

## Order-disorder character of the $(3 \times 3)$ to $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase transition of Sn on Ge(111)

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The  $\alpha$  phase of Sn/Ge(111) has been investigated from 120 K up to 500 K, using synchrotron radiation core-level photoemission. By means of photoelectron diffraction experiments, we verified that the rippled structure of the low-temperature  $(3 \times 3)$  phase is preserved in the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phase at room temperature, thus confirming the order-disorder character of the phase transition. We also found that at least two components are present in the Sn  $4d$  core-level spectra up to 500 K, i.e., about 300 K above the onset of the transition from the low-temperature  $(3 \times 3)$  phase to the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phase, thus excluding the occurrence of any displacive transition.

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The system formed by one-third of a monolayer (ML) of Sn adatoms atop the  $T_4$  sites of the Ge(111) surface ( $\alpha$  phase) exhibits a transition from a low-temperature (LT)  $(3 \times 3)$  phase to a high-temperature (HT)  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phase. This transition is gradual, reversible, and has a critical temperature  $T_c \sim 220$  K. The phase transition was attributed to the manifestation of a commensurate surface charge-density wave state in the LT phase stabilized by many-body effects, in particular by electron correlation.<sup>1-4</sup> Later on, an order-disorder model,<sup>5</sup> invoking dynamic fluctuations as microscopic driving mechanism,<sup>6</sup> has been proposed to explain the published data. The research then focused on the role of surface defects<sup>7,8</sup> and the determination of the surface structure<sup>9-12</sup> in an attempt to discriminate between the two interpretations.

At present, the  $(3 \times 3)$  structure has been determined with a good agreement between surface x-ray diffraction<sup>9,10</sup> (SXRD) and photoelectron diffraction<sup>12</sup> (PED) measurements. At low temperature, the Sn adatoms occupy inequivalent  $T_4$  sites, with one Sn adatom (out of three within the unit cell) protruding above the surface. This inequivalency is also confirmed by photoemission experiments, where at least two components (with intensity ratio close to 1:2) are required to fit the Sn  $4d$  spectrum properly.<sup>5,11-14</sup>

For the structure of the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phase at room temperature (RT), only SXRD measurements are available.<sup>9,10</sup> They slightly favor a structure with equivalent Sn adatoms, thus suggesting that the transition is indeed due to a pseudo-Jahn-Teller effect,<sup>9</sup> i.e., it would be a displacive phase transition. This result is hardly conciliating with a very recent He diffraction study of the  $(3 \times 3)$  order parameter, which indicates the occurrence of a three-state Potts order-disorder phase transition at  $T_c \sim 220$  K.<sup>15</sup> Moreover, the hypothesis of a displacive transition at 220 K is also not compatible with the core-level photoemission experiments, where the inequivalency between the Sn atoms seems to remain also in the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phase, since the Sn  $4d$  line shape does not change significantly from  $\sim 100$  to 150 K up

to room temperature.<sup>5,6,13,16</sup> This discrepancy urges PED structural measurements of the RT phase.

The hypothesis of a displacive transition, being recently suggested to be driven by a phonon softening,<sup>17</sup> asks for experiments in a more extended temperature range. To our knowledge no data have been published at temperatures higher than 300 K, while it is well known that the displacive phase transitions are always accompanied by an intermediate disordered stage around the critical temperature,<sup>18-20</sup> manifesting the change in surface corrugation only at a temperature substantially higher than  $T_c$ . It is therefore of utmost importance to have a clear indication of the order-disorder character of the transition around  $T_c$  and to know if the two components observed in the Sn  $4d$  core level spectra at LT and RT are also present far from  $T_c$ , up to the highest temperature where this phase is stable ( $\sim 550$  K).<sup>21</sup>

By means of photoelectron diffraction (PED) measurements, we have already shown that in the  $(3 \times 3)$  phase the observed splitting of the Sn  $4d$  core levels in two components derives from adatoms with different bonding configuration.<sup>11</sup> A vertical ripple of 0.3 Å between the Sn adatoms has been estimated by simulations, with one adatom out of three that protrudes above the surface. In particular, the adatom at the higher height level is associated to the Sn  $4d$  component with the larger binding energy.<sup>12</sup> The three nearest-neighbor Ge atoms follow the Sn adatom vertical distortion, i.e., their bond angle and length remain almost unchanged. This rippled structure is in good agreement with both the SXRD experiments<sup>9</sup> and recent density-functional theory (DFT) calculations<sup>22,23</sup> for the LT  $(3 \times 3)$  phase.

In this paper, we report on the evolution of the Sn  $4d$  core levels and on their PED patterns at different temperatures. The measurements were performed at the ELETTRA Synchrotron facility in Trieste, in the ultrahigh vacuum end stations of the ALOISA (Refs. 24 and 25) and SuperESCA (Ref. 26) beamlines. The Sn  $4d$  core-level photoemission spectra presented here were measured at the SuperESCA beamline with an overall energy resolution better than 120 meV. The PED experiments were performed at the ALOISA beamline.

