Order-disorder transition of the (3×3) Sn/Ge(111) phase

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We have measured the long-range order of the α phase of Sn on the Ge(111) surface throughout the $(3 \times 3) \rightarrow (\sqrt{3} \times \sqrt{3})R30°$ phase transition. The transition has been found of the order-disorder type with a critical temperature $T_c \sim 220$ K. The expected three-state Potts critical exponents are shown to be consistent with the observed power-law dependence of the (3×3) order parameter and its correlation length close to T_c, thus excluding a charge-density wave driven phase transition.

Growing attention has been drawn during the past few years to the α phase (1/3 monolayer) of both Pb and Sn on Ge(111), which undergoes a transition from the room-temperature (RT) $(\sqrt{3} \times \sqrt{3})R30°$ phase to the low-temperature (LT) (3×3) one. On the basis of scanning tunnelling microscopy (STM) experiments, this transition was claimed to be the manifestation of a surface charge-density wave (SCDW), i.e., a periodic redistribution of charge, possibly accompanied by a small periodic lattice distortion, which determines a change of the surface symmetry.[1–4] This model interpretation would imply relevant effects of electronic nature, such as magnetism of the LT phase[3] and electron correlation effects.[5] As further experiments with different techniques were being performed to explore the properties of this system, increasing doubts were cast about the SCDW model. The research was then focused on the determination of the atomic structure of the RT and LT phases, in an effort to discriminate between different transition models, as well as on the study of the role played by defects, which were seen to stabilize the LT phase[6,7] and to determine a metal to semiconductor transition.[8]

At present, the atomic structure of the LT (3×3) Sn/Ge(111) phase has been determined with a substantial agreement between x-ray diffraction (XRD)[9,10] and photoelectron diffraction[11] measurements. The Sn atoms occupy the T_4 sites above the Ge(111) lattice, but one Sn atom, out of three, per unit cell, is vertically displaced by ~ 0.3 Å in the outward direction. This distortion strongly affects the substrate lattice too, where the three nearest-neighbor Ge atoms are found to follow the Sn atom in its vertical displacement. The most recent calculations in the local-density approximation reproduce quite exactly this vertically rippled structure.[12,13]

The RT phase structure is a more controversial issue. The analysis of the most recently published XRD measurements slightly favors a structure where the vertical ripple disappears and the Sn atoms occupy equivalent T_4 sites at the same height level.[9] On the basis of this observation, and taking into account the strong distortion of the substrate too, a short interaction range displacive phase transition (pseudo-Jahn-Teller distortion) appeared to describe the system behavior more adequately than a long interaction range SCDW.[14] On the other hand, the spectroscopic measurements give a result that seems incompatible with both the STM and

XRD measurements. The Sn $4d$ core level spectrum associated with the α phase, can be fitted with two components (with intensity ratio of 1:2), which have been attributed to the two types of Sn atoms in the LT (3×3) phase.[11,15–17] The same two components are found for both the LT and RT phases, i.e., the vertical ripple is expected to remain also at the RT $(\sqrt{3} \times \sqrt{3})R30°$ phase.[15,16,18,19] This result clearly points to an order-disorder character of the transition. In addition, a model based on molecular dynamics calculations has shown that the Sn atoms can jump between the two height levels, but the ratio between the number of up and down atoms remains equal to 1:2, even above the transition temperature, where the jumping rate would be beyond the STM time resolution.[18]

Most strikingly, all the experimental efforts for discriminating among the possible transition models have been devoted to the determination of the local atomic structure of the two Sn phases. To our knowledge, the diffraction techniques (both electrons and x rays) have not been employed to quantitatively study the temperature behavior of the diffraction pattern, i.e., of the surface order parameter that describes the thermodynamics of the whole system. We have thus performed He atom scattering (HAS) experiments to directly measure the surface order parameter, thus characterizing the phase transition. This experimental technique is only sensitive to the surface charge density (like STM), in addition it is a long-range order probe and offers the advantage of a short interaction time (10^{-13} s).

