Surface Charge Ordering Transition: α Phase of Sn/Ge(111)

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(Received 20 June 1997)

We have identified and characterized a charge-density wave transition ($T_c \sim -60\,^{\circ}\mathrm{C}$) in the low-coverage α phase of the Sn/Ge(111) interface both experimentally and theoretically. Charge ordering is accompanied by a structural distortion from $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ to (3×3) symmetry. Density-functional theory calculations are unable to correctly reproduce the observed ground state and, more importantly, indicate that Fermi surface nesting does not play a role in this transition. Both signal the importance of many-body effects in this system. Experiment and theory indicate that the Sn/Ge(111) overlayer is fundamentally different from the Pb/Ge(111) overlayer previously reported. [S0031-9007(97)04249-X]

PACS numbers: 73.20.At, 61.16.Ch, 68.35.Md, 71.45.Lr

A charge-ordered state, or charge-density wave (CDW), incorporates a symmetry-lowering periodic redistribution of valence charge driven by a reduction in the system's total electronic energy, resulting in a small periodic lattice distortion [1]. This phenomenon is most likely to occur in reduced dimensions [2,3], for example, in the layered perovskites [4]. The loss of coordination at a crystal surface might also be expected to invite CDW formation, but few genuine instances of *surface* charge-density waves have been reported to date. One clear example was recently discovered at the Pb/Ge(111)-α vacuum interface [5]. This low-density overlayer transforms from the room-temperature (RT) $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ structure to the low-temperature (LT) (3×3) ground state. Charge ordering ($\sim$0.5 Å corrugation) and accompanying lattice distortion occur gradually and reversibly with $T_c \sim -20\,^{\circ}\mathrm{C}$. Density function theory calculations indicate the charge-ordered (3×3) structure is the ground state of this system [5]. The opening of a $E_g \sim 65$ meV band gap below T_c (later confirmed by photoemission measurements [6]) *must* be the consequence of correlation effects [5]. We therefore conjectured that although enhanced electron-phonon coupling (enabled by Fermi surface nesting) drives this transition, many-body interactions stabilize the ground state.

Our motivation to study the α phase of Sn/Ge(111) was threefold. First, seeking verification that Pb/Ge(111) charge ordering is not an isolated quirk of nature resulting from Pb's exotic properties, we considered the other isostructural adsorbate/substrate combinations that exist. Al, Ga, In, Sn, and Pb all form the same low-density overlayer atop both Si(111) and Ge(111) [7,8]. However, overlayers composed of the trivalent species (Al, Ga, In) will probably not undergo a CDW distortion, as they are semiconducting [7] with an even number of electrons per unit cell at RT.

Second, it is imperative to test several theoretically derived concepts, including Fermi surface nesting, and the idea that the CDW ground state is a Mott-Hubbard insulator [5]. Intuitively, the Sn overlayer bandwidth w should be less than that of the Pb overlayer, because the metallic r_{Sn} is $\sim$10% smaller than r_{Pb}. For the same reason one expects the on-site Coulomb repulsion U to be larger for the Sn overlayer. Consequently, we expected a larger correlation gap U-w [9,10] and therefore a higher CDW transition temperature for Sn overlayer CDW.

The third reason for studying Sn/Ge(111)-α is the core level study by Göthelid *et al.* [11]. They interpreted their observation of two Sn 4d core level peaks in the RT Ge(111)-$(\sqrt{3} \times \sqrt{3})R30^{\circ}$-Sn phase as indicating fluctuations between metallic and nonmetallic phases. This is consistent with CDW critical temperature T_c near RT, higher than for the Pb overlayer (as would be expected from the above argument).