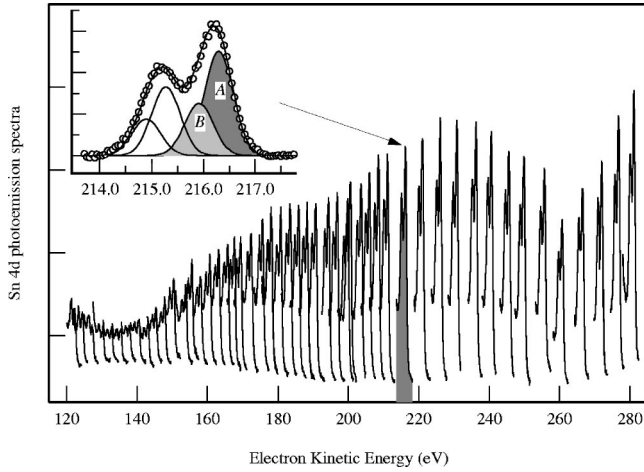


FIG. 1. Sn  $4d$  photoemission spectra taken in normal emission from the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phase at RT. Each spectrum has been taken at a different photon energy. The data have been normalized to the photon flux. The overall intensity slope clearly shows the Cooper's minimum for the Sn  $4d$  core level at the lowest energies. The spectrum taken at  $h\nu \sim 245$  eV is shown in the inset panel together with the fit to two doublets, after background correction.

Details about the sample preparation and PED experiment at ALOISA are given elsewhere.<sup>12</sup> At the SuperESCA beamline, the  $\alpha$  phase was prepared by dosing 1/3 ML of Sn on a clean Ge(111)- $c(2 \times 8)$  surface kept at RT. The optimum coverage and annealing treatment for the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  and  $(3 \times 3)$  phases were checked by optimizing the intensity of the low-energy electron diffraction (LEED)  $(3 \times 3)$  extra spots of the LT phase and the intensity of the Sn induced surface band at the Fermi level in the photoemission spectra. This feature is indeed very sensitive to the quality of the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phase.<sup>4,16</sup> We have investigated also the  $(2 \times 2)$  phase of Sn/Ge(111), obtained by dosing  $\sim 0.2$  ML of Sn and annealing at 450 K. The temperature stability during measurements was better than  $\pm 10$  K.

In Fig. 1, we show the Sn  $4d$  core-level photoemission spectra taken at room temperature in normal emission geometry for photon energies between 120 and 300 eV. In these experimental conditions, the photon energy dependence of the photoemission spectra (after normalization to the photoemission cross section) mainly reflects the vertical distance between the Sn adatom and the Ge atom directly underneath, thus enhancing the sensitivity to the vertical distortions of the adatom layer.<sup>11</sup> In fact, the Sn vertical ripple is the main structural parameter involved in the phase transition, since it is expected to disappear in the high-temperature phase if a displacive transition takes place. A detailed description of the Sn  $4d$  core-level analysis in terms of two spin-orbit split doublets is given in Ref. 12, where high-resolution spectra have been studied to determine the fitting parameters used for the successive analysis of the PED data taken in the LT phase. Also in the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phase at 300 K, the Sn  $4d$  core levels have a shape that cannot be fitted with a single spin-orbit split doublet.<sup>5,6,13,16</sup> At least one additional doublet is needed to improve appreciably the quality of the fit (see the inset panel of Fig. 1).

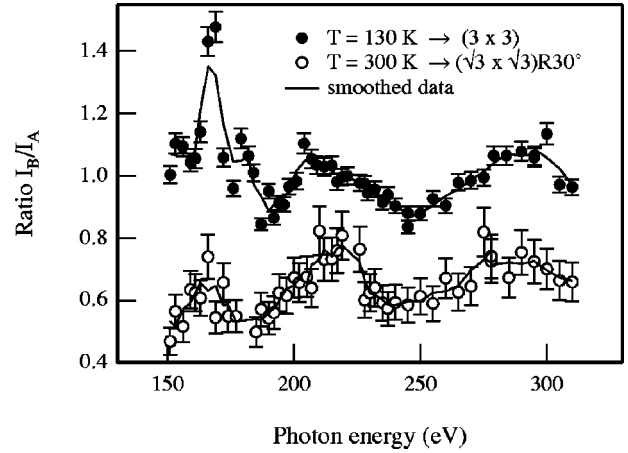


FIG. 2. Intensity ratio between the minority  $B$  and the majority  $A$  components of the Sn  $4d_{5/2}$  core levels at 130 K (filled circles) and 300 K (open circles). The data at 130 K have been vertically shifted by 0.4 units for the sake of clarity. The smoothed data (full lines) are also shown as a guide to the eye.