The experiment has been performed with a compact HAS apparatus which is described in more detail elsewhere.[20] A 20.1-meV He beam ($k = 6.3$ Å^{-1}) has been used for the present measurements; the corresponding instrumental resolution and angular reproducibility yield a transfer width exceeding 1200 Å. The measurements have been performed on different samples from the same Ge(111) wafer. The surface has been cleaned by 1-keV Ar$^+$ ion bombardment and annealing up to 1100 K, thus obtaining a good $c(2 \times 8)$ pattern. Sn has been evaporated at $T_{cell} = 1220$ K from a Knudsen cell hosted into a liquid-nitrogen cryopanel. The base pressure never exceeded 1×10^{-9} mbar during evaporation and remained at 2×10^{-10} mbar during the measurements.

For the preparation of the (3×3) phase of Sn on Ge(111), we have followed a procedure slightly different from the
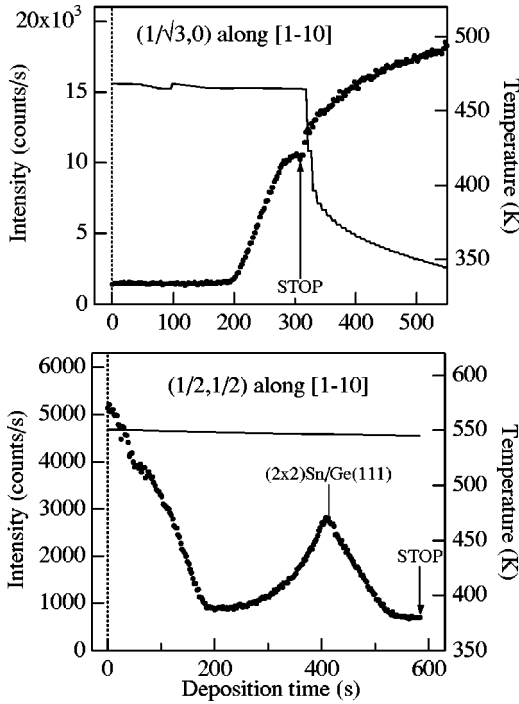
FIG. 1. Upper panel: intensity of the $(1/\sqrt{3},0)$ peak taken along the $[1\bar{1}0]$ direction during Sn deposition at an approximate rate of 15 min/ML (filled markers, left axis). The surface temperature is also reported (full line, right axis). Lower panel: intensity of the $(1/2,1/2)$ peak [with labeling relating to the $c(2\times8)$ clean surface phase] taken along the $[1\bar{1}0]$ direction during Sn deposition at an approximate rate of 30 min/ML (filled markers, left axis). The surface temperature is also reported (full line, right axis). The occurrence of the intermediate (2×2) Sn phase is also labeled.

FIG. 2. He diffraction patterns ($k_{He}=6.3$ Å^{-1}) taken from the α phase of Sn on Ge(111) at 140 K. Upper panel: measurement along the $[1\bar{1}0]$ direction, the intensity is on a logarithmic scale. The fractional order peaks can be equivalently labeled as $[\pm(n/\sqrt{3}),0]$, relating to the $(\sqrt{3}\times\sqrt{3})R30°$ phase, or $[\pm(n/3),\pm(n/3)]$, when relating to the (3×3) phase. Lower panel: measurement along the $[112]$ direction. The fractional order peaks $[\pm(n/3),0]$ are characteristic of the (3×3) phase. A mean (3×3) domain size of 200 Å is estimated from the width of the $[\pm(n/3),0]$ peaks.

standard one reported in the literature, where Sn is usually evaporated on samples held at RT and successively annealed to $T_s\sim500$ K. We have monitored the intensity of the diffraction peak $(1/\sqrt{3},0)$ along the $[1\bar{1}0]$ surface direction while depositing at $T_s\sim500$ K (see upper panel of Fig. 1). After 2/3 of the total exposure used in our work (~10 min), the $(\sqrt{3}\times\sqrt{3})$ pattern starts to appear, but the deposition is stopped only at the maximum intensity of the $(1/\sqrt{3},0)$ peak. The surface is then left to cool down. Alternatively, one can monitor the half-integer peaks of the $c(2\times8)$ pattern up to their disappearance, which only occurs after the formation of the intermediate (2×2) Sn/Ge(111) phase[11] (see lower panel of Fig. 1). The latter procedure is less accurate in the coverage calibration. The diffraction patterns of the (3×3) phase taken at 140 K are shown in Fig. 2 along both the $[112]$ and $[1\bar{1}0]$ directions. The diffraction peaks along the $[112]$ are characteristic of the (3×3) phase, while those along the $[1\bar{1}0]$ direction belong to the RT $(\sqrt{3}\times\sqrt{3})R30°$ phase too.

