Temperature Dependence of Surface States with $3\times3-\sqrt{3}\times\sqrt{3}$ Phase Transition on Sn Adsorbed Ge (111) Surface

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The phase transition between $\sqrt{3}\times\sqrt{3}$ and $3\times3$ structures on Sn adsorbed Ge(111) surface is discussed in terms of an order-disorder structural transition. The Monte Carlo calculation is performed to obtain the surface electronic states with a tight-binding model. The calculated reciprocal-space-projected density of states can reproduce both experimental results of the high and low temperature phases by the angle resolved ultraviolet photoemission spectroscopy measurements. [DOI: 10.1380/ejssnt.2010.349]

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I. INTRODUCTION

The Ge(111) surface covered by 1/3 monolayer of Sn is known to undergo a phase transition at approximately 210 K from the $\sqrt{3}\times\sqrt{3}$ structure of the high temperature phase (HT phase) to the $3\times3$ structure of the low temperature phase (LT phase). This phase transition has been discussed in terms of a charge density wave (CDW) [1, 2]. On the other hand, diverse experimental studies have provided evidences that this phase transition is understood as an order-disorder structural transition [3]. It is believed that Sn atoms adsorb on three-fold hollow sites. Here, the Sn atoms may take two types of positions normal to the surface [4]. We refer to the Sn atoms with different “heights” as up and down Sn atoms hereafter. At high temperatures, each Sn atom fluctuates between the up and down positions, and the up-down configuration of the Sn atoms is disordered, resulting in an averaged $\sqrt{3}\times\sqrt{3}$ structure. On the other hand, at low temperatures, each Sn atom takes either the up or down position with the up-down configuration of the Sn atoms forming the $3\times3$ ordered structure [3].

Uhrberg et al. and Kidd et al. measured the surface electronic states of both the $\sqrt{3}\times\sqrt{3}$ and $3\times3$ phase by angle resolved photoemission [6, 7]. Two surface bands are observed in both HT and LT phases. As the periodicity of the surface system changes before and after the phase transition, the folding effect is expected to change the UPS spectrum before and after the phase transition. However, the results of Uhrberg et al. do not show the change caused by the folding effect, and the dispersions are similar between the HT and LT phases. Quantitatively, the position of the surface bands slightly differ between the HT and LT phases. In addition, Kidd et al. observed the extended Fermi edge on $M-\Gamma$ line of the surface Brillouin zone for the $\sqrt{3}\times\sqrt{3}$ HT phase.

In this paper, we construct a theoretical model for describing the phase transition in terms of an order-disorder phase transition. We further introduce a theoretical model and a calculation method for treating the surface electronic states at finite temperatures when the system is in the disordered state and contains short-range ordering [5]. We perform Monte Carlo simulations to demonstrate the change in the electronic states associated with the change in the lattice structure in the phase transition. We compare and discuss the results with the experiment.

II. MODEL

Figure 1 schematically shows the surface structure of the Sn adsorbed Ge(111) surface. The back ground triangular lattice indicates the $1\times1$ structure of the clean Ge(111) surface. Each $\sqrt{3}\times\sqrt{3}$ cell indicated by the thick lines contains a Sn atom. We consider three equivalent sublattices of the adsorbates on this surface system, each of which is indicated by the different shades of the circles representing Sn atoms in each of the sublattices. In the $\sqrt{3}\times\sqrt{3}$ HT phase, the Sn atoms fluctuate between the up and down positions, so that all the adsorbed Sn atoms are equivalent. In the $3\times3$ LT phase, the Sn atoms in two of the sublattices take the down (or up) position while the Sn atoms in the remaining sublattice take the up (or down) position. All the Sn atoms in the same sublattice take the same up or down position though there are still arguments regarding which of the two positions constitute the majority [3, 4].

