X-ray Diffraction Study of Charge-density-wave Phase Transition on In/Cu(001)

There is a growing interest in phase transitions in ultrathin films and wires. This is due in part to the technological trends toward electronic devices with dimensions much smaller than those of the currently used ones. The phenomena of interest include Peierls-type charge-density-wave (CDW) phase transitions, which are driven by the electron–phonon interaction in metallic materials with low-dimensional electron systems and are associated with changes in transport properties, which thus potentially useful in applications such as switching and memory.

As solid surfaces and interfaces provide quasi-two-dimensional electron systems, efforts have long been made to the observation of CDW transitions restricted to a few atomic layers on surfaces. Recently, intriguing surface phase transitions [1] have been found and a Peierls-type scenario was suggested as the driving mechanism. These phase transitions have received wide attention. However, in spite of extensive investigations, the driving mechanism is still a matter of intense controversy. The confusion is partly due to the difficulty of quantitatively characterizing phase transitions restricted to a few atomic layers on surfaces. Since the CDW phase transitions are driven by electronic and lattice degrees of freedom coupled with each other, it is desirable to study the dynamical behavior of the electrons and the lattice during the phase transition; this, however, has not yet been realized for these surface phase transitions.

Most recently, we have studied the phase transition on the Cu(001) surface covered with 0.63 ML of In. Grazing-incidence surface X-ray diffraction (GISXRD) [2] was used to observe the critical behavior of the lattice [3]. Angle-resolved photoelectron spectroscopy (ARPES) was used to study the temperature dependence of the CDW energy gap [4]. Only by combining these two classes of experimental data, we have succeeded in constructing a comprehensive picture of the CDW phase transition on this surface [3].

Figure 1 shows scanning-tunneling-microscopy (STM) images for the high-temperature (HT) p(2×2) and low-temperature (LT) c(4×4) phases. The phase transition is reversible. We have found by ARPES that the energy gap is formed at the Fermi level during the phase transition from the HT to LT phase. The energy gap coincided with the Brillouin zone of the LT c(4×4) phase, which indicates that the transition is a Peierls-type CDW transition. We also determined the temperature dependence of the absolute energy gap (energy interval between lower and higher bands). Upon elevating the temperature, the energy gap gradually decreases from 120 to ~300 K, decreases more significantly from 300 to ~370 K, and changes steeply above ~370 K to reach zero at $T_{c(elec)}$ = 405 K. The behavior is apparently in accordance with that predicted by the BCS gap equation and could be interpreted as indicative of the weak-coupling CDW phase transition, which assumes dominant contribution of electronic entropy. However, the GISXRD experiment carried out at beamline **BL13XU** clearly shows that this is not the case.

Typical diffraction profiles measured near the transition temperature are shown in Fig. 2. At low temperatures, the profiles can be well fitted with a single Lorentzian with a width of ~0.002 r.l.u., which corresponds to a transfer width of ~200 nm. Above 345 K, the profile gets broader and can be fitted with the sum of two components, a long-range one with the same width as those at low temperatures and a short-range one with a variable width, as shown in the middle panel of Fig. 2. The long-range component disappears just above 345 K and the short-range component decreases in intensity and gets broader with increasing temperature.

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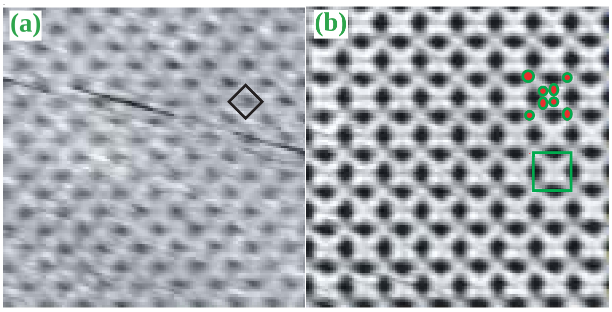

Fig. 1. STM images of **(a)** high-temperature p(2×2) and **(b)** low-temperature c(4×4) phases.

same width as those at low temperatures and a short-range one with a variable width, as shown in the middle panel of Fig. 2. The long-range component disappears just above 345 K and the short-range component decreases in intensity and gets broader with increasing temperature.