The full diffraction patterns for a few temperatures have been taken throughout the transition. Along the $[1\bar{1}0]$ direction, both the integer and fractional order peaks display the same behavior, i.e., an exponential intensity decrease due to the Debye-Waller (DW) attenuation without any variation of their angular width. It must be concluded that the $(\sqrt{3}$
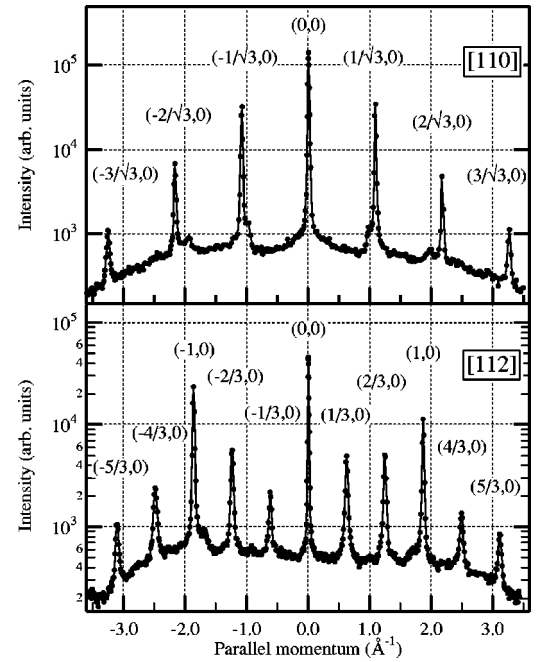
$\times\sqrt{3})R30°$ long-range order is maintained throughout the 130–300 K temperature range.

The diffraction pattern behavior along the $[112]$ direction is much different as reported in Fig. 3. In this case the specularly reflected peak and the integer peaks display the same exponential DW intensity decrease,[21] while the fractional order peaks present a steeper decrease with an inflection point at about 180 K. This observation is in contrast with the CDW model, whose predicted static distortion of the surface corrugation should strongly affect the He diffraction pattern. In particular, the expected metallicity of the RT phase[3,8] should flatten the surface charge density, thus leading to an increase of the He specular intensity [as observed for the $c(2\times8)$ $\rightarrow(1\times1)$ transition on the Ge(111) surface[22]]. In addition, the full width at half-maximum (FWHM) of the (0,0) and $(0,\pm1)$ peaks remains unchanged, while the fractional order peaks display a strong broadening as the temperature increases. This latter indicates a strong (3×3) domain-wall proliferation, thus suggesting the occurrence of an order-disorder phase transition.[23] In proximity of such an order-disorder equilibrium phase transition, all the thermodynamic quantities scale as power laws of the reduced temperature $t=(T_c-T)/T_c$. The corresponding critical exponents are only determined by the surface symmetry and they indicate the universality class of the phase transition. According to Landau's symmetry rules, this phase transition is expected to
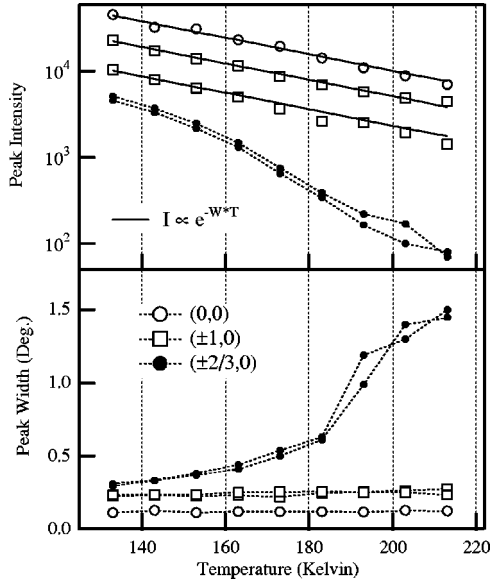
FIG. 3. Temperature behavior of the diffracted peak intensity and width (FWHM) taken along the [112] direction. The integer order peaks (open markers) and the fractional ones (filled markers) have been taken from the same surface of Fig. 1, yielding a mean (3×3) domain size of 200 Å. Upper panel: the peak intensity is reported on a logarithmic scale to put in evidence the deviation from the Debye-Waller attenuation of the fractional order peaks. Full lines are best fit to the DW factor e^{-WT} with $W=0.022$ K^{-1}. Lower panel: the diffraction peak FWHM is reported.

