Real-Time Microscopy of Two-Dimensional Critical Fluctuations: Disordering of the Si(113)-(3 × 1) Reconstruction

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Using low-energy electron microscopy, we have studied the critical fluctuations associated with the disordering of the (3 × 1) reconstruction on Si(113). We not only observe and quantify the increased spatial correlations near T_c, but also the associated slowing down of the relaxation of long wavelength critical fluctuations. The dependence of the slowing down on correlation length is consistent with theories for phase transitions with nonconserved order parameters. In addition, we show that steps limit the size of the correlation length, as is often conjectured. [S0031-9007(96)01062-9]

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Large scale fluctuations at critical points are a striking manifestation of atomic level thermal fluctuations. Since the first observations of critical opalescence in light scattering from CO_2 in 1869 by Andrews, scattering experiments (by light, x rays, neutrons, and electrons) have been the most widely used method for studying critical fluctuations [1]. In most cases, scattering experiments determine time averages of spatial fluctuations. For example, the magnitude and correlation length of fluctuations in the degree of order at an order-disorder transition can be studied by measuring the amplitude and width of a diffracted x-ray beam associated with that order. Although the dynamics of critical fluctuations in fluid and magnetic systems have been extensively studied with scattering techniques, it is far more difficult to study the dynamics of solid-state structural transitions, despite their importance. Recently, important progress was made using x-ray intensity fluctuation spectroscopy [2], where scattering of coherent x rays gives rise to temporal fluctuations in the speckle pattern near T_c. However, this promising method is still in its infancy, and the experiments are very demanding even with the brightest x-ray sources presently available.

In this paper we present a time-and-space resolved study of the disordering of the Si(113)-(3 × 1) surface reconstruction at 693 °C, using low energy electron microscopy (LEEM). In short, this second order, two-dimensional phase transition is imaged in real space (spatial resolution ~40 nm) and in real time (time resolution ~30 ms), and recorded live on videotape. Since the ordered and disordered phases give different contrast, the image becomes noisy due to critical fluctuations. Near T_c the size of the fluctuations exceeds the microscope resolution, and at the same time, the fluctuations undergo critical slowing down. From these observations we can directly relate the spatial coherence length ξ of the fluctuations to the decay time τ_{rel} of long wavelength fluctuations, and determine the dynamical critical exponent z [1,3]. In addition, the intensity of the fluctuations shows a strong increase near T_c, related to the divergence of the specific heat, allowing an estimate of the critical exponent α [1].

Our results are in all respects consistent with previous x-ray and low energy electron diffraction (LEED) studies of this phase transition. But while previous visualizations of critical fluctuations have largely depended on numerical simulations, in this work the transition is directly observed in real space and real time. The video record provides an overwhelmingly large, but rapidly acquired database which can be used for subsequent quantitative analysis.

Extensive diffraction measurements [4–6] of the threefold degenerate (3 × 1) reconstruction [7] on Si(113) have shown that it disorders continuously in a second order transition at about 700 °C. One reason this transition is of interest is that it is a possible realization of the chiral three-state Potts model [8,9]. Although characteristics of chiral behavior have been observed in the transition, the measured critical exponents β, γ, and ν are close to those of the standard three-state Potts model. The estimates of the critical heat exponent α perhaps tend to be greater than the Potts value of $1/3$, ranging from 0.25 to 0.8 [4,5]. These relatively large values of α aid the observation of the transition with microscopy. An important feature revealed by the diffraction experiments (and also observed in our experiment) is that correlations in the disordered phase are highly anisotropic. At 0.1% of T_c, correlations in the $[1\bar{1}0]$ direction are a factor of 10 smaller than in the transverse $[\bar{3}\bar{3}2]$ direction [6].

In our experiments, the Si(113) surface was cleaned by heating to 1250 °C for a few seconds. The surface was then observed using LEEM [10] in mirror mode (i.e., under imaging conditions in which the electrons are reflected just in front of the sample), as it was cooled and heated through the phase transition. Concurrently, LEED was used to monitor the degree of (3 × 1) order. As has been previously reported [4–6], we found that T_c varied from run to run by about 20 °C, although during each run the transition was reversible. At approximately 1 °C increments near the transition, LEEM sequences lasting about a minute were recorded onto video tape. T was typically stable to better than 0.5 °C during these sequences. At high T, (113) oriented terraces have a

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uniform bright intensity. At low T the terraces are darker, presumably due to a difference in work function between the ordered and disordered phases. At intermediate T, the fluctuations characteristic of a second order transition appear in an extremely distinctive way, as we now discuss in detail.

