

Periodic lattice distortion accompanying the charge-density-wave transition for Sn/Ge(111)

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(Received 26 February 1999)

The periodic lattice distortion (PLD) accompanying the charge-density-wave (CDW) transition (at -60°C) in the α phase of Sn on Ge(111) has been determined by combining the distinct sensitivities of low-energy electron diffraction (LEED) and surface x-ray diffraction (SXRD). New LEED I - V data combined with a SXRD analysis yield a significant lattice distortion. The PLD accompanying the CDW transition is a $0.37\text{-}\text{\AA}$ vertical rippling of the Sn atoms accompanied by a perpendicular (0.17 \AA) and parallel (0.12 \AA) distortion of the first-layer Ge atoms, consistent with a band Jahn-Teller-like distortion. [S0163-1829(99)01128-5]

A charge-density-wave (CDW) transition has been observed for thin films (α phase with $\frac{1}{3}$ monolayer density) of Pb and Sn on the (111) surface of Ge, using a variable temperature scanning tunneling microscope (STM).^{1,2} STM images reveal a (3×3) symmetry in the low-temperature CDW phase with the filled and empty state images being complimentary.^{1,2} Electron-diffraction studies of both of these systems show that there is a commensurate lattice distortion that accompanies the CDW transition, from a room-temperature $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure (labeled $\sqrt{3}$) to a (3×3) low-temperature structure.^{1,2} For the Pb film, first-principles density-functional calculations confirmed that the CDW (3×3) phase was in fact the ground state of the system, and that the Fermi contour of the high-temperature $\sqrt{3}$ phase, confirmed by angle-resolved photoemission measurements,³ had a shape that would suggest Fermi surface nesting.¹ It was proposed, based on these calculations, that the transition was driven by Fermi surface nesting,¹ but stabilized by electron correlation effects, since experiments showed that this CDW transition was accompanied by a metal-to-nonmetal transition,^{1,4} unexplainable with band theory.

At first glance, the behavior of the Sn film is very similar to that of the Pb film. The CDW transition is at -60°C compared to -20°C for Pb, the STM images are nearly identical, and the commensurate lattice distortion, as seen with low-energy electron diffraction (LEED), is qualitatively similar. Upon close inspection, the details are significantly different. First-principles density-functional calculations show that the CDW configuration is not the ground state for

Sn/Ge.² Both theory^{2,5} and experiment⁶ indicate that Fermi surface nesting is not an appropriate model for this transition, and there is no metal-to-nonmetal transition for Sn/Ge.^{2,6} Scandolo *et al.*⁵ proposed, based on theoretical calculations, that the $\sqrt{3}$ phase is paramagnetic and is unstable towards a commensurate spin-density wave with periodicity (3×3) and magnetization $\frac{1}{3}$. Le Lay *et al.*⁷ proposed, based on core-level data, that dynamic fluctuations between the sp^3/sp^2 hybridization states at room temperature would condense into a (3×3) low-temperature phase. A key to determining the origin of the CDW transition in the Sn/Ge(111) system is the structure of the periodic lattice distortion accompanying the electronic transition.

A recent surface x-ray-diffraction (SXRD) study of the PLD for the Sn/Ge system reported a quite surprising structure, which in several ways is counterintuitive.⁸ The best fit to the experimental data was a structure that had no measurable distortion in the Sn layer and a $0.2\text{-}\text{\AA}$ lateral distortion of three of the nine surface Ge atoms. The scattering rods associated with the new (3×3) structure were very weak and consequently the data set unique to the (3×3) was limited. The width of the Sn-induced rod associated with the (3×3) CDW phase gave a correlation length of $90\pm 20\text{ \AA}$. We have utilized LEED I - V measurements to examine the surface structure in detail. In principle, the enhanced surface sensitivity of LEED compared to SXRD should allow for a more detailed determination of the Sn-Ge bonding configuration. What we find is that the structure (for both phases) determined by LEED I - V is, at face value, inconsistent with the SXRD structure. A structure consistent with both LEED

and SXRD can be obtained if the specific sensitivities of each technique are understood and utilized.