In this Letter, we present LT scanning tunneling microscopy (STM) images that reveal a charge-ordering transition for the Sn/Ge(111)-α system. As with the Pb overlayer, low-energy electron diffraction (LEED) indicates a structural transition from the RT $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ symmetry to the LT (3×3) coinciding with the CDW formation. However, there are many significant discrepancies between the two systems that beg a more sophisticated explanation than we originally offered. Most importantly, electron-energy-loss spectroscopy (EELS) measurements show that, unlike the Pb overlayer transition, both phases of the Sn overlayer are metallic—contradicting the expectations presented above. Also, density-functional theory calculations fail to identify the observed 3×3 distorted Sn ground state as lowest in total energy although such calculations were successful in verifying the Pb ground-state charge rearrangement. This is most surprising because these same calculations also predict that the Sn overlayer Fermi surface is nearly identical to that of the Pb overlayer. Finally, this Fermi surface shape is not nested with the proper magnitude and direction to definitively account for the observed transition (as previously speculated [5]).

Sn/Ge(111)-α consists of $\frac{1}{3}$ monolayer of equivalent Sn adatoms spaced $\sim$7 Å apart in a hexagonal array of T_4 sites atop the bulk truncated germanium lattice [8]. This interface is easily produced by Sn deposition onto the clean Ge(111)-$c(2 \times 8)$ surface, followed by a brief anneal. RT LEED, EELS, and STM measurements indicated the interface to be clean and well ordered. The well-converged electronic structure calculation results presented here were accomplished using the Ceperley-Alder treatment of exchange and correlation [12] and the generalized gradient approximation [13] with a plane wave cutoff of 10–12 Ry, and up to the equivalent of 4320 k points per 1×1 surface Brillouin zone. The response functions shown here were calculated in the Lindhard approximation to screening [3] using a model pseudofree electron band.

Figure 1 shows a map of the Sn overlayer's unoccupied (empty state—left) and occupied (filled state—right) density of states in a pair of registry-aligned STM images acquired at both RT (top) and LT (bottom). Each protrusion imaged is directly identifiable as the electron cloud associated with a single surface adatom [14]. At RT, all adatoms appear with equal intensity in STM; the $(\sqrt{3} \times \sqrt{3})R30°$ unit cell is indicated.

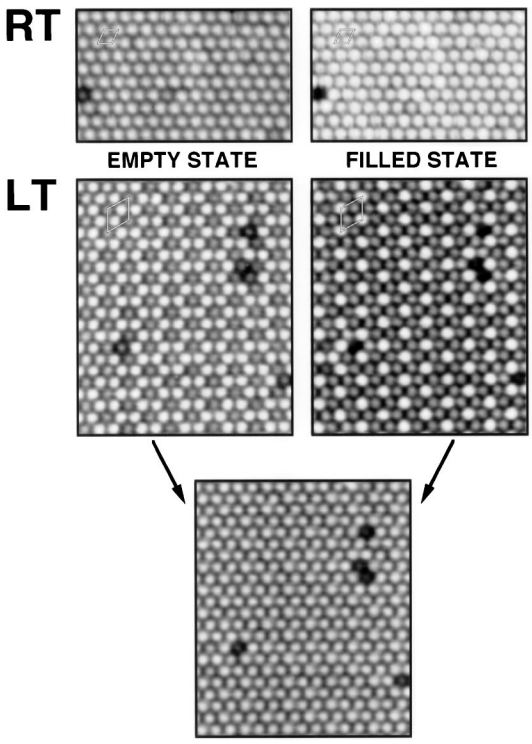

FIG. 1. Registry aligned 105×60 Å^2 STM images showing an atomically resolved map of the Sn overlayer's unoccupied ($V_{\text{sample}} = +1.0$ V; left) and occupied ($V_{\text{sample}} = -1.0$ V; right) density of states. These data were acquired at RT and LT ($T \sim 60$ K). An average of the two LT images is shown at bottom. Images were acquired with constant tunnel current, and processed slightly to remove sample inclination and noise, and enhance contrast.

With decreasing temperature, however, this overlayer's symmetry spontaneously changes. Adatoms no longer appear equivalent, and a new (3×3) unit cell can be identified. *Complimentarity between the filled state and empty state guarantees these data indicate a real valence charge rearrangement and do not contain significant information about any accompanying periodic lattice distortion (PLD);* this honeycomb-style pattern is identical to that observed with Pb/Ge(111)-α [5]. The absence of bond reorganization or mass transport is further verified in the average of these two LT data sets, which approximates the RT condition of equivalent adatoms in a hexagonal array. The defects visible throughout Fig. 1 (one at RT and five at LT) are Ge atoms substitutionally occupying overlayer adatom sites [15]. In STM of Sn/Ge(111)-α, single domains were observed to be as much as 60 000 Å^2, a factor of 40 larger than any achieved in the Pb/Ge(111) system.

