

Growth Kinetics of O/W(110) at High Coverage

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We study the phase separation of the O/W(110)- $p(2\times 1)+p(2\times 2)$ system with LEED as it is quenched from an "infinite"-temperature initial state to within its coexistence region. Novel features of this system are the fourfold degeneracy of the ordered phases and their finite densities. The measured growth exponent is consistent with the Lifshitz-Slyozov prediction $x = \frac{1}{3}$. Diffusion activation energies measured with two independent methods are consistent with each other and lead to $E \approx 0.58$ eV.

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Recent studies of systems under strongly nonequilibrium conditions, realized after a quench that forces the system from a high- to a low-symmetry state, have revealed certain universal characteristics. Extensive theoretical work¹⁻⁵ on models with Monte Carlo simulations and some experimental work⁶⁻⁹ have suggested that the growth of the lower-symmetry phase, as measured by its average domain size L , is universal; i.e., it depends on few general parameters and not the details of the system. It usually obeys a power law

$$L = A(T)t^x, \quad (1)$$

with the exponent x classifying systems into different growth classes.

The estimation of the exponent x is computationally difficult because its range is limited to $0 \leq x \leq \frac{1}{2}$ and excellent statistics are required. It is well established, however, that $x = \frac{1}{2}$ for systems^{10,11} with nonconserved order parameter [both for conserved (Kawasaki) and nonconserved (Glauber) particle number] and that $x = \frac{1}{3}$ for systems¹²⁻¹⁵ with conserved order parameter which phase separate into high- and low-density phases. This latter case was worked out originally by Lifshitz and Slyozov for small volume fraction of one of the phases. The mechanism leading to $x = \frac{1}{3}$ involves the evaporation of monomers, mainly from smaller domains, and their diffusive transport until they encounter and condense on domains further away. Growth is effectively accomplished with the larger domains growing bigger and the smaller ones eliminated. Recently, this mechanism has been extended^{13,14} to the case of finite volume fraction when the two phases occupy comparable amounts. It has been argued and verified with computer simulations that the exponent is still $x = \frac{1}{3}$, because the rate of evolution is still limited by the long-range mass transport through the matrix. Only at early times can diffusion along the interfaces separating the interconnected domains lower the exponent x . At the next level of complexity of the phase-separation process, one would like to examine the effect of multidegeneracy and nonzero densities of both ordered phases. Multidegenerate ordered phases have been studied theoretically be-

fore with both nonconserved and conserved dynamics on systems in a single-phase region separated by a second-order line. Originally, it was believed^{10,16,17} that the growth exponent x decreases with the number of degenerate ground states p , and if p is larger than the spatial dimensionality, growth is logarithmic. Recent work^{18,19} on systems with conserved dynamics has suggested, however, that although growth freezing is possible at zero temperature, at finite temperature the exponent x approaches the value $\frac{1}{2}$ asymptotically. This was shown on models with next-nearest-neighbor jumps¹⁸ (in addition to the nearest-neighbor ones) or by allowing a stable precursor state.¹⁹ The effect of multidegeneracy, however, has not been tested for the phase-separation process, especially on experimental systems. The O/W(110)- $p(2\times 1)+p(2\times 2)$ system provides such a possibility because two ordered, fourfold-degenerate states coexist at low enough temperatures. Both phases have finite densities ($\theta_{2\times 1} = 0.5$, $\theta_{2\times 2} = 0.75$) and the density difference ($\Delta\theta = \theta_{2\times 2} - \theta_{2\times 1} = 0.25$) is smaller than the difference ($\Delta\theta = 1$) in the models of phase separation that are usually studied.

