

## Temperature dependence of the charge-density-wave energy gap on In/Cu(001)

S. Hatta, H. Okuyama, M. Nishijima, and T. Aruga\*

*Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan*

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A charge-density-wave (CDW) phase transition on In/Cu(001) with In coverage of 0.63 ML has been studied with angle-resolved photoelectron spectroscopy. Because of the quasi-two-dimensional electronic structure, the upper and lower bands of the CDW ground state were observed at a  $k$  point slightly offset from  $k_F$  of the high-temperature phase. The two bands transformed to a metallic band at 405 K. Tracing the upper-band minimum and the lower-band maximum, we determined the temperature dependence of the CDW order parameter. The dependence indicates that the electronic entropy plays an important role in the transition. We discuss the enhanced contribution of electronic entropy to the free energy due to underlying bulk metallic states.

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Peierls-type charge-density-wave (CDW) ground states originate from the instability of low-dimensional electronic systems. At low temperatures (LT), the response functions of low-dimensional electronic systems show strong singularity at a wave vector spanning the Fermi surface. Such a system is unstable toward the formation of a periodic lattice distortion.<sup>1</sup> Once a CDW ground state arises, the energy gap  $2\Delta$  is formed at the Brillouin-zone boundary. The size of  $\Delta(0)$  at absolute zero temperature is determined by the strength of the electron-phonon ( $e$ -ph) coupling.

The free energy of a CDW ground state is generally described by electronic energy, electronic entropy and lattice entropy terms. In the limit of weak  $e$ -ph coupling, electronic terms dominate the temperature dependence of the free energy and  $\Delta(T)$  is expected to obey a continuous analytic equation.<sup>1</sup> There have been, however, few studies conducted directly on the temperature dependence of an overall CDW energy gap because of experimental difficulties, while the temperature dependence of the lattice distortion amplitude has been sometimes studied instead.<sup>2-4</sup>

A CDW energy gap is defined as the difference between a lower-band maximum and an upper-band minimum. While angle-resolved photoelectron spectroscopy (ARPES) is a powerful method to determine the electronic structure of matters, it is usually difficult to determine the CDW gap size by this method since it is sensitive only to occupied electronic states. In literature it was often assumed that the middle of the CDW gap was located at the Fermi level ( $E_F$ ), which enabled ones to equate  $\Delta$  with the binding energy of the occupied state maximum.<sup>5-10</sup> The assumption, however, is not guaranteed in general, in particular, for systems with a two-dimensional (2D) Fermi surface. In such a system, the surface Brillouin-zone (SBZ) boundary for a CDW phase does not completely coincide with the Fermi wave vector  $k_F$  for the high-temperature (HT) phase, and hence the reference energy at which the upper and lower bands encounter with each other at the transition temperature  $T_c$  does not agree with  $E_F$ . It is therefore desirable to observe both the upper and lower bands in order to determine the CDW gap size exactly.

A phase transition has been observed at  $\sim 400$  K on In/Cu(001) with 0.63-ML coverage. The low-energy elec-

tron diffraction (LEED) showed the periodicity of the LT and HT phases as  $c(4 \times 4)$  and  $p(2 \times 2)$ , respectively.<sup>11</sup> The In-induced surface resonance band originating from a hybridization between Cu  $4sp$  and In  $5sp$  states was observed,<sup>12</sup> which constitutes a circular Fermi surface in the HT phase.<sup>13</sup> It was found that in the LT phase an energy gap across  $E_F$  is formed in the vicinity of the Fermi surface crossing the  $c(4 \times 4)$  SBZ boundary. In the ARPES spectra taken at or below 300 K, only the lower band was observed and its maximum was located at  $\sim 600$  meV below  $E_F$ , which indicates that the LT  $c(4 \times 4)$  phase is stabilized by the Peierls mechanism.<sup>11</sup> Strong variation of the CDW gap size in the  $k$  space was also observed. This behavior is interpreted as due to the  $k$  dependence of the  $e$ -ph coupling.

In the present work, we investigated by ARPES the temperature dependence of the CDW gap on the  $c(4 \times 4)$  surface. By selecting a  $k$  point so that the CDW gap is developed about the reference energy lower than  $E_F$ , both the upper and lower bands for the CDW ground state were observed. With increasing temperature the CDW gap size was gradually decreased and the two bands were eventually merged into a metallic band at 405 K. Thus we succeeded in directly estimating the temperature dependence of the CDW order parameter. The dependence implies that the electronic entropy plays an important role for the surface phase transition.