Preparation and characterization of the Sn/Ge interface have been adequately described in previous papers.^{2,6} Normal incidence LEED I - V data were collected with a commercial video-LEED system in a magnetically shielded vacuum chamber operated at a pressure less than 1×10^{-10} Torr. The experimental LEED I - V data sets were formed by averaging all recorded equivalent beam intensities as a function of incident electron energy. Measurements at room temperature of the $\sqrt{3}$ phase utilized nine inequivalent beams $\{(\frac{1}{3} \frac{1}{3}), (\frac{2}{3} \frac{2}{3}), (\frac{1}{3} \frac{4}{3}), (\frac{4}{3} \frac{1}{3}), (0 \ 1), (1 \ 0), (1 \ 1), (0 \ 2), \text{ and } (2 \ 0)\}$ with a total energy range of $\Delta E = 1300$ eV. The CDW (3×3) structure was determined at 100 K using 11 inequivalent beams $\{(0 \ \frac{2}{3}), (\frac{2}{3} \ 0), (\frac{1}{3} \ \frac{1}{3}), (\frac{2}{3} \ \frac{1}{3}), (\frac{2}{3} \ \frac{2}{3}), (\frac{1}{3} \ \frac{4}{3}), (\frac{4}{3} \ \frac{1}{3}), (0 \ 1), (1 \ 0), (0 \ 2), \text{ and } (2 \ 0)\}$ over an energy range of 1165 eV.

Analysis of the LEED I - V spectra was carried out using standard multiple-scattering algorithms combined with automated-tensor LEED.⁹ Thirteen atomic phase shifts of Ge (Sn) were employed in our calculations, which we derived using the muffin-tin potential approximation with a Ge (Sn) muffin-tin radius of 1.5436 (4.0889) a.u.¹⁰ Electron attenuation was included by the energy-dependent imaginary part of the optical potential V_{oi} , modeled by the equation $V_{oi} = C \{E/(200/27.21 + V_{or})\}^{1/3}$, where E is the incident electron energy (eV), C is a constant optimized during the search, and V_{or} is the real part of the optical potential, which is a constant optimized during the search. The agreement between the experimental and calculated spectra is judged by the Pendry R factor (R_p), where $R_p \leq 0.25$ for an acceptable structure, and the error bar in the structural determination follows the definition of Pendry.¹¹

Since the PLD distortion accompanying the CDW transition is defined as the change in the structure between the $\sqrt{3}$ high-temperature and the (3×3) low-temperature phases, it is critical to start with a well-defined structure for the high-temperature phase. The basic structure of the $\sqrt{3}$ phase was determined by SXRD in 1987 (Ref. 12) and refined with a more extensive data set in 1998.⁸ Column 2 of Table I lists the structure for this phase determined by the recent SXRD study⁸ where the quality of the fit is measured with R_2 .¹³ Column 3 is the best-fit structure from our LEED I - V analysis. A comparison of columns 2 and 3 shows that there is, at face value, qualitative disagreement between the two structures. The vertical height of the Sn atoms above the Ge surface is appreciably different, and while LEED shows that the first three or four layers of Ge are contracted towards the bulk, SXRD shows a general expansion. This difference can be quantified by looking at the R factors shown at the bottom of the table.

The answer to this puzzle is contained in the relative sensitivities of each technique, which can be understood in the plot of momentum transfer normal to the surface, shown in Fig. 1. LEED is a backscattering process, with comparatively high momentum particles, so that the momentum transfer perpendicular to the surface is inherently large. In contrast surface x-ray-scattering experiments utilize a low angle of incidence with smaller perpendicular momentum transfer. At the same time, the interaction strengths of the two probes (electrons and photons) are quite different. The present LEED analysis is consequently more sensitive to perpendicu-

TABLE I. Comparison of the LEED, SXRD, and combined LEED/SXRD structure for Ge(111)-($\sqrt{3} \times \sqrt{3}$) $R30^\circ$ -Sn. Δd_i is the vertical distance of the i th plane with respect to the position of an ideally bulk truncated surface. d_{Sn} is the vertical distance of the Sn from the first Ge layer. The geometry of this surface is shown in Fig. 1 of Ref. 8.