We deduced from these data the long-range order parameter, susceptibility, and correlation length, which are shown as functions of temperature in Fig. 3. Also shown are power-law curves with a sole fitting parameter of T_c and fixed exponents, $\beta = 1/8$, $\gamma = 7/4$, and $\nu = 1$. The curves are in good agreement with the data, which show unambiguously that an order-disorder phase transition classified into 2D using universality class takes place at $T_{c(\mathrm{lattice})} = 345$ K.

The seemingly contradicting results of ARPES and GISXRD point to a scenario that suppose the cooperative roles of electronic and phonon entropy terms. The system is characterized by two energies: The zero-temperature CDW energy gap (~ 800 meV) determines the CDW condensation energy. A relatively large gap size leads to the enhanced effect of fluctuation. On the other hand, the energy separation of the upper CDW band from the Fermi level (< 200 meV) governs the excitation of bulk electrons to the upper band and thus the electronic entropy of the system. We thus conclude that the phase transition on the In/Cu(001) surface is a CDW phase transition driven concertedly by the electronic and phononic entropies.

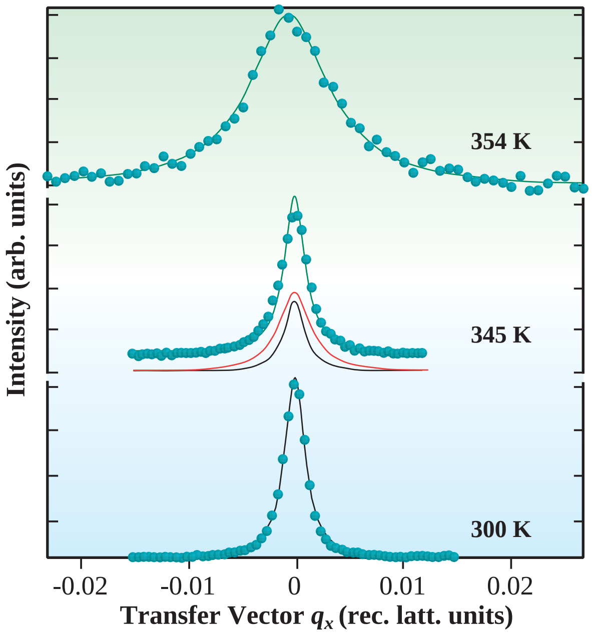

Fig. 2. Typical diffraction profiles measured for In/Cu(001) near the transition temperature.

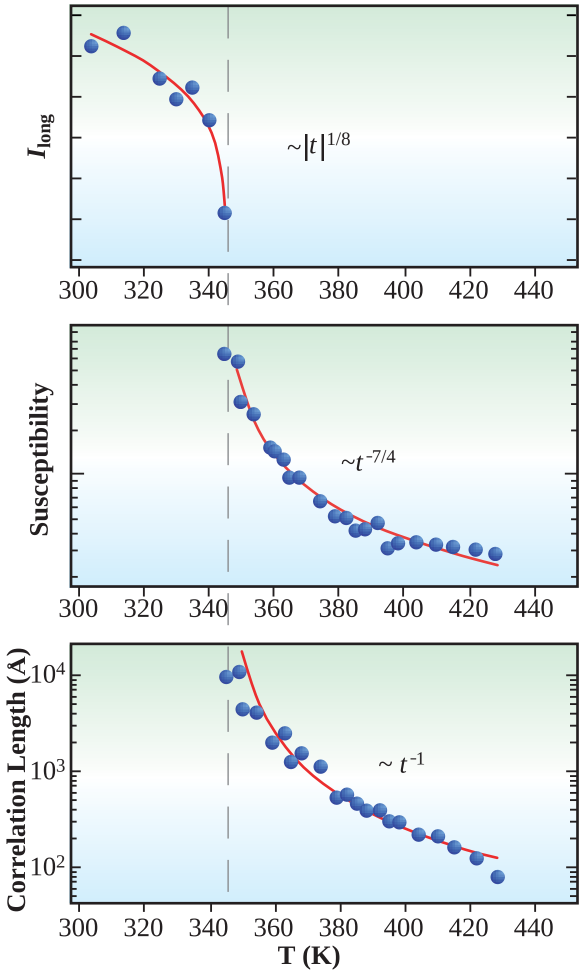

Fig. 3. Temperature dependences of long-range order parameter I_{long}, susceptibility, and correlation length. $t = (T - T_c)/T_c$, where T_c denotes the transition temperature.

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