RT LEED data indicate a $(\sqrt{3} \times \sqrt{3})R30°$ surface symmetry consistent with the RT data of Fig. 1. With decreasing sample temperatures, however, strong new diffraction maxima emerge indicating that a significant PLD of the same (3×3) symmetry has occurred concomitantly with charge rearrangement. This transition is observed to be gradual and reversible with a T_c well below RT ($T_{c\text{-Sn}} \sim -60\,°\text{C} < T_{c\text{-Pb}} \sim -20\,°\text{C}$ [5]), contrary to our expectations. The relative intensities of the observed (3×3) diffraction pattern *nonrigorously* indicates that the LT Sn overlayer's PLD is smaller than that of the Pb overlayer.

Our EELS data are shown in Fig. 2(a), and verify the metallic nature of the RT $(\sqrt{3} \times \sqrt{3})R30°$ overlayer—the measured loss function shows no discrete onsets. LT EELS data indicate the new Sn/Ge(111)-α ground state is still metallic, consistent with the single particle picture of these bands (electron counting) [5]. We did find a very weak excitation at 90 meV, but attributed little significance to it—a more thorough discussion can be found in Goldoni and Modesti [16]. For comparison, similarly acquired EELS data from the LT Pb/Ge(111)-α interface are also shown in Fig. 2(a) (a dramatic 65 meV band gap is indicated). Again, the lack of a metal-nonmetal transition in the Sn overlayer is contrary to our preliminary expectations.

Figure 2(b) shows the calculated ground-state band structure of the Sn/Ge(111)-α phase around the Fermi energy. It compares well to the RT dispersion measured with photoemission [16]. The large dots indicate the Sn-p_z-like surface band ($S1$) that causes the $(\sqrt{3} \times \sqrt{3})R30°$ structure to be metallic. The total calculated width w of the $S1$ state is 0.66 eV. Although $S1$ is the only occupied band with appreciable Sn-p_z character, only 15% of it is localized at the Sn adatom—its main weight is between the second and third Ge layers. Thus, w is determined by both the adatom orbital overlap and its hybridization with underlying Ge states. This strong hybridization with the substrate explains why the Sn/Ge(111)-α bandwidth

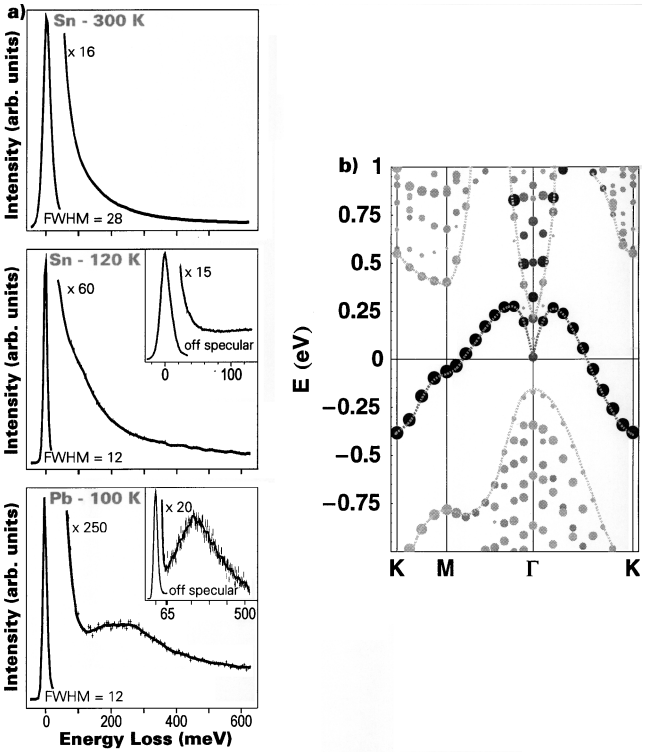

FIG. 2. Electronic structure of the Sn/Ge(111) system: (a) Specular EELS data of the RT and LT Sn overlayer phases and the LT Pb overlayer phase (impact energy = 7 eV; insets = 5° off specular). (b) Calculated band structure of the Sn-alpha phase; gray level indicates Sn-p_z character (black is highest).