belong to the three-state Potts universality class, due to the threefold symmetry of the triangular surface lattice.

To check the consistency of the order-disorder hypothesis, we have followed in more detail and with larger statistics the temperature dependence of one of the diffraction peaks characteristic, of the (3×3) long-range order, which disappears above the critical temperature T_c. The temperature dependence of the diffracted peak has been found reversible, provided that the (3×3) domains extend at least a few hundreds of Å. The analysis of the temperature behavior of the $(-2/3,0)$ peak is reported in Fig. 4. In this case, the measurements were taken from a surface displaying a (3×3) mean domain size of 400 Å, i.e., twice that of Fig. 3.

In the proximity of the transition temperature, the diffraction intensity for parallel momentum exchange **K**, close to the reciprocal lattice vector **G**$=(-2/3,0)$, can be written as[24]

$$I(\mathbf{K},T)=\rho^2(T)\delta(\mathbf{K}-\mathbf{G})+\chi(\mathbf{K}-\mathbf{G},T), \qquad (1)$$

where ρ stands for the order parameter and χ is the order-parameter susceptibility, which accounts for the order fluctuations close to T_c (Fourier transform of the order-parameter correlation function). The order parameter vanishes at T_c as $\rho\sim t^\beta$, and the fluctuations scale as $\chi\sim|t|^{-\gamma}$. As a consequence, the order-parameter susceptibility is the only contribution to the $(-2/3,0)$ diffraction peak above the transition temperature and determines the peak shape. The susceptibility can be approximated to a Lorentzian and its width is proportional to the inverse of the (3
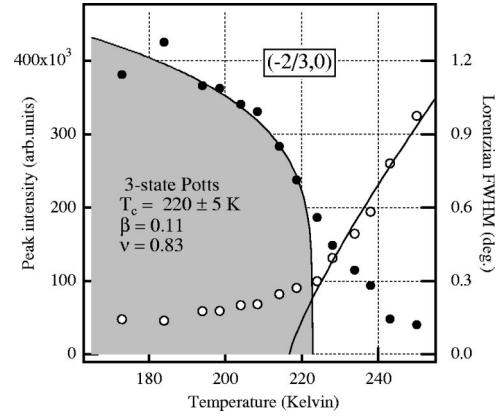

FIG. 4. Temperature dependence of the $(-2/3,0)$ He diffraction peak taken along the [112] direction from a surface with a (3 $\times3$) mean domain size of ~400 Å. The peak intensity (filled circles, left axis) and the Lorentzian FWHM (open circles, right axis) were obtained by fitting the data to a Voigt function. A Gaussian broadening of 0.2° (FWHM), due to the instrumental resolution, has been used. The peak intensity has been corrected for the DW factor, as obtained from Fig. 2. The full line is a fit of the Lorentzian widths to $|t|^\nu$ with the predicted three-state Potts exponent $\nu=0.83$, thus yielding $T_c=217$ K. The shaded line represents the expected behavior, $\beta=0.11$, of the order parameter for the critical temperature of 223 K.