We use an Ising-type model to handle the surface system. We assume that the experimentally observed LT phase to be the ground state, that is, the Sn atoms in the same sublattice are ordered to either up or down positions with two sublattices at the same height and one different. Then, we consider a degree of freedom with two values for each Sn atom and attribute the “spin” $-1$, to the majority “height” and “spin” 1 to the minority “height”. We take up to the second nearest neighbour interactions. We assume a ferromagnetic-type interaction between the

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Sn atoms within each sublattice, so that the Sn atoms tend to stay in the same position. On the other hand, we assume an antiferromagnetic-type interaction between the Sn atoms in different sublattices. As it is a triangular lattice, these interactions raise a frustration in the system. To suppress this frustration, one may introduce an external field, long-range interactions, or many-body interactions. For convenience, we chose to introduce a three-body interaction. Then the system can be described by the following Ising Hamiltonian:

\[ \mathcal{H}_{\text{lat}} = J_1 \sum_{(\ell, \ell')} S_{\ell} S_{\ell'} + J_2 \sum_{(\ell, \ell')} S_{\ell} S_{\ell'} + V \sum_{(\ell, \ell', \ell'')} S_{\ell} S_{\ell'} S_{\ell''}, \]

where the summations in the first and the second term are taken over the nearest neighbour pairs and the next nearest neighbour pairs, respectively. The summation in the third term is taken over the combination of indices that constructs a nearest neighbour triangle. Here, \( S_\ell \) indicates the upper or lower position of the \( \ell \)-th Sn atom and takes the value either 1 or \(-1\). We refer to it as the “spin”, hereafter. \( J_1 \) is the two-body interaction parameter between the nearest neighbour Sn atoms, which belong to different sublattices. \( J_2 \) is the two-body interaction parameter between the second nearest neighbour Sn atoms, which belong to the same sublattice. \( V \) is the three-body interaction parameter between three nearest neighbour Sn atoms in a triangular arrangement. Other types of three-body interactions are possible. However, as introducing these other interactions does not generate any qualitative differences, we only include the triangular three-body interaction for simplicity.

The parameters are set to reproduce the transition temperature as in Table I. The parameter values for reproducing the transition temperature are not unique. Nevertheless, macroscopic properties such as the total energy or the specific heat are not sensitive to the parameter values and taking different values do not influence the basic nature of the system as long as the transition temperature is reproduced.

We only consider the surface electronic states and handle them with a tight binding approximation. This treatment neglects the intra-atomic Coulomb interaction that is major many-body effect causing the Mott insulator transition reported on this surface system at much lower temperatures [9]. However, this one-body approach is enough powerful to discuss about the CDW transition strongly coupled with lattice displacements. We consider a single electronic state per \( \sqrt{3} \times \sqrt{3} \) unit cell localized around a Sn atom. This electronic state assumes one of the electronic states induced by the Sn atom. The site energy and the transfer integral depend on the “height” of the atom, so that they are functions of the “spin” value. We do not consider the overlap integrals for simplicity. Then, the Hamiltonian for the surface electronic states is expressed as follows:

\[ \mathcal{H}_{\text{ele}} = \sum_{\ell} \epsilon(S_\ell) c_{\ell}^\dagger c_\ell + \sum_{(\ell, \ell')} t_1(S_{\ell}, S_{\ell'}) \left( c_{\ell}^\dagger c_{\ell'} + c_{\ell'}^\dagger c_\ell \right) + \sum_{(\ell, \ell', \ell'')} t_2(S_{\ell}, S_{\ell'}, S_{\ell''}) \left( c_{\ell}^\dagger c_{\ell'} c_{\ell''} + c_{\ell'}^\dagger c_{\ell''} c_\ell \right). \]

Here, \( c_\ell \) and \( c_\ell^\dagger \) are the annihilation and creation operators for the electronic state localized around the \( \ell \)-th Sn atom and \( S_\ell \) is the “spin” of the \( \ell \)-th Sn atom. \( \epsilon(S_\ell) \) is the site energy. \( t_1(S_{\ell}, S_{\ell'}) \) and \( t_2(S_{\ell}, S_{\ell'}, S_{\ell''}) \) are the nearest and the next nearest neighbour transfer integrals for the electronic transfer between electronic states localized around the \( \ell \)-th and \( \ell' \)-th Sn atoms. The transfer integrals are considered up to the second nearest neighbour, so that the second and the third summations are taken over the nearest and next nearest neighbour pairs of Sn atoms, respectively. \( \epsilon(S_\ell) \), \( t_1(S_{\ell}, S_{\ell'}) \) and \( t_2(S_{\ell}, S_{\ell'}, S_{\ell''}) \) are parameters that characterized the model. We use the values indicated in Table II. The values are set to reproduce the experimental electronic structure in the \( 3 \times 3 \) LT phase.

