Critical behavior of the $p(2\times1)$-O/W(110) system

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We have investigated the critical behavior of a two-dimensional phase transition of the $p(2\times1)$ oxygen overlayer on a W(110) surface, using high-resolution low-energy-electron diffraction (LEED). The temperature dependence of a characteristic $(\frac{1}{2}0)$ LEED spot of the $p(2\times1)$ structure reveals a power-law divergence for the susceptibility and correlation length of the critical scattering near the transition temperature of 709 K. Two independent exponents estimated from line-shape analyses are $\beta=0.19\pm0.05$ and $\gamma^-=1.48\pm0.34$ for $T<T_c$, showing significant deviations from those of the two-dimensional (2D) Ising model. Other exponents estimated by the scaling relations agree qualitatively with experimental values. We further observe that the exponent η near T_c also shows large deviation from the theoretical value. We find that these nonuniversal values for the exponents are consistent with the 2D XY model with cubic anisotropy.

I. INTRODUCTION

With the recent advent of numerious high-resolution experimental techniques, intensive studies of the critical behavior of two-dimensional chemisorbed adlayers, which often exhibit order-disorder phase transitions, have been made to test the rich theoretical predictions.[1-11] By identifying a system into one of the universality classes, we obtain valuable information such as fluctuation correlation functions and interatomic or molecular interactions.

Despite the inevitable nonideal experimental conditions including finite-size effects and limited capability of approaching an exact transition temperature T_c, many systems of various symmetries have been successfully studied to extract critical exponents well fitted to the corresponding universality classes of the Ising model[1,2] the three-state[3,4] or four-state Potts model,[5] and the XY model with cubic anisotropy.[6,7]

The system O/W(110) has been studied extensively in the past with little effort concerning the critical properties.[8-10] The system shows a series of low-energy-electron-diffraction (LEED) patterns: the $p(2\times1)$, $p(2\times2)$, and (1×1) phases at oxygen coverages 0.5, 0.75, and 1.0 monolayers (1 ML$=1.42\times10^{12}$ atoms/cm^2), respectively.[8] In this work, we report results of a high-resolution low-energy-electron-diffraction (HRLEED) study of the $p(2\times1)$ phase at the saturation coverage of 0.5 ML. At this coverage, the system satisfies requirements for a study of critical behavior; it becomes closed in a limited range of temperature and shows an order-disorder transition with a transition temperature T_c near 700 K. Moreover, the substrate remains unconstructed, in contrast to the H/W(110) system,[11] so that the critical properties are effectively caused by adatom-adatom lateral interactions.

II. EXPERIMENT

The measurements were made with a HRLEED diffractometer similar to that used previously,[12] which has a spatial resolution of about 3000 Å. The effective transfer width was determined from a measurement of full width at half maximum (FWHM) of a normal reflection (01) as a function of the incident electron energy E, where we observe an oscillatory behavior from the surface step structures. By choosing a relative minimum of FWHM at $E=160$ eV, the maximum transfer width was found to be about 500 Å. We note that the effective transfer width was not limited by the apparatus transfer function but by the crystal imperfections. The tungsten single-crystal sample was a ribbon shape of dimensions $5\times30\times0.25$ mm^3 and its surface was carefully oriented to within $\pm0.2°$ of the (110) plane and thoroughly cleaned in ultrahigh vacuum using a well-known recipe.[11] The base pressure during the measurements was maintained below 1×10^{-10} Torr.

The sample was resistively heated with gated heating current. Temperature was measured with a W5%Re/W25%Re thermocouple spot welded to the rear surface of the sample and the temperature variation during a measurement was about ±1 K. In order to find the saturation coverage (0.5 ML) of the $p(2\times1)$ phase, intensity and FWHM of a half-order spot $(\frac{1}{2}0)$ vs oxygen coverage were obtained and then the best-defined $p(2\times1)$ phase having maximum intensity and minimum FWHM was taken as the saturation coverage. No attempt was made to determine the absolute coverage of oxygen in this work.

We assured the closeness of this $p(2\times1)$ phase by observing no significant change of its shape and FWHM of the $(\frac{1}{2}0)$ spot after repeated cycles of heating (up to $1.2T_c$) and cooling down to room temperature. It is also

important to note that the FWHM vs E curves for the normal spot and the half-order spot agree in their peak positions of the oscillations, which implies that no serious substrate reconstruction was induced by the adsorbates.