Experiments were done with an ARUPS10 (VG Microtech) electron spectrometer and a high-flux He discharge lamp in combination with a toroidal mirror monochromator (Specs) which yielded He-I $\alpha$  radiation (21.22 eV) with a high spectral purity. The total-energy resolution was 45 meV, and the acceptance angle was  $1^\circ$ . The Cu(001) sample was cleaned by repeated cycles of Ar ion sputtering and annealing at 800 K. Indium was evaporated from an alumina crucible. The well-ordered  $c(4 \times 4)$  surface at room temperature was made by postannealing as reported in the previous work.<sup>11</sup> The cleanness of the sample was checked by observations of the Cu(001) surface state at  $\bar{M}$  and a sharp LEED pattern. The phase transition was confirmed by LEED. We were able to heat the sample by a tungsten filament at the back of the sample. The filament currents were modulated to

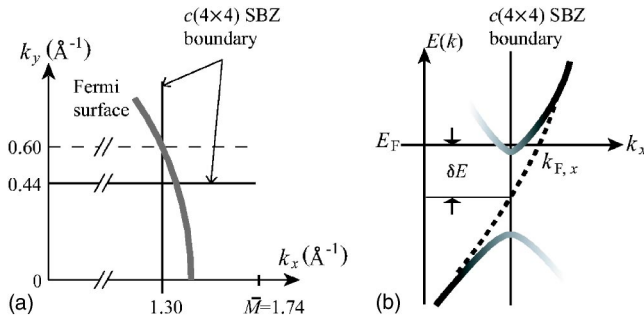


FIG. 1. (a) The relation between the Fermi surface of the  $p(2 \times 2)$  surface and the  $c(4 \times 4)$  SBZ boundaries. (b) Schematic of the CDW gap opening asymmetrically to  $E_F$ . The heavy solid lines show the upper and lower bands in the low-temperature phase and the heavy broken line shows the metallic band in a high-temperature phase.

measure photoelectrons during currentless periods by synchronizing and gating the detector electronics appropriately.

Figure 1(a) shows schematically the Fermi surface for  $p(2 \times 2)$  and the  $c(4 \times 4)$  SBZ boundaries. The  $k_x$  and  $k_y$  axes are defined along the  $[100]$  and  $[010]$  directions, respectively. For the  $p(2 \times 2)$  surface, the Fermi surface crosses the  $c(4 \times 4)$  SBZ boundary at  $k_y \sim 0.6 \text{ \AA}^{-1}$ . At  $k_y < 0.6 \text{ \AA}^{-1}$ ,  $k_{F,x}$  exceeds the  $c(4 \times 4)$  SBZ boundary and the energy gap would open with respect to the reference energy,  $\delta E$ , lower than  $E_F$  as shown in Fig. 1(b). This makes it possible to observe the upper and lower bands by ARPES at temperatures near  $T_c$ . On the other hand, the energy-gap size rapidly becomes small where we come too much apart from the crossing. We therefore measured the surface resonance band along  $k_x$  at  $k_y = 0.51 \text{ \AA}^{-1}$ .

Figures 2(a)–2(c) shows the surface resonance mapped at various temperatures. The high intensity is shown bright. The intensity is normalized to the Fermi distribution function at each temperature, which allows us to observe the electronic states up to  $\sim 0.2$  eV above  $E_F$ . The  $c(4 \times 4)$  SBZ boundary is located at  $k_x = 1.30 \text{ \AA}^{-1}$ . At 305 K, the surface resonance band is backfolded at the  $c(4 \times 4)$  SBZ boundary, and its maximum is located at 590 meV below  $E_F$ . In the previous work,<sup>11</sup> the metallic band did not completely disappear in the LT phase, due to the remnant  $p(2 \times 2)$  domains stabilized by surface incompleteness such as defects. In our experiment,