As one cools from high T, the transition first shows up as increased fluctuations in image intensity on a time scale close to the video rate (1/30 s). To characterize these fluctuations, we measured the total intensity $I_L(t)$ in square regions of size L on step-free (113) terraces as a function of time t. Figure 1 shows $I_L(t)$ for $L = 170$ nm at 699 °C and 693 °C. Inspection of the LEED pattern at 699 °C reveals a diffuse (3×1) beams: there is only short ranged (3×1) order. At high T, the observed fluctuations appear spatially random. If the observed fluctuations were spatially random, then the time averaged Fourier spectrum should be white, independent of wave number q. The actual spectrum shows an isotropic peak at $q = 0$, consistent with white noise spatially convoluted with a 2D isotropic Gaussian with a full width of 40 nm. Since this width is independent of T at high T, we interpret it as the instrumental resolution of the LEEM in mirror mode. So, at high T each region of the images separated by distances greater than the instrumental resolution is fluctuating independently in time, implying that the correlation length ξ of fluctuations on the surface is smaller than the instrumental resolution.

As T decreases, the magnitude of the image fluctuations increases, as shown by comparing the 693 °C fluctuations plotted in Fig. 1 with the 699 °C fluctuations. To quantify this, Fig. 2 shows the T dependence of the mean square intensity $\langle I_L^2 \rangle - \langle I_L \rangle^2$, taking the averages over time, for $L = 170$ nm. The intensity fluctuations increase until they reach a peak at about 693 °C, after which they begin to decrease. Observation of the LEED pattern at 690 °C shows that the surface has long-range (3×1) order [11].

To understand the factors which govern these intensity fluctuations, we suppose that the surface potential (and thus image contrast) of each region of the surface is determined by an average of the *local* environment of the surface atoms in that region. At second order transitions, such averages have the same critical properties as the energy [12]. The mean square fluctuations of energylike quantities diverge near the critical point like the specific heat C, i.e., as $\epsilon^{-\alpha}$, where $\epsilon = |T - T_c|/T_c$. So, the mean square fluctuation of the random image fluctuations should have the form $\langle I_L^2 \rangle - \langle I_L \rangle^2 \propto L^2 C \propto L^2 \epsilon^{-\alpha}$ [13]. We thus interpret the peak in the image fluctuations observed in Fig. 1 as due to the divergence of the specific heat at $T_c \approx 693 \pm 1$ °C. Given the limitations of the data, it is difficult to give an accurate estimate of α. The lines in Fig. 2 show fits by $\epsilon^{-\alpha}$ with a T independent background (in part due to shot noise in the image), and a symmetric amplitude on either side of the transition (as expected for the three-state Potts model). The solid line shows the fit with α fixed to the Potts value of one-third. The dashed line shows a fit when α is 0.6, which is in the middle of the range of previous diffraction estimates [5]. The fit is slightly better for more of the data, although there is little statistical difference between the two fits. The magnitude of the fluctuations is reasonable for a second order transition. From Fig. 2, near T_c the critical part of the mean square fluctuations per (3×1) unit cell is about equal to the square of the average image intensity. The total difference in the image intensity between the ordered and disordered states is observed to be roughly a quarter of the average intensity. So the mean square fluctuations per unit cell are about $1/(0.25)^2 = 16$ times the square of the image contrast. This number is typical

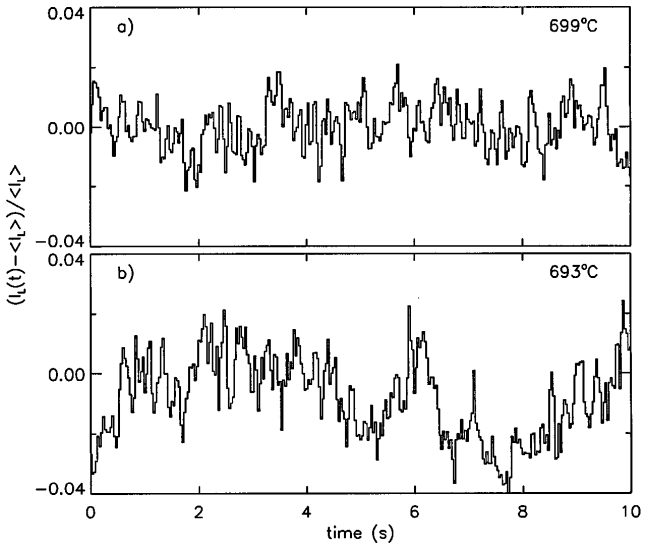

FIG. 1. Time dependence of the image intensity fluctuations at two temperatures: (a) 699 and (b) 693 °C.

