (2003).
[7] A.A. Demkov et al. Phys. Rev. B **52**, 1618 (1995).
[8] J. Ortega, R. Pérez and F. Flores, J. Phys.: Condens. Matter **14**, 5979 (2002), and references therein.