Parameters (\AA)	SXRD	LEED I - V	LEED/SXRD
d_{Sn}	+1.910 (± 0.20)	+1.750 (± 0.11)	1.75
Δd_1	+0.088 (± 0.10)	-0.024 (± 0.04)	-0.018
Δd_2	+0.028 (± 0.05)	-0.042 (± 0.05)	-0.030
Δd_3	+0.085 (± 0.03)	-0.067 (± 0.05)	-0.059
Δd_4	+0.052 (± 0.02)	-0.027 (± 0.06)	-0.030
Lateral d_1	0.050 (± 0.02)	0.030 (± 0.15)	0.050
Vertical d_2	+0.609 (± 0.04)	+0.562 (± 0.04)	0.556
Vertical d_4	+0.410 (± 0.04)	+0.463 (± 0.06)	0.426
Lateral d_4	0.040 (± 0.02)	0.182 (± 0.17)	0.040
$\langle u \rangle_{\text{Sn}(z,xy)}$	(0.280,0.320)	(0.333,0.333)	(0.280,0.300)
$\langle u \rangle_{\text{Ge}(1,2)}$	(0.180,0.140)	(0.244,0.190)	(0.160,0.140)
$\langle u \rangle_{\text{Ge}(3,4)}$	(0.170,0.160)	(0.109,0.109)	(0.160,0.130)
$\langle u \rangle_{\text{Ge bulk}}$	0.084	0.109	0.084
R_p/R_2	0.450/0.012	0.220/0.034	0.239/0.014

lar distortions and outermost layers, while the SXRD study, with which we are comparing, is more sensitive to the parallel distortions and deeper layers. It is important to note that the small perpendicular momentum transfer shown in Fig. 1 for SXRD is not an inherent property of this technique. The significant improvement in beam intensity at a third generation synchrotron would appreciably enhance the perpendicular sensitivity of SXRD.

Given the sensitivities of the two different techniques, we have searched for a structure consistent with both data sets. The first step was to assume that the lateral distortions found by SXRD were correct and allow the LEED search program to vary only the vertical distortions. This produced a structural model with $R_p = 0.239$, almost as good as the best-fit structure shown in column 3 ($R_p = 0.22$). When this new structural model was compared to the SXRD data, a value of $R_2 = 0.014$ was obtained. This process was then iterated; that is, the vertical positions obtained by LEED are assumed and the SXRD data are fit to obtain a new set of lateral distortion, etc. Iteration did not improve the fit. The structural model

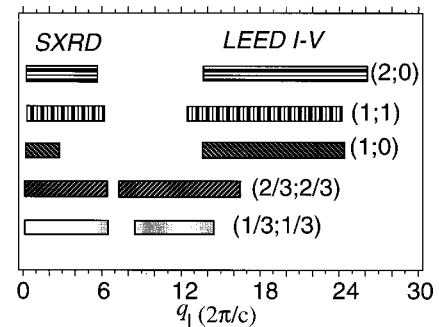


FIG. 1. A comparison of the perpendicular momentum transfer for different beams. The SXRD range is taken from Ref. 8 and the LEED from this work. $c = 9.80 \text{ \AA}$ is the repeat distance going into the bulk, three bilayers.

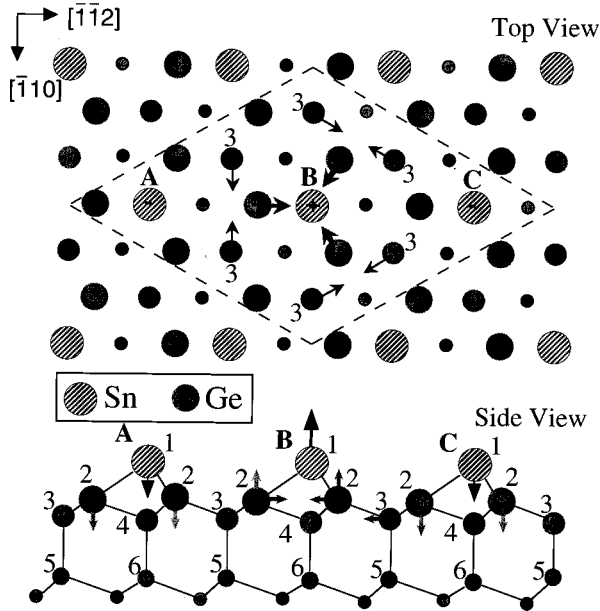


FIG. 2. Structural model of Ge(111)-(3 \times 3)-Sn. The top is a view from above the surface and the bottom is a side view. The arrows show the direction of the distortion-induced charge ordering transition with respect to the $\sqrt{3}$ phase, i.e., the difference between the (3 \times 3) and $\sqrt{3}$ structures.