Figure 2 shows the electronic bands for possible \( 3 \times 3 \) and \( \sqrt{3} \times \sqrt{3} \) ordered structures with these parameters.
overlaid on the angle resolved photoemission results of Uhrberg et al. [6]. Here again, the parameter values for reproducing the experimental electronic structure in the 3×3 LT phase are not unique. We select the present parameter set as they are rational and simple. The nearest neighbour electronic transfer is set with the same value except between electronic states localized around Sn atoms in minority positions, the absolute value of which is set smaller than the others. The second nearest neighbour is set with the same value for all combinations of the Sn atom positions. Consequently, the band for the 3×3 ordered structure with all Sn atoms at position 1 appears on the lower experimental band for the √3×√3 phase, and the band for the 3×3 ordered structure with all Sn atoms at position −1 appears on the higher experimental band for the 3×3 phase near the K point.

In this scheme, the high temperature phase is essentially a disordered system. In such a disordered system, the wavenumber is not a good quantum number. Thus, the band structure cannot be discussed in the usual energy-wavenumber dispersion. To discuss the electronic states in the reciprocal space for disordered structures, we define a quantity that we call the reciprocal-space projected density of states (RDOS) [5]. Denoting the n-th eigenenergy of the Hamiltonian (eq. (2)) as \( E_n \), the n-th eigenfunction as \( |n⟩ \), and the Bloch function corresponding to the wavenumber \( \mathbf{k} \) as \( |\mathbf{k}⟩ \), the RDOS, \( \hat{D}(\mathbf{k}, \varepsilon) \), for electrons with wavenumber \( \mathbf{k} \) and energy \( \varepsilon \) is expressed as:

\[
\hat{D}(\mathbf{k}, \varepsilon) = \sum_n |⟨\mathbf{k}|n⟩|^2 \delta (\varepsilon - E_n),
\]

Here, \( |\mathbf{k}⟩ \) is basis for projecting the density of states (DOS), \( \hat{D}(\varepsilon) = \sum_n \delta (\varepsilon - E_n) \), to the reciprocal space.
FIG. 5: Left panels are the density plots of RDOS, which is roughly corresponding to the band mapping by ARUPS measurement. The filled and open circles represent the experimental results of ARUPS for $\sqrt{3}\times\sqrt{3}$ and $3\times3$ surfaces. Right panels are snapshots where bright circles indicate up atoms site of Sn adsorbates.

With this RDOS, the DOS is expressed as:

$$D(\varepsilon) = \sum_{\vec{k}} D(\vec{k}, \varepsilon).$$

(4)

We evaluate this RDOS to examine the electronic structure of the system. The RDOS provides the band mapping in the reciprocal space that can be compared with the experimental results of ARUPS measurements. The band mapping reflects only DOS. In order to reproduce the photo electron spectra themselves we need the complete information about matrix elements of photo electrons. Particularly, the band mapping for ordered structure has too sharp shape to compare with the experimental spectra because of the delta-function like DOS.

III. CALCULATION

We perform Monte Carlo simulations based on the Metropolis algorithm using the two models. In each Monte Carlo step, the configurations of the Sn atom position are first updated based on the Isin model using the Metropolis algorithm. We take a system consisting of $72\times72$ of the $\sqrt{3}\times\sqrt{3}$ cells with periodic boundary condition. First, 10,000 samples are generated to ensure the equilibrium, and lattice-related physical quantities are averaged over further 10,000 samples. The electronic states are calculated with the tight binding model for a part of the configuration generated by the Metropolis algorithm containing $24\times24$ of the $\sqrt{3}\times\sqrt{3}$ cells with the periodic boundary condition applied. The electronic states are calculated by the numerical diagonalization method. With the eigenfunctions obtained, the RDOS is calculated based on eq. (3) except that the delta function is replaced by a gaussian due to the nature of a numerical calculation. The RDOS is averaged over 1,000 samples.