The photon energy dependence of the intensity ratio  $I_B/I_A$  between the minority  $B$  and the majority  $A$  components of the Sn  $4d_{5/2}$  core levels at 130 and 300 K is shown in Fig. 2. This presentation of the PED data allows a direct evaluation of any change of the Sn vertical ripple, in particular, the disappearance of the ripple would yield a constant intensity ratio without any energy modulation. In addition, the comparison between the intensity ratio below and above the transition is not affected by the systematic errors of extracting the anisotropy  $\chi$  function. These errors can be large around 130 eV, because of the pronounced Cooper minimum. The error bars in Fig. 2 represent the maximum error in the intensity ratio, as obtained by the fitting procedure of Ref. 12, and it mainly arises from the uncertainty on the energy shift between the  $A$  and  $B$  components and their linewidth. The intensity ratio  $I_B/I_A$  below and above the phase transition is very similar, confirming that, also in the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phase at RT, there are two inequivalent types of Sn adatoms with different bonding geometry (different vertical distances between Sn and the underneath Ge atom). Thus the rippled structure is maintained up to RT. This result differs from that obtained by SXRD experiments<sup>10,9</sup> [where the surface corrugation was claimed to change from the  $(3 \times 3)$  to the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phase], and indicates that the phase transition at  $T_c \sim 220$  K has an order-disorder character.

Since the two spectral components are unambiguously assigned to two adsorption sites with different Sn heights, we can detect any structural modification of the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phase by simply measuring the Sn  $4d$  spectrum as a function of the temperature. In particular, an eventual merge of the two spectral components in a single one would be the fingerprint of a displacive transition. We have reported in Fig. 3 the line shapes of the Sn  $4d$  core-level spectra of 1/3 ML of Sn/Ge(111) measured from 120 to 500 K with a photon energy of 198 eV and an emission angle of  $55^\circ$  from the surface normal. These spectra have been fitted to Doniach-Sunjic (DS) doublets convoluted with a Gaussian. The Gaussian takes into account both the instrumental

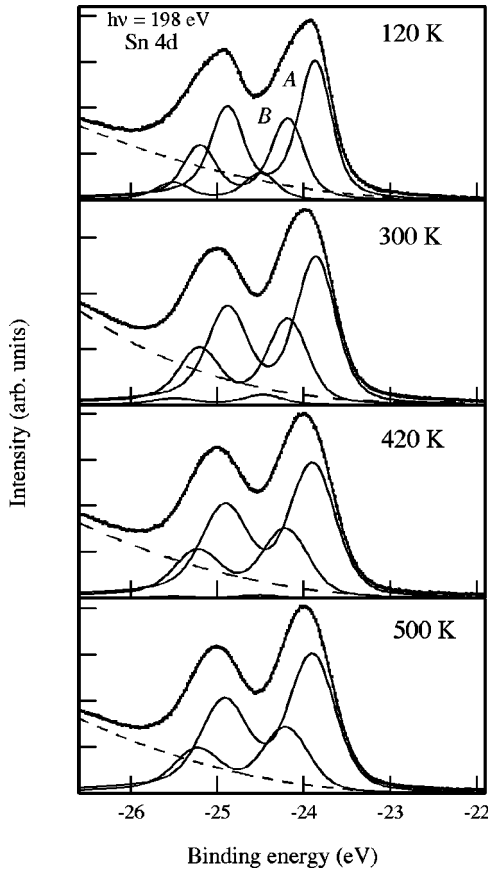


FIG. 3. Fit of the Sn  $4d$  core levels with three DS spin-orbit split components in the  $(3 \times 3)$  phase at 120 K, and in the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phase at 300, 420, and 500 K. The fits yield a Lorentzian width of 0.2 eV with a branching ratio of  $0.63 \pm 0.01$  and an intensity ratio of 0.52–0.6 between the  $B$  and  $A$  components.

broadening (120 meV) and the temperature-dependent phonon broadening, that is much larger. The free parameters were the energy position of the doublets, their intensities, the Gaussian full width at half maximum (FWHM) (assumed to be the same for all the doublets), the asymmetry of the DS line, and the branching ratio. The spin-orbit splitting was set to 1.02 eV (according to Refs. 13 and 28 and a polynomial function was used for the background caused by the low-energy tail of the Ge  $3d$  core levels at about 29 eV of binding energy.