III. RESULTS AND DISCUSSION

A series of intensity profiles of $(\frac{1}{2}0)$ spot along the (10) direction at various temperatures are presented in Fig. 1. We clearly observe line broadening and decrease of intensity with increasing temperature. These changes contain not only the critical scattering but also the Debye-Waller effect (e^{-2MT}). After the Debye-Waller factor corrections[13] using $2M=7.3\times10^{-3}$ K^{-1} and background subtractions, we fitted the profiles by

$$I(\mathbf{q},T)=I_0(T)\delta(\mathbf{q}-\mathbf{q}_0)+\chi(\mathbf{q}-\mathbf{q}_0,T)\ , \tag{1}$$

where the first and second terms represent the long-range order (LRO) and the long-range fluctuation (LRF), respectively. Here $\mathbf{q}$ is a momentum transfer of the LEED electron to the surface and $\mathbf{q}_0$ is a characteristic wave vector of the $p(2\times1)$ phase. The first term dominates for $T\ll T_c$ with the delta function suitably modified as a function of finite width due to the finite-size effect. The second term, a susceptibility term representing the critical scattering, becomes more important as T approaches T_c and diverges at T_c for an ideal sample. It turns out that the profiles in Fig. 1 are best fitted by a Lorentizan squared (L^2) for the LRO plus a Lorentzian (L) for the LRF. As pointed out by Mukamel *et al.*,[14] this indicates that the LRO on the present surface was limited by numerious point defects. The Lorentzian form of the susceptibility is given by

$$\chi(\mathbf{q}-\mathbf{q}_0,T)=\frac{\chi_0(T)}{1+\xi(T)^2(\mathbf{q}-\mathbf{q}_0)^2}\ , \tag{2}$$

where ξ is a correlation length of the LRF, which diverges at T_c.

Results of the fits for $I_0(T)$ and $\chi(T)$ are shown in Fig. 2, where LRF increases at the expense of LRO as T approaches T_c. Because of the finite-size effect, the susceptibility does not diverge to infinity at T_c. The solid curves are theoretical fit curves by $I_0\propto|t|^{2\beta}$ and $\chi\propto|t|^{-\gamma}$, where $t\equiv(T_c-T)/T_c$ is a reduced temperature. In order to extract the exponents β and γ, we used $T_c=709$ K, where LRO vanishes. With this T_c, we obtained $\beta=0.19\pm0.05$ for a limited temperature range of $0.027\le t\le0.083$. This procedure is further justified by finding a relative minimum of the *goodness of the fit* parameter as we vary one of the fit parameters while keeping others fixed.[15] However, we notice that the resulting values of the exponents are sensitive to each step of the procedure, for example, the background subtraction and the choice of T_c.

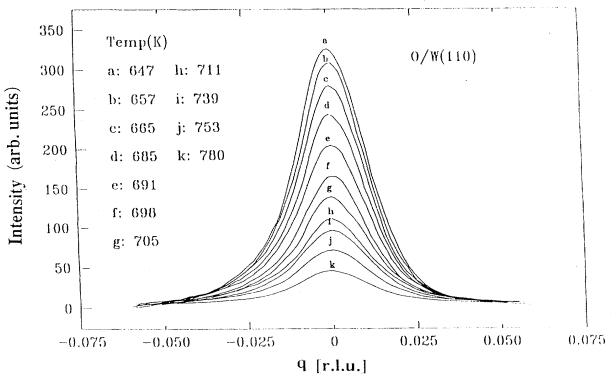

FIG. 1. Temperature dependence of a $(\frac{1}{2}0)$ LEED spot profile for the $p(2\times1)$-O/W(110) superstructure. The profiles are best fitted by L^2+L(Lorentzian), where L^2 and L represent long-range order and long-range fluctuation respectively.

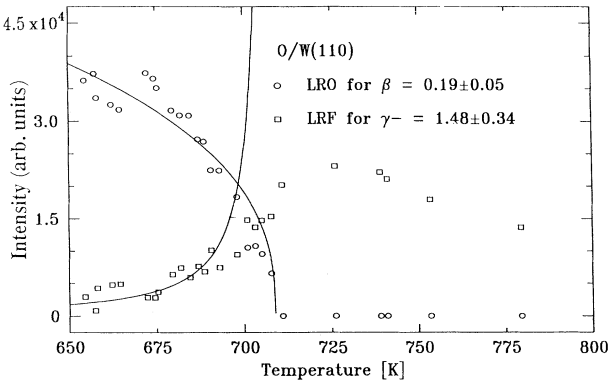

FIG. 2. Temperature dependence of $I_0(t)$ for LRO(○) and $\chi_0(t)$ for LRF (⊓) of the $p(2\times1)$ structure where t is a reduced temperature. Solid curves are fits to the power laws as described in the text for the limited ranges of temperature $0.027\le t\le0.083$ for LRO and $0.055\le t\le0.083$ for LRF to minimize the finite-size effect. The critical exponents β and γ were estimated from these fits for $T<T_c$.