We study this system at high coverage, $\theta \approx 0.68$. The experiments were carried out in a UHV chamber with base pressure $(6-8) \times 10^{-11}$ Torr equipped with a commercial LEED diffractometer, a single-pass cylindrical-mirror analyzer for Auger spectroscopy, and a mass spectrometer for background-gas analysis. The sample can be heated to 800 K by radiation and 2200 K for oxygen desorption by electron bombardment. During the electron bombardment, the sample holder was electrically connected to the filament so only desorption from the crystal was possible. This provides a very clean crystal before dosing, free of contamination. The sample could be cooled to a temperature of 130 K by thermal contact with a liquid-nitrogen Dewar. Diffraction patterns were imaged with a SIT video camera, frame averaged, digitized, and stored for spot-profile analysis on an IBM-AT computer.

Initially, oxygen was dosed with the crystal cold. The coverage, $\theta = 0.68$, as measured by Auger spectroscopy is between a perfect (2×1) and a perfect (2×2) super-

structure. It is known that there is no diffusion at $T=130$ K, so the adatoms are frozen in an "infinite"-temperature configuration. The crystal is quenched up into the temperature range 351–384 K, and the superstructure spots appear gradually. This temperature range was selected because at lower temperatures no appreciable growth can be measured and at higher temperatures growth was too fast for the detector.

The observed (2×2) diffraction pattern does not uniquely determine the real-space configuration. Either (2×1) domains coexisting with (2×2) domains or pure (2×2) domains are consistent with the (2×2) diffraction pattern. The first possibility has been suggested²⁰ from a schematic completion of the phase diagram which was determined with equilibrium measurements. A theoretical study²¹ of a lattice gas, with a weak fifth-neighbor interaction modeling the system, has suggested no coexistence between (2×1) and (2×2) domains, only (2×2) domains. In Fig. 1, we plot the peak intensity of the $(\frac{1}{2}, \frac{1}{2})$ spot versus the peak intensity of the $(\frac{1}{2}, 0)$ spot for several growth temperatures. It is clear the relation deviates from linearity as time increases. This suggests that both (2×1) and (2×2) domains are present; otherwise, if only (2×2) domains existed, the linearity would extend over the entire curve. This is additionally supported by the comparison of the final full width at half maximum (FWHM) of the spots obtained at the end of growth. The $(\frac{1}{2}, 0)$ -spot FWHM is narrower than the $(\frac{1}{2}, \frac{1}{2})$ FWHM by approximately 15%. If only (2×2) spots were present, then the FWHMs would have been the same. This demonstrates how useful information about the equilibrium phases and the determination of the phase diagram of an overlayer can be obtained from these nonequilibrium experiments.

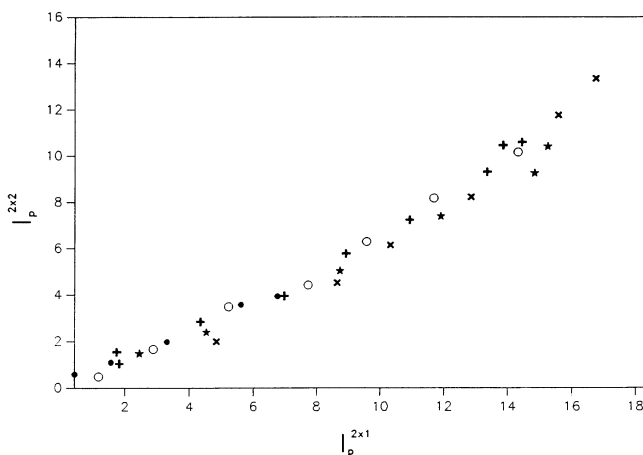


FIG. 1. Plot of the peak intensity $I_p^{2 \times 2}$ of the $(\frac{1}{2}, \frac{1}{2})$ spot vs the peak intensity $I_p^{2 \times 1}$ of the $(\frac{1}{2}, 0)$ spot. The deviation from linearity shows that both (2×1) and (2×2) domains coexist on the substrate. Different symbols correspond to different quench temperatures.