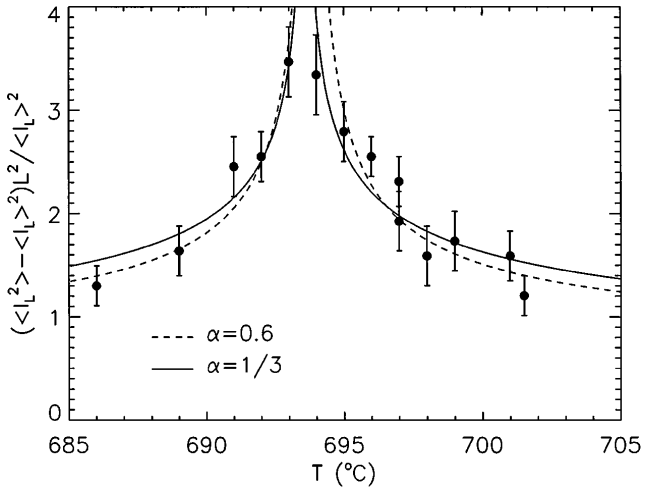

FIG. 2. The time average of the mean square fluctuations in image intensity of 170 nm square regions of the surface as a function of T. The peak near 693 °C locates the critical point. L^2 is in units of the (3×1) unit cell area, i.e., 1.27 nm × 1.15 nm. The fits are described in the text.

of the order of magnitude of the ratio of the mean energy or density fluctuations to the square of the energy or density changes for 2D lattice gas models of surface phase transitions within 0.1% of T_c [14].

Associated with the increased magnitude of fluctuations at a second order phase transition, fluctuations near T_c become more correlated. Figure 3(a) shows a sequence of images of the surface at 693 °C. The images show the expected enhanced spatial correlations along the $[\bar{3}\bar{3}2]$ direction. To measure this enhanced correlation, we calculated the spatial autocorrelation function $g(r) = \langle [I(r + r') - \langle I \rangle][I(r') - \langle I \rangle] \rangle$ along this direction. [Here I was the intensity of each (8.5 nm × 8.5 nm) pixel of the image.] Again, the thermodynamic averages were made by averaging over several thousand video frames. Figure 4(a) plots $g(r)$ for two T's. The increased correlation length as one approaches T_c is clearly visible. To measure the correlation length ξ, we fit $g(r)$ by $A \exp(-r/\xi)$ [15]. Far above T_c, the 40 nm resolution of the instrument limits the smallest observable correlation length. Near T_c the measured ξ becomes at least 80 nm. Correlations in the transverse $[1\bar{1}0]$ direction are always too short, compared to the instrumental resolution, to be detected. This anisotropy is consistent with the x-ray diffraction observations of the phase transition; the maximum ξ measured in the $[1\bar{1}0]$ direction (at $\epsilon \sim 0.001$) was only ~30 nm [6].

As the correlations become longer ranged and the magnitude of the fluctuations becomes larger, they also become slower. The presence of longer time components in the fluctuations near T_c (see Fig. 1) is already an indication of critical slowing down. To quantify these fluctuations, we computed the time autocorrelation function of $I_L(t)$: $c(t) = \langle [I_L(t + t') - \langle I_L \rangle][I_L(t') - \langle I_L \rangle] \rangle$. Figure 4(b) shows plots of $c(t)$ for the same T's as shown in Fig. 4(a). As expected, associated with the increase in correlation length the relaxation time of the fluctuations increases. In much the same way as computer simulations are analyzed [16], we determine the relaxation time by fitting $c(t)$ to $\exp(-t/\tau_{\mathrm{rel}})$. τ_{rel} is changing from around 160 ms at high T to at least 720 ms within a degree of T_c.