is not smaller than that of Pb/Ge(111)-α [6,16]—in contradiction to our expectations. The predicted extended nature of the $S1$ state also suggests that our speculation concerning the difference between the Sn and Pb on-site Coulomb repulsions U is incorrect.

The inset of Fig. 3 shows the calculated Sn overlayer holelike Fermi surface (FS) centered on $\overline{\Gamma}$. This shape is nearly identical with that of the Pb overlayer FS, with at most 1% deviation in all directions, and compares well to the measured RT FS [6]. Both are well fit ($\theta = 0° \rightarrow 360°$) by a harmonic expansion,

$$k_{\mathrm{Sn}}(\theta)/\text{Å}^{-1} = 0.383\,03 - 0.049\,021\cos(6\theta) + 0.001\,080\,8\cos(12\theta) - 0.000\,516\,42\cos(18\theta)\,,$$

$$k_{\mathrm{Pb}}(\theta)/\text{Å}^{-1} = 0.382\,19 - 0.052\,836\cos(6\theta) + 0.001\,284\,6\cos(12\theta) - 0.000\,799\,67\cos(18\theta)\,.$$

Contrary to our speculation for the Pb system [5], this shape is not well nested along 0°. To illustrate this point, we calculated the momentum-resolved Lindhard approximation to the dielectric response (Fig. 3) of a pseudo-free-electron band with angular-dependent effective mass appropriately chosen to exactly yield the calculated FS

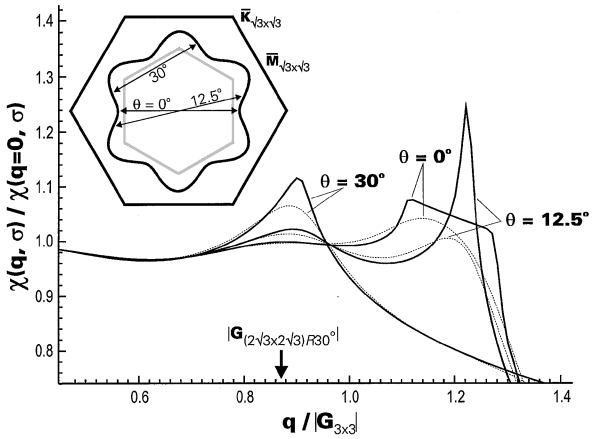

FIG. 3. Angle specific $T \sim 0$ (solid) and RT (dashed) normalized Lindhard response functions based on the calculated FS. Inset shows the Ge(111) $(\sqrt{3} \times \sqrt{3})R30°$ surface Brillouin zone (outer hexagon) containing the calculated Fermi contour for the Sn overlayer.

shown. As expected, the electronic response along $\theta = 0°$ is not strongly peaked because, in that direction, no opposing parallel regions of FS exist. It seems unlikely that the *cusp* along $\theta = 0°$ could result in a giant Kohn anomaly because it is 11% off commensurate ($\sim 1.11 G_{3\times3}$). By means of simple comparison, one would more likely expect the broad *peak* along $\theta = 30°$ to bring about a $(2\sqrt{3} \times 2\sqrt{3})R30°$ distortion because it is only 4% off commensurate ($\sim 1.04 G_{(2\sqrt{3}\times2\sqrt{3})R30°}$), but this is not observed. Therefore, it follows that the CDW transition is not driven by enhanced electron-phonon coupling enabled by strongly nested FS—that is, if the single particle FS is the correct representation of this system. Note that our calculation of the response function did not include either many-body interactions [17] or crystal local field corrections [18]. Maldague [17] has shown that exchange and correlation effects can bring about peaks in the response of a 2D material, even when there is no nesting present. Lastly, it is also worth mentioning the small nested sections along $\theta \sim 12.5°$ (not a high-symmetry direction). This leads to an enhanced response which will likely result in an anomalous softening of the phonon spectrum at momentum $\sim 1.2|G_{3\times3}|$ (0.73 Å^{-1}).