Besides the  $A$  and  $B$  components, a third weak doublet was required to fit properly the  $(3 \times 3)$  phase spectra at 120 K. This component is attributed to the Sn atoms surrounding Ge substitutional impurities in the  $(3 \times 3)$  overlayer, according to the measurements of Uhrberg *et al.*<sup>16</sup> We observed that the third component intensity decreases by increasing the temperature up to disappearance at 420 K. This is possibly due to limits of the fitting procedure in detecting such a faint feature when the main components become increasingly broader.<sup>16</sup> The energy shift between the  $A$  and  $B$  components does not change between 120 and 500 K (see the upper panel of Fig. 4), while the corresponding Gaussian width gradually broadens from  $\sim 0.3$  eV up to  $\sim 0.5$  eV. The Sn  $4d$  core-level line shape at 500 K is more symmetric and can be fitted

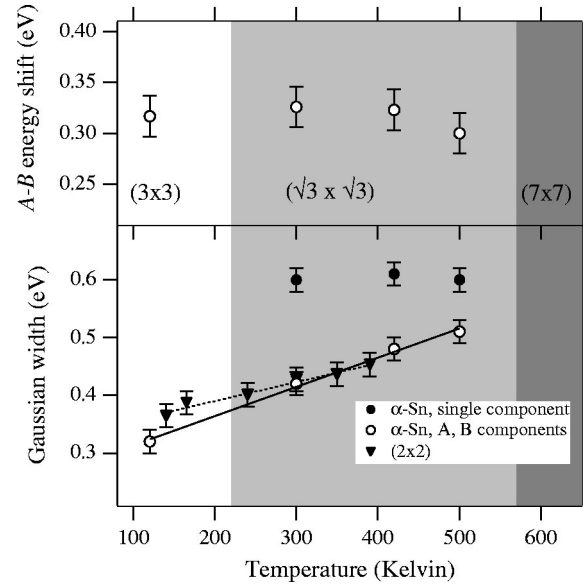


FIG. 4. Upper panel: temperature dependence of the energy shift between the  $A$  and  $B$  components as obtained by the fit to the Sn  $4d$  spectra in Fig. 3. Lower panel: temperature dependence of the Gaussian FWHM as obtained from Fig. 3 (open circles). The filled circles show the Gaussian FWHM obtained by fitting the spectra of the  $\alpha$  phase to a single spin-orbit split component (DS type). The Gaussian FWHM of the Sn  $4d$  spectra, taken in the  $(2 \times 2)$  phase at 0.2 ML, is also reported (filled triangles). Full and dotted lines are linear fits to the temperature behavior of the FWHM's.

to a single DS doublet, thus yielding a Gaussian FWHM of  $\sim 0.6$  eV, a value much larger than that of the components used to fit the low-temperature spectra.

In order to discriminate between the model with a single component at 500 K and that with  $A$  and  $B$  components, we have followed the temperature dependence of the Gaussian FWHM of these components in the  $(3 \times 3)$ , in the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  and in the  $(2 \times 2)$  phases of Sn on Ge(111). The corresponding temperature dependences are reported in Fig. 4. The values obtained for the  $A$  and  $B$  components of the  $\alpha$  phase and for the  $(2 \times 2)$  phase show a linear increase with the temperature, with a slope of  $(0.5 \pm 0.02) \times 10^{-3}$  eV K<sup>-1</sup> and  $(0.32 \pm 0.03) \times 10^{-3}$  eV K<sup>-1</sup>, respectively. This result is consistent with the linear increase ( $\sim 0.2 \times 10^{-3}$  eV K<sup>-1</sup>) observed for the surface components of the  $3d$  core levels of the clean Ge(111) surface in a wider temperature range.<sup>27</sup> The fit of the  $\alpha$ -phase core levels with a single component yields a Gaussian width which does not change with the temperature, while the quality of the fit declines as the temperature is lowered (being definitely insufficient already at 300 K). If the 500-K spectra contained a single component, there would be a jump of  $\sim 0.2$  eV of the FWHM between 300 and 500 K, with about a threefold increase in the temperature derivative of the core-level width. This implies that the thermal broadening of the Sn  $4d$  core levels would be strongly nonlinear, in contrast to the data of the Sn  $(2 \times 2)$  phase, the clean Ge(111) surface, and other semiconductors surfaces.<sup>28,29</sup> As a consequence, the temperature dependence of the FWHM's reported in Fig. 4 strongly

supports a deconvolution of the Sn  $4d$  core-level spectra with at least two DS doublets up to 500 K.

In conclusion, we have measured the temperature and energy dependence of the Sn  $4d$  core levels of Sn/Ge(111). By means of energy-dependent PED, we found that the vertical distortion, obtained for the two kinds of Sn adatoms in the LT ( $3 \times 3$ ) phase, is also present in the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  phase at RT, i.e., the transition at  $\sim 220$  K has an order-disorder character. In addition, we have shown that the two

components of the photoemission spectra, reflecting the inequivalence of the Sn adsorption sites, are present up to 500 K. This result leads us to discard the occurrence of a displacive character of the transition even at temperatures much higher than  $T_c = 220$  K.

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