The value of β obtained in this study is larger than $\beta=0.125$ of the two-dimensional (2D) Ising model. It is interesting to note that such large deviations were also reported for other nonuniversial XY system, a $p(2\times2)$-H/W(110)[6] and a $p(2\times2)$-O/Mo(110).[7] As discussed below, since the scaling laws assure the relations between the measured exponents, these deviations are not caused by experimental uncertainties but are characteristics of the nonuniversal system. As discussed previously, this may be interpreted as an indication that the transition belongs to the universality class of the 2D XY model with cubic anisotropy.[16] The deviation of exponent β may imply that the anisotropy field strength h_4 (see Ref. 16) is finite rather than infinite as in the 2D Ising system, to cause the exponents nonuniversal.

The susceptibility exponent for $T<T_c$, γ^-, was also determined in similar fashion and found to be 1.48 ± 0.34. We also notice some deviation of γ from the Ising value of $\frac{7}{4}$. Grzelakowski *et al.* reported similar deviations for the $p(2\times2)$-O system for $\beta=0.19\pm0.02$ and $\gamma=1.20\pm0.10$ (Ref. 7). A temperature range of $0.055\le t\le0.083$ was taken for the fit since it includes most of the data that show significant variations while minimizing the finite-size effects. Unfortunately the data above T_c are too spare to estimate γ^+.

In Fig. 3, we show a plot of the correlation length ξ as a function of temperature with a theoretical curve $\xi(t) \propto |t|^{-\nu}$ appearing as a solid curve. The correlation length exponent ν estimated for the same temperature range as for γ, is $\nu^- = 1.23 \pm 0.27$. Since theories predict that only two exponents are independent while others can be estimated from several scaling relations, by taking β and γ as two independent exponents, we obtain $\nu^- = \beta + \gamma^-/2 = 0.93 \pm 0.22$, which agree qualitatively with the independent experimental estimation within acceptable limits of error. We also interpret the deviation of the exponent ν from the Ising value of $\nu = 1$ to be a result of the finite anisotropic field h_4. Considering the inevitable nonideal experimental conditions mentioned earlier, the deviations might be thought as not being significant, which means that h_4 may be strong enough to keep the system close to the 2D Ising class.

Although the transition may remain close to the 2D Ising system, the unique character of nonuniversal exponents of the 2D XY with cubic anisotropy is also revealed in another independent estimation of the exponent η. From the scaling relation $\eta = 2\beta/\nu$, we calculate $\eta = 0.41 \pm 0.20$, which shows a rather large deviation from the Ising or four-state Potts model value of 0.25. This value of η is accidentally identical to that reported earlier, which was deduced from the scaling relation $\eta = 2 - \gamma/\nu$ (Ref. 7). Since the Lorentzian form for LRF at T_c is valid only when η is negligibly small, we estimated an effective exponent η, using a formula proposed by Fisher and Burford[17] for $T \neq T_c$:

$$\chi(\mathbf{q}, T) = \frac{\chi_0(T)(1+\phi_0 q^2 \xi^2)^{\eta/2}}{(1+\phi_1 q^2 \xi^2)}, \tag{3}$$

where ϕ_0 and ϕ_1 are constants with $\phi_0 \approx 0.3$ and $\phi_1 \approx 1.0$ very close to T_c. Note that in Eq. (3), $\chi_0(T)$ is independent of η but $\xi(T)$ is affected somewhat by η. By selecting the smallest $t = 0.003$, we fitted the profile as presented in Fig. 4 to produce $\eta = 0.38 \pm 0.12$, in reasonable agreement with the estimation of 0.41 ± 0.20 by the scaling relation. This rather large value of η may approach the theoretical value of 1/4 as T approaches T_c. Interestingly, the choice of $T_c = 709$ K is further supported by negative values of η as shown in Fig. 4(b) for temperatures other than T_c. As we move away from T_c, η becomes more negative, which is unphysical since $\xi(r) \propto r^{2-\eta}$.