In contrast to our earlier results for the Pb overlayer [5], we do not find any calculated instability of the Sn/Ge(111)-α phase towards a 3×3 reconstruction—despite the fact that both systems have nearly identical Fermi surfaces. That is, any distortion of the Sn overlayer (from the condition where all adatoms are equivalent) raises the total calculated energy of the system. As these calculations rigorously include the electron-phonon interaction energy, but only approximately consider electron-electron interaction energies, this prediction offers further support to the idea that the observed ground state involves more than just a giant Kohn anomaly. Even though the low-temperature Sn overlayer is *not* a Mott-Hubbard insulator, correlation effects are largely

responsible for the symmetry reduced ground state. This is consistent with the conclusions of a recent high resolution photoemission study [16].

As is illustrated in Fig. 3, features in the momentum-resolved electronic response of a material broaden with increasing temperature, as the FS becomes less sharply defined due to thermally excited e^--hole pairs. Even above T_c evidence of such attenuated screening can still be observed, for example, in Friedel oscillations [19]. Figure 4 illustrates this effect with a filled state STM image of the Sn overlayer acquired at RT. In response to the presence of an impurity (next-nearest neighbor substitutional Ge adatoms highlighted by arrows), a localized electronic rearrangement, identical in appearance to the LT CDW, has formed. We expect the symmetry of the LT and RT charge rearrangements to be identical because the same vectors dictate both [20]. Such local charge oscillations possibly explain the split Sn $4d$ core levels observed above T_c [11].

At first glance, the properties of the Sn/Ge(111)-α CDW seem consistent with our understanding of the physics of reduced-dimension materials: charge ordering and structural distortion are of the same symmetry, there exists a metallic band at both RT and LT in accordance with the rules of electron counting, T_c is lower than for the Pb/Ge(111)-α, and the structural distortion seems less pronounced than that of Pb/Ge(111)-α (both are consistent with our observation $E_{g\text{-Pb}} > E_{g\text{-Sn}}$). However, certain aspects of this system still require clarification. Certainly, the differences between the isovalent Sn/Ge(111)-α and Pb/Ge(111)-α interfaces are not presently understood. Also, the absence of appreciable electronic response (in the Lindhard approximation) at $G_{3\times3}$ suggests two distinct possibilities: (1) The existing structure in $\chi(\theta = 0°)$ is pronounced enough to cause a phonon softening that evolves, shifts in momentum, and locks-in to a commensurate distortion with decreasing temperature, and (2) these CDW transitions are driven mainly by correlation effects and not just electron-phonon coupling. The latter seems more likely.

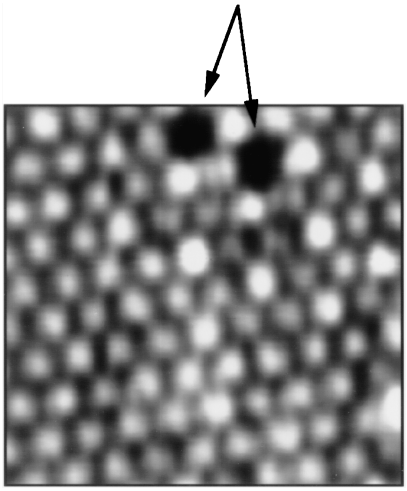

FIG. 4. 66×63 Å^2 RT filled state ($V_{\text{sample}} = -1.0$ V) STM data of the Sn overlayer containing a localized 3×3 electronic rearrangement in response to the pair of defects at the top of the image.

This research was funded by the National Science Foundation: DMR-9510132 and INT-9307334. H. H. W. acknowledges the donors of the Petroleum Research Fund administered by the American Chemical Society for their support. ORNL is managed by Lockheed Martin Energy Research Corp. for U.S. DOE under Contract No. DE-AC05-96OR22464. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. DOE under Contract No. DE-AC04-94AL85000.

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