The inverse square root of the second moment of the spot profile at time t ,

$$q(t) = \left(\frac{\sum_{i=1}^n q^2 S(q, t)}{\sum_{i=1}^n S(q, t)} \right)^{-1/2}, \quad (2)$$

increases with time and is proportional to the average domain size of the ordered domains. The above summation is carried out over the entire Brillouin zone. $S(q, t)$ was measured along the close-packed direction. Heating-time intervals were increased progressively by approximately a factor of 2, since we are expecting a power-law growth. Each growth curve of different temperature was least-squares fitted by the power law [Eq. (1)] to determine the growth exponent x . We find that x lies within the range 0.31 ± 0.03 . Only at the highest temperature is x below this range. However, substantial growth occurs at this temperature even during the initial shortest time interval of 0.25 min, so saturation effects might be more important. Figure 2 shows the growth curves plotted against t^x and straight-line fits through the data.

The use of $q(t)$ as a measure of the time dependence of the average domain size L is more accurate than the peak intensity. The latter is more sensitive to instrumental broadening. On the other hand, $q(t)$ is a weighted average over the entire Brillouin zone, and thus, for points further away from the peak, the profile is flatter and the instrumental effects are limited. The FWHM (corresponding to domains of linear dimensions approximately 30 Å) of a profile at the end of the growth is approximately 2.5 times larger than the instrument response function.

The temperature dependence of the growth rate in Eq. (1) can be related^{22,23} to the diffusion activation energy. Nonequilibrium experiments, in addition to addressing the question of universality, can provide diffusion activa-

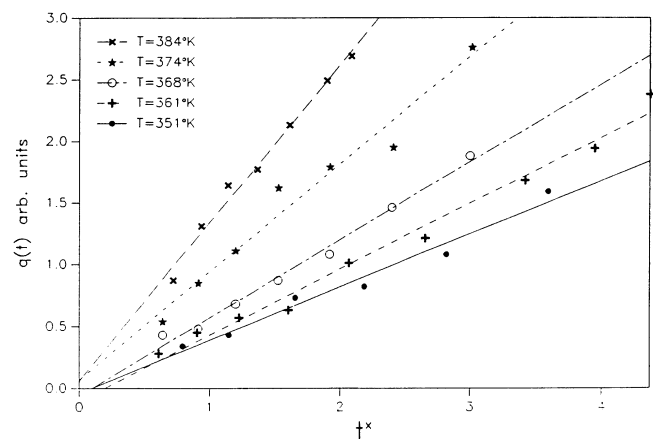


FIG. 2. Plot of $q(t)$, the inverse square root of the second moment of the angular profile $S(q, t)$ vs t^x for five temperatures shown in the figure. The slopes of these lines are used to extract the growth-rate activation energy.

tion energies which can be used²² to extract adsorbate-adsorbate and substrate-adsorbate interactions. The two known models where analytic work is possible (the Lifshitz-Cahn-Allen growth law,¹⁰ applicable to a $p=2$ system with nonconserved dynamics, and the Lifshitz-Slyozov law¹²) and recent Monte Carlo simulations²⁴ on a model with $p=2$ and conserved dynamics show that the diffusion coefficient appears on the right-hand side of Eq. (1) with the same exponent x as time. This has been generalized^{22,23} for any growth law, Eq. (1), by a dimensional argument. Since there is no time in the left-hand side of Eq. (1) [and under the assumption that the only time dependence of $A(T)$ is through D], D , which has dimensions of inverse time, must have the same exponent as time to eliminate the overall time dependence of the right-hand side in Eq. (1). It follows that D is proportional to $A^{1/x}$, so the diffusional activation energy is $1/x$, the growth-rate activation energy. Figure 3 shows Arrhenius plots of the growth rate determined from Fig. 2. We obtain $E_A=0.19$ eV for the growth rate activation energy. Dividing by the growth exponent, we find $E_D=0.58$ eV for the diffusion activation energy. We estimate the uncertainty in the diffusion activation energy to be $\pm 10\%$.