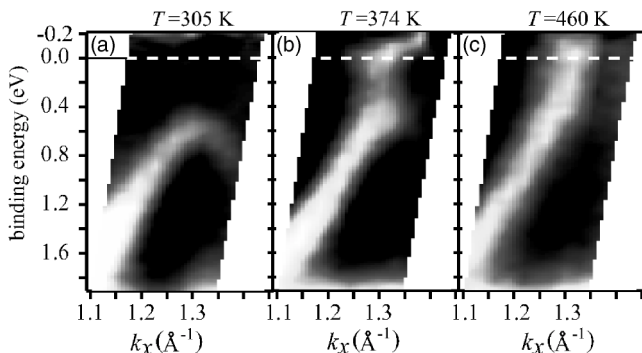


FIG. 2. (a)–(c) The surface resonance band mapped at 305, 374, and 460 K, respectively. The white dashed line denotes  $E_F$ .

using the samples prepared carefully, such bands were not observed at low temperatures as shown in Fig. 2(a). At 374 K, while the surface resonance band is still backfolded to the higher binding energies, the maximum moves to  $\sim 500$  meV, and an additional band is observed around  $E_F$ . This is in good agreement with what was expected in Fig. 1(b). The spectral weight is concentrated on the extended-zone-scheme dispersion in Fig. 2(b), probably because of the photoemission matrix-elements effect. The surface resonance band crosses  $E_F$  at  $k_x = 1.34 \text{ \AA}^{-1}$  at 460 K, where the surface has the  $p(2 \times 2)$  periodicity.

Since the upper and lower bands are shifted to opposite direction in energy, the energy balance should be examined. For the bands at  $k_y = 0.51 \text{ \AA}^{-1}$ , the integrated electronic energy for  $1.1 \leq k_x \leq 1.5 \text{ \AA}^{-1}$  shows monotonous decrease, which indicates that the energy decrease due to the downward shift of the lower band is greater than the increase due to the upward shift of the upper band. Although such an estimation for a part of  $k$  space does not represent the total electronic energy balance of the two-dimensional system, it is expected that the electronic energy decrease with temperature lowering is achieved at most of  $k$  space. A study revealing the anisotropic gap distribution over the entire SBZ must be very interesting. For this system, however, there are experimental difficulties such as the bulk band disturbing the surface band features in the spectra.

The spectra at  $(k_x, k_y) = (1.30 \text{ \AA}^{-1}, 0.51 \text{ \AA}^{-1})$ , which is the turning point of the surface resonance band, for temperatures below and just above the gap closing are shown in Fig. 3. The intensities of the spectra above room temperature are normalized to the Fermi distribution functions. In the normalized spectra, the only data points with raw counts higher than  $\sim 100$  are shown. Above 365 K, two peaks indicated by inverse triangles approach each other with increasing temperature. It is notable that the binding energy of the upper-band minimum depends on temperature, supporting that the upper band we call here is an upper branch of the CDW state. Finally, they are merged into a single peak between 400 and 410 K. We hence determined that the phase transition occurred at 405 K.

Figure 4 shows the binding energies of both the lower-band maximum and the upper-band minimum at temperatures from 120 to 410 K. The shift of the lower-band maximum below 300 K is significant as seen in the spectra at the bottom of Fig. 3, which shows the energy shift of  $\sim 50$  meV between 120 and 305 K in good agreement with the previous result.<sup>11</sup> This cannot be accounted for by the fluctuation effect, which might be important near  $T_c$ , and indicates that the electronic terms undergo significant changes even below 300 K.

It might be interesting to compare the observed temperature dependence with that expected for the weak-coupling CDW (WCDW) phase transition. In the weak-coupling limit, the temperature dependence of  $\Delta$  is given by a nonlinear equation,

$$\frac{1}{\lambda} = \int_0^{\epsilon_0} \tanh\left(\frac{\epsilon_k}{2k_B T}\right) \frac{d\epsilon_k}{(\epsilon_k^2 + \Delta^2)^{1/2}}, \quad (1)$$