For fluctuations with wavelengths larger than ξ, the dynamical theory of critical slowing down [3] predicts that the relaxation time should diverge as one approaches the critical point as $\tau_{\mathrm{rel}} \propto \xi^z$, where z is the dynamical critical exponent. Theoretically, z is found to be around 2 for systems where the fluctuations do not have to conserve any quantity, and around 4 when the fluctuations conserve the order parameter. Since the order parameter is not conserved during surface reconstructive transitions (the surface does not phase separate into reconstructed and non-reconstructed regions at low T), one expects $z \approx 2$. Figure 5 plots τ_{rel} vs ξ as extracted from Figs. 4(a) and 4(b), yielding $z = 1.9 \pm 0.3$. Recent estimates of z for the three-state Potts model with nonconserved dynamics give about 2.2 [16]. From this estimate of z, we can estimate the time scale of the atomic events responsible for the observed fluctuations; extrapolating τ_{rel} of Fig. 5 to lengths of the size of (3 × 1) unit cell (~1 nm) gives approximately 10^{-4} s. This is a reasonable number for Si surfaces—it is comparable to the time between random

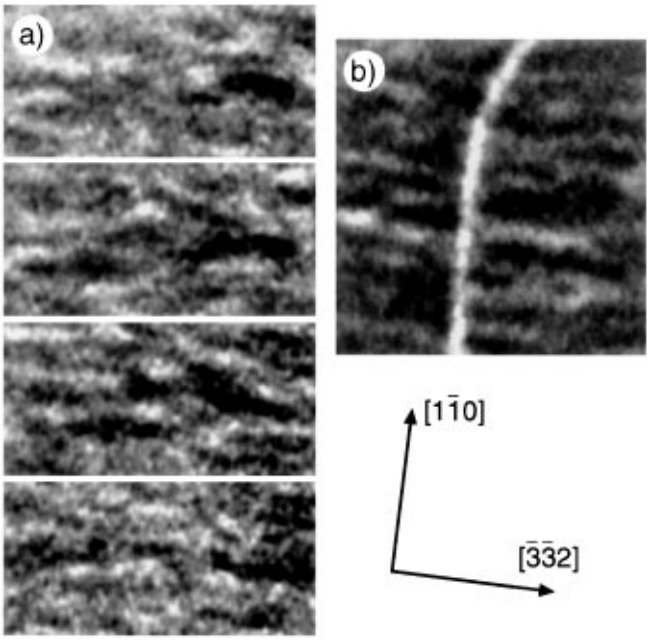

FIG. 3. (a) A sequence of images of Si(113) near the critical point. Each (0.5 μm × 1 μm) image is separated by 0.4 s, and averaged over the previous 0.4 s. Extended correlations are clearly seen in the $[\bar{3}\bar{3}2]$ direction. (b) A square μm image of the intensity near T_c crossed by a step bunch (light vertical line). We find no correlations in image intensity across this step bunch.

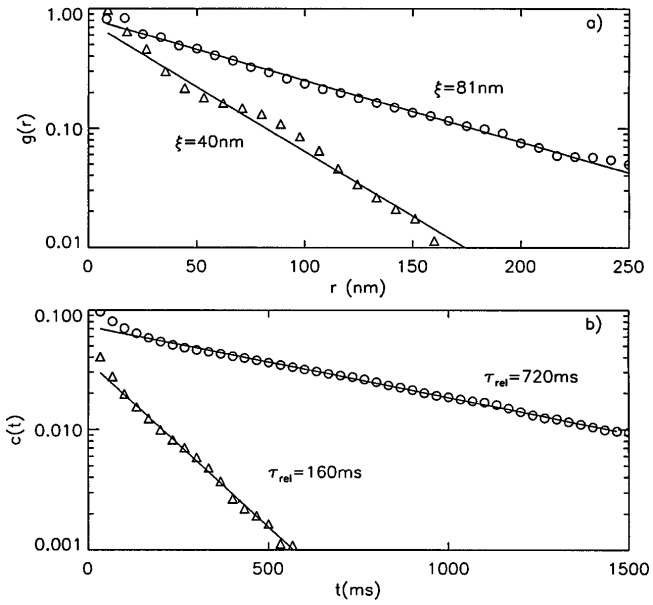

FIG. 4. (a) The spatial autocorrelation function $g(r)$ of the image intensity along the $[\bar{3}\bar{3}2]$ direction for two T's. (b) The temporal autocorrelation function $c(t)$ of the image intensity summed over 170 nm square regions for the same T's. The triangles are for $T = 695$ °C; the circles are for a T within 1 °C of T_c.