It is also possible to extract a diffusion activation energy from the measurements without relying on the value of the growth exponent x . By inspecting the growth curves at different temperatures, one determines the various times $\tau(T)$ that the average domain size reaches a fixed value L_0 . We only assume that in Eq. (1) the diffusion coefficient and time appear as a combination (Dt) on the right-hand side, but no specification of the functional form of the growth law or the exponent x is needed. Since L_0 is the same for all temperatures, it follows that $D(T)=\text{const}/\tau(T)$. Hence a plot of $\tau^{-1}(T)$ vs $1/T$ can provide the diffusion activation energy. This es-

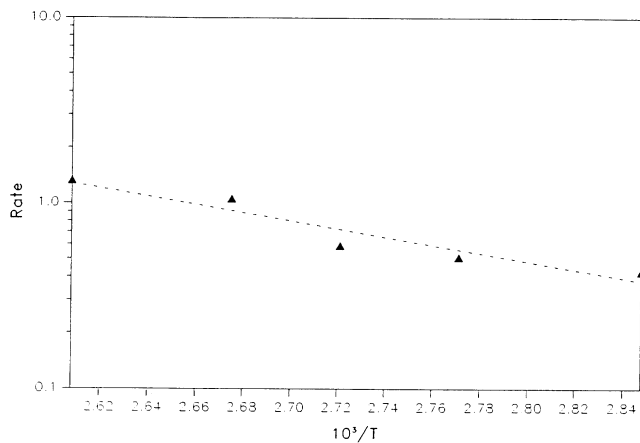


FIG. 3. Growth rates extracted from the time dependence of $q(t)$ vs $1/T$. The diffusion activation energy $E=0.58$ eV is determined from the growth-rate activation energy divided by the growth exponent x .

timate has the advantage of being independent of the measured value of the growth exponent. We find for the diffusion activation energy $E_D=0.52$ eV, within the range of the previous estimate.

At the same time, the consistency of the activation energy measured by the two methods strengthens the reliability of the measured exponent $x=0.31 \pm 0.03$. Actually, the ratio of E_D measured from the times $\tau(T)$ required to attain a certain length L_0 to the measured E_A can be used as an independent measure of the growth exponent x .

The measured exponent $x=0.31 \pm 0.03$ is consistent with the exponent $x=\frac{1}{3}$ predicted by the Lifshitz-Slyozov theory. Is this expected? As we described above, the requirement of mass transport through the region separating the growing domains determines the $t^{1/3}$ growth law. It is clear that mass transport is needed in the present system. The (2×1) phase acts as a "sea" through which monomers evaporating from the (2×2) domains diffuse to condense on larger (2×2) domains, and conversely, the (2×2) phase acts as a "sea" for the (2×1) domains to grow. The separating phases have nonzero densities ($\theta_{2 \times 1}=0.5$, $\theta_{2 \times 2}=0.75$) instead of the fully occupied ($\theta_{1 \times 1}=1$) and fully emptied ($\theta_{(1 \times 1)\text{holes}}=0$) phases of the ferromagnetic Ising model used for phase-separation simulations, but this does not affect the requirement of mass transport. Furthermore, the four-fold degeneracy of the separating phases does not change the growth exponent. It has been demonstrated²⁵ in computer simulations that the ground-state degeneracy has no effect on the growth exponent for systems with Glauber dynamics. Although it requires larger computational effort, this has been also suggested^{18,19} to be true for systems that obey Kawasaki dynamics. The above results apply to systems that are quenched into a single-phase region, where the growing domains of different degeneracy are adjacent to each other. The independence of the growth exponent on degeneracy should be expected on stronger grounds for the case of phase separation, because domains of different degeneracy do not share boundaries and slowing down due to topologically stable configurations is less probable. Recent simulations²⁶ on a lattice gas model with (2×1) and (2×2) coexisting phases have demonstrated that the growth exponent for the phase separation of these two phases, out of an initial random configuration, is $x=\frac{1}{3}$, in agreement with our experimental results.

In summary, we studied the phase separation of a system in an initially "infinite" temperature into two multidegenerate finite-density ordered phases. The growth exponent is consistent with the Lifshitz-Slyozov theory of phase separation with the degeneracy and density having no effect. We also extracted a diffusion activation energy of $E \approx 0.58$ eV by using two independent methods.

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