which gives the best fit to both sets of data is presented in column 4 of Table I. The LEED/SXRD [LEED] structure gives a Sn-Ge bond length of 2.86 Å [2.87 (\pm 0.18) Å], with a “pinching” in of the three Ge atoms in the surface plane by 0.05 Å [0.03(\pm 0.15) Å] (see Fig. 1 in Ref. 8). Within experimental error all Ge-Ge bond lengths are the same as the bulk value of 2.45 Å for both LEED and LEED/SXRD structures. This structure does have an angular distortion in the Ge-Ge bond compared to the ideal sp^3 hybridization.

A structure of the low-temperature (3 \times 3) phase determined by SRXD has already been published, where the PLD was attributed to the motion of the Ge atoms in the surface plane [Ge(2B) in Fig. 2] surrounding one of the three Sn atoms (B). There was no significant vertical distortion of either the Sn atoms or the Ge surface atoms.⁸ When this structural model is compared to the LEED I - V data, the resulting $R_p=0.70$ is totally unacceptable. The best fit to the LEED data (column 2 of Table II) produces a very different structure with appreciable vertical rippling in both the Sn layer (0.36 Å), one atom up (B) and two down (A and C), accompanied with a lateral (0.20 Å) and vertical (0.16 Å) distortion of the first Ge layer. When this structure, determined by LEED, is compared to the SXRD data, the agreement is again poor, $R_2=0.022$ compared to the value of 0.0066 reported for the fit to the SXRD original structural model.⁸ Again, as we did for the room-temperature $\sqrt{3}$ phase, we have searched for a structure that is compatible with both the LEED I - V and SXRD data. In this search, Sn atoms A and C have been constrained to have the same relative position and the SXRD fitting procedure has more parameters than used originally. Table II lists in column 3 the distortions that are experimentally significant for the LEED/SXRD structure.

Generally speaking, it is clear what has occurred. The

TABLE II. Structural distortion measured with LEED, the combination of LEED and SXRD, for the low-temperature (3 \times 3) phase compared to the room-temperature $\sqrt{3}$ phase. The geometry of the surface is shown in Fig. 2.

Structural parameters (Å) with respect to $\sqrt{3}$ structure	LEED I - V		LEED/SXRD
	(A)	(C)	
Δ Sn (A and C)	-0.101	-0.061	-0.015
Δ Sn (B)	+0.294		+0.355
Δd_1 (A and C)	-0.077		-0.036
Δd_1 (B)	+0.086		+0.134
Lateral 1-B	0.199		0.117
Lateral 3	0.260		0.148
$\langle u \rangle_{\text{Sn}}(z,xy)$	(0.293,0.293)		(0.210,0.221)
$\langle u \rangle_{\text{Ge}}(1,2)$	(0.178,0.117)		(0.143,0.044)
$\langle u \rangle_{\text{Ge bulk}}$	0.078		0.032
R_p/R_2	0.20/0.0220		0.24/0.0108

surface has reduced its symmetry to lower its energy. This occurs through a vertical rippling of the Sn layer which induces distortion in the Ge first bilayer (see Fig. 2). All of the resulting distortion results in changes in bond angles trying to minimize any changes in the bond lengths. Consider first the structural changes associated with Sn(B). The outward displacement of Sn(B) accompanied by inward and upward motion of the Ge(2B) atoms creates an appreciable increase in the tetrahedral bond angle [Sn-Ge(2)-Ge(4)], from 65.5° for the $\sqrt{3}$ phase to 77.1° for the (3 \times 3) phase. There is also a change in the Ge tetrahedral bond angle defined by Ge(2B)-Ge(4B)-Ge(6B), from 118° for the $\sqrt{3}$ to 122° for the (3 \times 3). Therefore, the bonding of the Sn to the Ge in the B site becomes more s - p_z -like.¹⁴ The downward motion of Ge atoms 2A and 2C causes a slight increase in the distortion in the tetrahedral formed by Ge(2A)-Ge(3A)-Ge(5A), driving Sn atoms A and C to be more p_x - p_y bonded. The tetrahedral formed by the three Ge(2) atoms, the second-layer Ge(3) atom, and the third-layer Ge(5) atom is more complicated to explain due to the lateral distortion of Ge(3). The Ge(3)-Ge(5) axis is tilted by 3.5° with respect to the surface normal. The three Ge(3)-Ge(2) angles (associated with type A, B, and C Sn) are distorted by +6°, +1°, and +6° with respect to the Ge(3)-Ge(5) axis. The azimuth bond angles in the plane perpendicular to the 3-5 axis are not identical, distorted to 127°, 115°, and 118°, with respect to the ideal value of 120°.