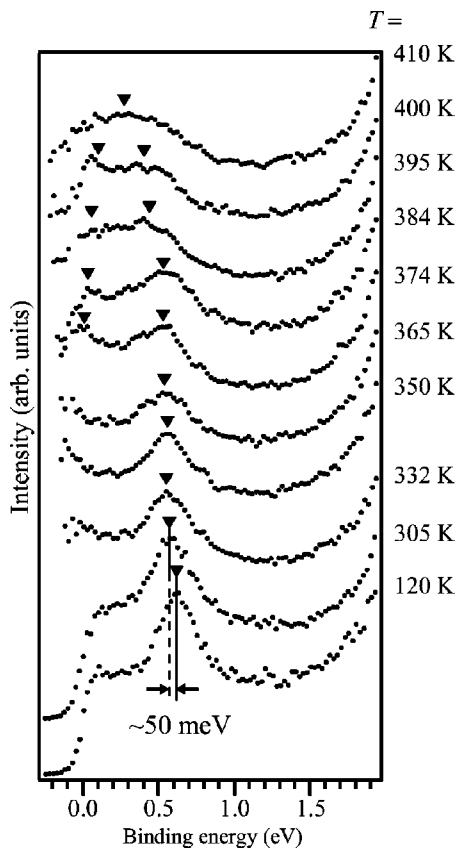


FIG. 3. Spectra between 120 and 410 K, at the  $c(4 \times 4)$  SBZ boundary. Intensities above room temperature are normalized by the Fermi distribution function. Inverse triangles indicate the upper-band minima and lower-band maxima.

where  $\epsilon_0$  denotes a cutoff energy and  $\lambda$  the dimensionless  $e$ -ph coupling constant.<sup>1</sup> An equation of the same form is also seen in the BCS theory for the superconductivity. This gives rise to a weak temperature variation at temperatures much below  $T_c$ , while in the region just below  $T_c$  the temperature variation approximates to  $\propto [1 - (T/T_c)]^{1/2}$ . We fitted Eq. (1) to the temperature dependence of the lower-band maximum and the upper-band minimum. The solid lines in Fig. 4 show the results of the fitting of Eq. (1), for the upper and lower bands, respectively, with adjustable parameters of  $\delta E$ ,  $\Delta_u(0)$ , and  $\Delta_l(0)$ .  $\Delta_u(0)$  and  $\Delta_l(0)$  are defined so that the upper-band minimum and the lower-band maximum have the binding energies of  $\delta E - \Delta_u(0)$  and  $\delta E + \Delta_l(0)$ , respectively, at  $T=0$ .  $T_c$  is fixed at 405 K. The comparison between the experiment and the theory seems to give fair agreement. The fitted values of  $\Delta_l(0)$  and  $\Delta_u(0)$  are  $310 \pm 30$  meV and  $550 \pm 150$  meV, respectively. Therefore the energy-gap size at the zero temperature is estimated to be  $860 \pm 180$  meV at  $T=0$ . The value of  $\delta E$  is 320 meV, which is shown by a dashed line in Fig. 4. This is in good agreement with the value of  $\sim 300$  meV expected from the metallic band dispersion at 460 K and the difference between  $k_{F,x}$  and the  $c(4 \times 4)$  SBZ boundary,  $0.04 \text{ \AA}^{-1}$ , at  $k_y = 0.51 \text{ \AA}^{-1}$ .

A linear dispersion relation is assumed for the HT phase in the usual WCDW theory, which gives rise to the  $\Delta(T)$  value common to the upper-band minimum and the lower-

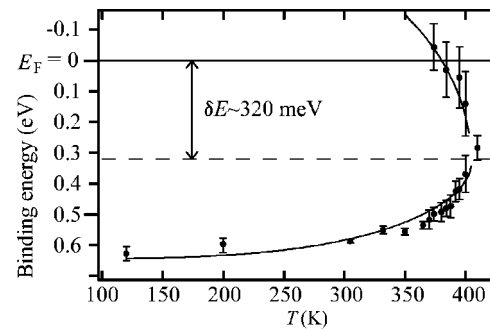


FIG. 4. The temperature dependence of the lower-band maximum and the upper-band minimum. The solid curves are the theoretical curves fitted for the data.

band maximum. The metallic band at 460 K, however, disperses more steeply toward the higher  $k_x$ , which necessarily results in  $\Delta_u(0)$  larger than  $\Delta_l(0)$ .

The temperature dependence of the lower-band maximum is roughly represented by the theoretical curve. The theoretical curve covers well the behavior at lower temperatures such as the energy shift between 120 and 300 K. This indicates the importance of the electronic entropy and energy as in the WCDW phase transitions. On the other hand, the observed temperature dependence is more rapid than the theoretical curve near the transition temperature. Most probably it is due to the fluctuation effect, which is neglected in the mean-field theory.