$\times3$) correlation length ξ, thus giving the spatial extent of the fluctuating domains. The susceptibility correlation length diverges at T_c as $\xi\sim|t|^{-\nu}$. The three-state Potts critical exponents assume the fractional values $\beta=1/9$, $\nu=5/6$, and $\gamma=13/9$.[25] Experimentally, the susceptibility contribution is convoluted with the instrumental profile (which is assumed to be a Gaussian). In the experiment we have measured the $(-2/3,0)$ peak profile at different temperatures and the analysis has been performed by fitting the data to a Voigt function with constant Gaussian width (corresponding to the Gaussian contribution obtained at the lowest achieved temperature). The resulting Lorentzian width is shown in Fig. 4 (open circles) together with the $(-2/3,0)$ peak intensity (filled circles).

The Lorentzian width displays a slight broadening below 220 K, possibly due to residual defects, while a much stronger broadening sets in above 220 K, when the order-parameter intensity is strongly reduced. This observation points to an order-disorder phase transition, where the order parameter ρ dominates the diffracted peak behavior below T_c, according to Eq. (1), and the Lorentzian should start to broaden after the disappearance of the term $I\propto t^{2\beta}$. For what concerns the critical exponents, we found a reasonable temperature range where the Lorentzian width can be fitted with the predicted $\nu=5/6$ critical exponent, thus giving a transition temperature of 217 K. This transition temperature does not yield a satisfactory power-law fit of the peak intensity. In this case, the expected $\beta=1/9$ exponent is obtained for a slightly higher transition temperature. This discrepancy (yielding a critical temperature $T_c=220\pm5$ K with a corresponding dispersion of $\pm20\%$ in the critical exponents) is due to the rounding of both the order parameter and its cor-

relation length close to T_c, and is to be related to the presence of defects within the (3×3) domains.

Both line and point defects produce a smearing of the equilibrium phase transitions.[26] In fact, several kinds of point defects have been observed by STM on the (3×3)Sn/Ge(111). Most of them are found to be Ge substitutional impurities within the Sn overlayer, which are shown to stabilize the LT phase in a local environment of the given (3×3) sublattice.[6] This case resembles the order-disorder $c(4\times2)\rightarrow(2\times1)$ transition on the (001) surface of both Ge and Si. Due to defects, the expected two-dimensional Ising critical exponents have been only recently found for Ge(001),[27] but are still lacking for Si(001).[28] This surface has been found to be strongly affected by point defects,[29,30] which have been demonstrated to reduce the order parameter below T_c and to smear out the transition.[31,32] A possible difference with the Sn/Ge system is the partial mobility of the Ge substitutional impurities [they were seen to lie on a single (3×3) sublattice at 120 K, as opposed to the random distribution observed above 165 K].[7] This observation led the authors of Refs. 6 and 7 to conclude that the transition is driven by a defect-defect interaction mediated by a SCDW, as a consequence the critical temperature was also predicted to decrease by decreasing the density of defects. From He scattering, the individual role of each kind of defect cannot be discriminated, but it is well observed that a larger (3×3) domain size yields a higher critical temperature T_c (compare the inflection points of Figs. 3 and 4, taken from (3×3) domains yielding a mean size of 200 and 400 Å, respec-

tively). This observation is consistent with both the coverage dependence of T_c for adsorbate order-disorder phase transitions (where it is demonstrated that the exact coverage, i.e., best surface quality, yields the highest critical temperature[33]) and the finite-size scaling laws for order-disorder phase transitions, where a reduced domain size is usually observed to yield a lower estimate of T_c.[34,35]

On the basis of the present experiments, the SCDW phase transition must be excluded, since a clear order-disorder behavior is displayed at the critical temperature. The occurrence of a late stage (higher temperature) displacive character of the $(3\times3)\rightarrow(\sqrt{3}\times\sqrt{3})R30°$ phase transition cannot be excluded *a priori* by the present study. In fact, all of the displacive phase transitions are expected to display an intermediate stage, where the order-disorder character dominates,[36,37] even for a large temperature range.[38] In the present case, an upper limit to the available temperature range is set to 550–600 K, where the $(\sqrt{3}\times\sqrt{3})$ phase is irreversibly decomposed into a new (7×7) phase. This temperature range is probably too small for displaying the onset of any displacive character.

Note added: During the manuscript refereeing, a theoretical model suggesting a displacive transition was also proposed,[39] while new photoemission and photoelectron diffraction data excluded this hypothesis up to 500 K.[40]

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