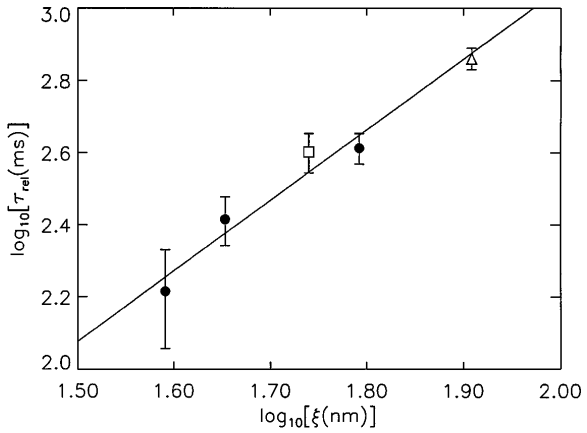

FIG. 5. Log-log plot of the relaxation time τ_{rel} vs correlation length ξ obtained from exponential fits such as those shown in Fig. 4. By fitting to $\tau_{\mathrm{rel}} \propto \xi^z$, we deduce $z = 1.9 \pm 0.3$. The solid circles are from the experimental run of Fig. 2; the other symbols are from different runs.

ad-dimer exchanges with step edges on Si(001) at similar T's, for example.

Surface structural transitions often involve a change in atomic density. In this case surface diffusion might limit the phase transition kinetics. In this scenario, one expects [3] that $z \approx 2 + \alpha/\nu \approx 2.7$ (using the values $\alpha \approx 0.6$ and $\nu \approx 5/6$ [4,6]). This value of z is only marginally consistent with Fig. 5. If fluctuations were limited by surface diffusion, the time scale of the fluctuations to would be influenced by the proximity of surface steps, which act as sources or sinks of adatoms. We did not observe any marked difference between relaxation times near and far away from step edges.

One difficulty often faced in interpreting measurements of correlation lengths obtained in diffraction experiments is the presence of defects such as surface steps, since these defects can limit the size of correlations. In microscopy, such effects can be minimized—we measured $g(r)$ on very rare micron sized step free regions of the surface, for example. The effects of defects on correlations can be also directly observed. The most common defect on our surfaces was bunched steps [17]. Figure 3(b) shows fluctuations near T_c on two terraces separated by such a step bunch. There are no obvious correlations in intensity, and indeed $g(r)$ is close to zero for r across the step bunch. Not unexpectedly, steps limit the size of correlations, as is often supposed.

In conclusion, we have observed critical fluctuations in a second order solid-state phase transition in real space, using LEEM. From our data we obtain a dynamical critical exponent $z = 1.9 \pm 0.3$, a value within the range of theoretical expectations. We observe the increase of the mean square fluctuation amplitude, directly related to the divergence of the specific heat. Finally, the presence of steps limits the allowable correlations length, as fluctuations are uncorrelated across atomic steps.

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[11] At low T there is some sign of imperfections in long range (3×1) order: ~ 1 μm long straight light streaks separated by several 100 nm run in the $[\bar{3}\bar{3}2]$ direction.
[12] See N. C. Bartelt, T. L. Einstein, and L. D. Roelofs, Phys. Rev. B **32**, 2993 (1985), and references therein.
[13] If the image intensity were determined by the local net order (as it might be in dark field imagining using an appropriate diffraction beam), then the mean square fluctuations would be proportional to the ordering susceptibility.
[14] For the Ising model the ratio of the critical part of the energy fluctuations to the square of the energy difference between ordered and disordered phase at $\epsilon = 0.001$ is 4.4. Similarly, the ratio of the density fluctuations to the total density change of the hard hexagon model (which has 3-state Potts exponents) at the same ϵ is 4.0 [R. J. Baxter, *Exactly Solved Models in Statistical Mechanics* (Academic, London, 1982)].
[15] We only used r's greater than the instrumental resolution to perform the fits. Energy fluctuations typically have shorter ξ's (as well as shorter τ_{rel}'s) compared to order parameter fluctuations, so the ξ's we obtain cannot be directly compared to diffraction measurements. Fits to simple exponentials always worked well. Very near T_c, $g(r)$ should decay as $1/r^{2-\alpha/\nu}$. We never observed this behavior, perhaps because ξ was never much greater than the spatial resolution.
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