In the WCDW theory, because the size of  $2\Delta$  is considered to be at most  $\sim 100$  meV, the occupancy distribution near  $E_F$  is sensitive to temperature, i.e., the electronic entropy dominates the temperature dependence of the free energy. In contrast, for a CDW ground state having a large energy gap as in the present case, the electronic entropy should become important only at very high temperatures ( $\geq 1000$  K). Instead, the lattice entropy can become dominant at lower temperatures in the temperature dependence of the free energy, and can cause an order-disorder transition, as described in the strong-coupling CDW (SCDW) scenario.<sup>14-18</sup> The order-parameter amplitude  $|\Delta|$  remains finite during the transition, while the coherence of the phase disappears.

It was suggested in the previous work,<sup>11</sup> based on a relation between the coverage ( $5/8$  ML) and the periodicity, that the phase transition is of an order-disorder type, which is supported by the agreement of the integer- and half-order LEED  $I$ - $V$  curves from the two phases. A sign of the onset of the order-disorder transition is visible in the temperature dependence of the LEED spot intensities, where the fourth-order spot shows rapid decrease from  $\sim 350$  K deviating the Debye-Waller slope. This may indicate that an order-disorder-type structural transition takes place at  $\sim 350$  K, which is  $\sim 60$  K lower than  $T_c$  for the electronic transition. This is in qualitative agreement with the SCDW scenario.

However, in the present case, the electronic entropy plays an important role even below the order-disorder transition. Moreover, although a small drop of the energy gap accompanying the order-disorder has been expected in a theoretical work on SCDW,<sup>14</sup> such a sign was not observed around 350

K in our data. In the SCDW theory it is assumed that the order-disorder transition temperature is much lower than the mean-field transition temperature. On the other hand, these transitions occur only within  $\sim 60$  K on In/Cu(001). In such a case, the electronic and lattice terms are not separable, which would yield previously unexpected behavior. The observed temperature dependence of the energy gap demonstrates that the electronic entropy plays a significant role.

The ratio of  $2\Delta(0)/k_B T_c$  has been used to classify CDWs into WCDW and SCDW. The value for one-dimensional WCDW is 3.52 within the mean-field approximation. The experimental values for actual one- or two-dimensional CDW materials lie in the range of 5-10. Our result corresponds to the ratio of  $\sim 17$ . It might be surprising that the temperature dependence shows the behavior similar to the WCDW theory in spite of such a large energy gap.

The CDW transition occurs on the surface of a metallic substrate in the present case. The bulk states of the Cu substrate have no energy gap across  $E_F$  around the  $c(4 \times 4)$  SBZ boundary. While the lower CDW band lies deep in energy below  $E_F$ , electrons can be excited thermally from the bulk band near  $E_F$  to the upper CDW band. This indicates that the effective gap size that governs the electronic entropy should be defined by the energy difference between the upper-band minimum and  $E_F$ . The upper-band minimum is located at  $\Delta_u(0) - \delta E = 230 \pm 150$  meV above  $E_F$  at  $T=0$ . Consequently,  $2\Delta(0)/k_B T_c$  is estimated to be  $\sim 7 \pm 4$ , which is a reasonable value for quasi-two-dimensional WCDW.

While the lower-band maximum remains at  $\sim 600$  meV under  $E_F$  at  $k_y = 0.44\text{-}0.60 \text{ \AA}^{-1}$ , the energy-gap size decreases

rapidly above  $k_y = 0.6 \text{ \AA}^{-1}$ . Below  $k_y = 0.44 \text{ \AA}^{-1}$ , the small gap opens below  $E_F$ . Therefore the upper-band minimum is always located closer to  $E_F$  than the lower-band maximum, in the  $k$  region where the large energy gap opens across  $E_F$ , which guarantees that the scenario discussed above is significant in the present case.

Thus the WCDW behavior in spite of the large CDW gap is ascribed to the coupling between the bulk metallic states and the surface resonances. While there have been few discussions on the contribution of bulk electronic structure on a surface CDW transition, this effect should be important in other surface CDWs on metals and narrow-gap semiconductors.

In summary, we measured the temperature dependence of the surface resonance band during the phase transition on In/Cu(001) with 0.63 ML. By selecting the appropriate part of the Fermi surface, we were able to observe the upper and lower bands, which encountered at 320 meV under  $E_F$  at 405 K. The temperature dependence of the energy gap showed a behavior very similar to that expected in the WCDW theory even though the lattice fluctuation is significant. The coupling of the bulk metallic states and the surface resonances leads to the effective energy gap smaller than the CDW gap and the enhanced contribution of the electronic entropy to the free energy.

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\*Email address: aruga@kuchem.kyoto-u.ac.jp

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