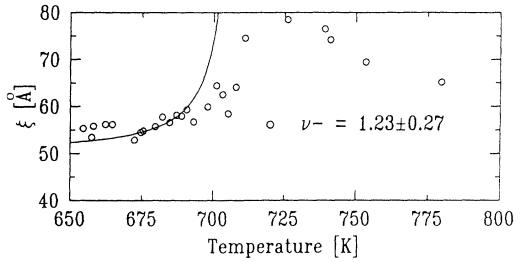

FIG. 3. Corresponding data (○) and fit (solid curve) as in Fig. 2, for the correlation length $\xi(t)$. The exponent $\nu^- = 1.23 \pm 0.27$ was obtained from the fit.

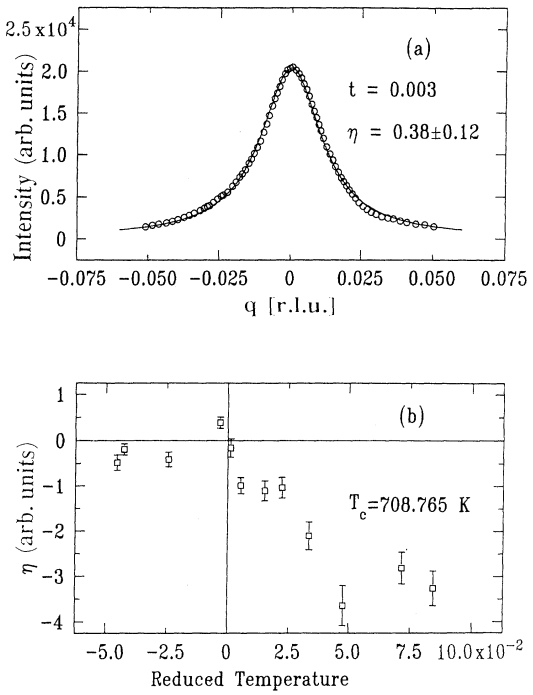

FIG. 4. (a) A profile of the $(\frac{1}{2}0)$ and theoretical fit (solid curve) near T_c ($t = 0.003$). The resulting exponent $\eta = 0.38 \pm 0.12$ is considerably larger than the Ising value of 1/4. (b) Temperature-dependent η showing a positive value only quite near to T_c, supporting the selection of T_c in this study. Physical implications of this abnormal behavior of η are discussed in the text.

Temperature-dependent η has been observed experimentally[7] and theoretically[18] in the phase transitions in the XY systems, where large values of η were also reported. Although the origin of this striking feature is not yet clear, Grzelakowski *et al.* discussed its nature in terms of the large acoustical vibration of the oxygen lattice.[7] The large Debye-Waller factor that we used for the $(\frac{1}{2}0)$ spot compared to 5.8×10^{-4} K^{-1} for the $(\frac{1}{2}\frac{1}{2})$ spot from the $p(2\times2)$-O structure[7] implies more significant T dependence of η as observed in this work. As mentioned earlier, the fact that the abnormal behavior of η and nonuniversal exponents are observed only for the 2D XY model with cubic anisotropy, strongly suggests an active role of the anisotropy fields in the systems. Theoretical calculations by Kaski *et al.*[9,10] show that the exponent η varies as a function of the anisotropy field strength within the range of $0.3 \leq \eta \leq 0.4$ for the $p(2\times1)$ phase of a centered rectangular system as in the O/W(110) system. Moreover, they also noticed that the thermal exponent $y_T (= \eta/\beta)$ can change sign when the field changes as a result of a finite-size effect. It is, of course, unphysical as mentioned earlier, but complies with the present experimental observation. For the $p(2\times1)$-O/W(110) structure, previous electron-energy-loss spectroscopy (EELS) studies showed that oxygen atoms occupy the quasithreefold hollow sites by which the substrate symmetry naturally allows potential anisotropy.[19]

IV. CONCLUSIONS

We have studied the critical behavior of an order-disorder phase transition $p(2\times1)$-$p(1\times1)$ as a function of temperature at 0.5 ML of oxygen chemisorbed on the W(110) surface. The experimentally determined values of the critical exponents show relatively large deviations compared to those of the 2D Ising model but are consistent with the scaling laws within the experimental accuracy. We further observe temperature-dependent η as reported previously for other XY systems. Therefore we confirm that the peculiar feature of η and deviations of the critical exponents are unique features for a nonuniversal system basically caused by an anisotropy field.

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