Figure 3 shows the long-range order parameter (LOP) defined by the structure factor corresponding to a $3\times3$ fractional spot and the generalized susceptibility that is calculated as the mean square of LOP divided by the temperature. As indicated by the sharp rise of the LOP and the sharp peak in the generalized susceptibility, which are characteristics of a second order phase transition, the phase transition takes place at approximately 210 K as we set up. Figure 4 shows the short-range order parameter (SOP) with the average of the “spin” value in each of the sublattices. The SOP is defined by $\langle S_\ell S_{\ell'} \delta(S_{\ell} - 1) \rangle$, where $\ell'$ are limited to nearest neighbors. That is the correlation of the “spin” values between a minority “spin” and its nearest neighbour sites together. The temperature dependence of the averaged “spin” within each sublattice shows a simular behaviour of the LOP. The averaged “spin” abruptly changes at the transition temperature whereas the SOP changes continuously even at the transition temperature and remains considerably above the transition temperature. This indicates that the system considerably retains the short-range ordering above the transition temperature though apparently random.

Figure 5 shows the RDOS for low and high temperatures and snapshot of the “up-down” configuration of the
Sn atoms, that is roughly corresponding to the STM image. At 50 K, the surface is mostly ordered to a 3×3 structure and the RDOS correspondingly has high intensity where the experimental surface bands for the 3×3 phase lies. At 270 K, the surface lacks short-range ordering and the RDOS has high intensity where the experimental surface bands for the √3×√3 phase lies.

**IV. DISCUSSION AND SUMMARY**

In this calculation, the tight binding parameters are set to reproduce the 3×3 states found in the experiment. Thus, it is only natural that the RDOS has high intensity at low temperatures where the experimental surface bands for the 3×3 phase lies. However, it is surprising that the RDOS at high temperatures automatically reproduces the experimental surface electronic bands [6] for the √3×√3 phase, including the extended Fermi edge reported by Kidd et al. [7], even though the parameters are set without considering the √3×√3 phase. When the surface is ordered, the electrons are scattered by the lattice with the scattering vector corresponding to the lattice vectors. When the surface randomness increases, the interference effect with diverse scattering vectors appears. Consequently, the RDOS contains weak contributions from the diverse types of scattering vectors. This effect on one hand blurs and broadens the RDOS, and on the other, influences where the RDOS has high intensity. As the contribution form smaller periodicity is considered to be larger, high intensity of the RDOS appears near where the bands for ordered states of the smallest periodicity lies, in this case, the √3×√3 ordered states as indicated in solid and dash-dotted curves in Figure 3, but where the contributions from larger periodicities also have high intensity. This softens the RDOS and results in the increase in the band position near the \( \bar{K} \) point at high temperatures.

Thus we can understand the surface electronic structure change accompanied with the phase transition in terms of an order-disorder phase transition. This results suggests that the CDW on this surface system is strongly coupled with the lattice displacements [8] like as one dimensional system. Therefore, the position of the adsorbed Sn atoms should be a good order parameter to describe this CDW phase transition.

To describe the phase transition observed on the Sn adsorbed Ge(111) surface and demonstrate the change in the electronic states through the phase transition, Monte Carlo simulations are performed using an Ising-type model for the lattice configuration and a tight binding model for the electronic states are constructed. At low temperatures, the surface is mostly ordered to 3×3 structure and the corresponding surface bands are observed. At high temperatures, the surface is mostly random. Consequently, the bands are blurred and softened reflecting the randomness of the surface. The change in the electronic states is due to the contributions from electron scattering vectors corresponding to larger periodicity of the lattice, which are abundant at high temperatures but do not exist at low temperatures.

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