The interplay between the electronic structure, the geometrical structure, and the lattice dynamics can now be understood, at least qualitatively. The system lowers its electronic energy by lowering the symmetry and the price paid in bond-angle distortions is less than the energy gained.¹⁴ The physics is nearly an ideal case of a band Jahn-Teller distortion, discussed by Friedel.¹⁵ A recent calculation by Ortega, Pérez, and Flores¹⁶ using a local-orbital self-consistent in local-density approximation (LDA), molecular-dynamics (MD) technique gave the first indications that this broken symmetry structure might be the ground state. They report a stable (3 \times 3) structure (40 meV per Sn atom) very similar to the structure presented in Table II, a vertical distortion in the

Sn of ~ 0.35 Å (one atom up, two down) accompanied by a vertical distortion in the Ge layer of ~ 0.20 Å.¹⁶ The structure is stabilized by the reduction in symmetry splitting the Sn-derived band into two bands with the one band being completely occupied. This lower band is primarily associated with the up Sn atom (*B* in Fig. 2). The $\sim 12^\circ$ increase in the Ge(*4B*)-Ge(*2B*)-Sn(*B*) bond angle enhances the *s*-*p_z* hybridization in the Sn(*B*) bonding, fully occupying the Sn-dangling hybrid.¹⁶ Therefore, the filled-state image in STM shows one bright Sn atom and two dark Sn atoms.² The upper band is partially occupied and primarily associated with the two down Sn atoms (*A* and *C*). The primarily *p_z* charge character for these atoms (*A* and *C*) is shoved above the Fermi surface, explaining the empty-state STM images.² The photoemission measurements reported in Ref. 16 show two bands consistent with this band Jahn-Teller-like distortion.

There are still numerous unanswered questions concerning the nature of the transition in these systems. If this is a band Jahn-Teller-like distortion at low temperature, there should be an appreciable increase in the rms motion of the atoms above the transition temperature. Tables I and II show that in fact the inverse happens. The effective Debye temperature is lower for the low-temperature phase. The second problem is that the published LDA calculation says that the (3×3) CDW configuration is not stable.² Even the LDA calculation for the Pb overlayer that predicted a stable (3

$\times 3$) structure (7 meV per Pb atom) had a very small (0.02 Å) vertical distortion in the Pb atoms (two up and one down) and an ~ 0.1 Å lateral distortion of the Ge.¹⁸ Ortega, Pérez, and Flores¹⁶ checked the validity of their local-orbital self-consistent approach by performing a plane-wave LDA calculation which gave a similar (3×3) structure, for which the calculated stability was only 5 meV per Sn atom. Our determination of the PLD should become the target for calculations of the CDW stabilizing force. It is essential to determine the stability of the structure presented in this paper using a *fully* converged LDA calculation. Most likely additional electron correlation effects will be important in the stabilization of both the Sn and Ge films. Avila *et al.*¹⁶ have already made this point, comparing the measured bandwidth (Sn derived) of ~ 0.5 eV with the calculated effective intra-site Coulomb interaction of 0.55 eV.¹⁷ In addition, it has been shown that defects can stabilize the CDW,² and theory has suggested that spin and magnetism are important in these systems.^{5,19,20}

We would like to thank Joe Carpinelli for his help at the beginning of this project. E.W.P. would like to thank Wolfgang Moritz for useful discussions. This work was funded primarily by NSF DMR-9801830. J.Z. was supported by NEDO (Japan). Much of the work was conducted at ORNL, sponsored by the Department of Energy, and managed by Lockheed Martin Energy Research Corp. under Contract No. DF-AC05-96OR22464.

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