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Specific-heat anomaly of Au(110)(1×2) studied by low-energy electron diffraction

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The specific-heat critical exponent α has been measured for the Au(110)(1×2) order-disorder phase transition using partially integrated low-energy electron diffraction intensities. The resulting value, $\alpha=0.02\pm0.05$, is consistent with the predicted Ising universality class of this transition. Evidence for a reduction in the effective critical temperature due to finite-size effects is also presented.

Studies of phase transitions on real surfaces provide important tests of our basic ideas about two-dimensional critical phenomena. The Au(110)(1×2) surface is an excellent model for studies of continuous order-disorder transitions. The clean surface is inert to the residual gases normally present in an ultrahigh-vacuum chamber so that much longer times are available for measurements than is usually the case. The phase transition is known to belong to the Ising universality class and the critical exponents β, γ, and ν have been measured by Campuzano *et al.*[1] Thus, Au(110)(1×2) can be used for more refined structures of critical behavior including the role of finite-size effects[2] and the kinetics of ordering.[3] In this report we use Au(110)(1×2) to apply a method proposed by Bartlet, Einstein, and Roelofs (BER)[4] for extracting the heat-capacity critical exponent α from low-energy electron diffraction (LEED) data. We also find evidence for finite-size effects in this system. It is also significant that the method of BER significantly expands the ability of LEED to study phase transitions, since the required measurements and analysis are simple, and multiple scattering is fully accounted for.

BER consider LEED intensities integrated over a small region centered around a reconstruction-induced fractional order beam. This integration reduces the sensitivity to long-range order so that the singular behavior near a phase transition is that of the average energy E. Thus, the exponent α is defined near the critical temperature T_c by[4]

$$E=E_0+a_1t\pm b_\pm|t|^{1-\alpha_\pm}+\cdots\ , \tag{1}$$

where E_0, a_1, b_+, and b_- are constant coefficients, $t\equiv(T-T_c)/T_c$ is the reduced temperature, and + and − refer to $t>0$ and $t<0$, respectively. Scaling predicts that $\alpha_+=\alpha_-$ and the ratio b_+/b_- is a universal quantity. For the Ising universality class, $\alpha_\pm=0$, which implies $b_+/b_-=1$.[5] As pointed out by BER, most real LEED instruments have a finite transfer width ω and are therefore only sensitive to correlations over a finite range $L_i\simeq\omega$, so that the required average is obtained automatically. Furthermore, since multiple scattering is short ranged,[4] its presence in LEED does not alter the analysis. BER show explicitly that as long as the diffracted intensity contains no information about the phase of the order parameter, the measured LEED intensity has the form

$$I(t)=\begin{cases}A_0-A_1t+B_-|t|^{1-\alpha_-}+\cdots, & t<0\\ A_0-A_1t-B_+|t|^{1-\alpha_+}+\cdots, & t>0\ ,\end{cases} \tag{2}$$

where A_0, A_1, B_+, and B_- are constants. As for Eq. (1), $\alpha_+=\alpha_-$ and $B_+/B_-=b_+/b_-$.

BER used Monte Carlo simulations for the $(\sqrt{3}\times\sqrt{3})R30$ and $p(2\times2)$ ordered phases on a triangular lattice to show that, depending on the range of t, integration of the intensity over more than about 0.83% of the Brillouin zone was sufficient for Eq. (2) to be valid for these cases. In general, the diameter of the integration region times the correlation length must be large. Since the integral of the intensity over the entire Brillouin zone is conserved,[6] the radius of the integration must also be much smaller than the diameter of the zone.

The largest value of $|t|$ for which Eq. (2) is valid is determined by the instrument and the influence of correction to scaling terms; the smallest depends on the perfection of the surface latttice. The smallest $|t|=t_{\min}$ is obtained when the correlation length ξ becomes comparable to the length scale L of the finite size regions;

$$t_{\min}\simeq(L/\xi_0)^{-1/\nu}\ , \tag{3}$$

where ξ_0 is the order of several lattice spacings. A more perfect surface results in a small $t_{\min}$. The largest value $|t|=t_{\max}$ occurs when ξ is comparable to the transfer width of the instrument ω;

$$t_{\max}\simeq(\omega/\xi_0)^{-1/\nu}\ , \tag{4}$$

unless there are important corrections to scaling beyond those indicated in Eq. (1).

The Au(110) sample is the same one used in a Rutherford backscattering study.[7] It was oriented to within $\pm0.5°$ of the (110) plane and cleaned in ultrahigh vacuum with 1-keV argon-ion sputtering followed by annealing at 1070 K. Temperature was measured with two type-K thermocouples[8] held against the side of the crystal by Pt mounting wires. The temperature was maintained constant to within ±0.2 K during each measurement. Diffracted intensities were measured with a movable Faraday collector whose circular aperture subtended 3.0×10^{-5} Sr at the sample. A retarding grid behind the aperture was

biased 0.9 V below the primary beam voltage. Only one value of the detector aperture was used; a more complete test of the validity of the BER method would require using several aperture sizes (i.e., varying the region of integration).

Figure 1 shows the intensity of the $(0,-\frac{1}{2})$ beam as a function of temperature for a 62-eV primary beam incident at 45° along the $[1\bar{1}0]$ direction. The inflection point provides an estimate of $T_C \simeq 695$ K.[4] Below 650 K, the measured full width at half maximum (FWHM) of this beam was 0.43 ± 0.02 nm^{-1} in good agreement with the value 0.42 nm^{-1} estimated for our LEED instrument using the procedure described by Park, Houston, and Schreiner.[9] For the results presented in Figs. 1 and 2, this instrument response corresponds to integration over a range of scattered wave vectors equal to about 5.6% of the (1×2) Brillouin-zone length along the $[1\bar{1}0]$ direction. Ratios of the FWHM measured for the $(0,-\frac{1}{2})$ and $(0,-1)$ beams were also in good agreement with calculated values and provide evidence that the beam width was dominated by instrumental effects rather than finite-size effects. This was not the case for Ref. 1.

Figure 1 also shows examples of a $(0,-\frac{1}{2})$ beam angular profile measured at 478 K by fixing the angle of incidence and the detector position and varying the incidence energy. Possible artifacts associated with this method are described elsewhere,[10] but are not important for the analysis reported here. The intensity far away from the maximum was used to define a linear background intensity due to thermal diffuse scattering (TDS) and intrinsic surface imperfections. Profiles measured at temperatures far enough above T_c, so that fluctuations in the (1×2) phase no longer contribute significantly, show this linear approximation to be accurate to better than 10% of the background intensity. After background subtraction, the exponential Debye-Waller dependence of the intensity was determined using data with $T < 600$ K. The effective Debye temperature was found to be 102.5 K in good agreement with previous estimates.[7,11] This value for the Debye temperture was assumed to apply over the entire temperature range of the data, $T \leq 900$ K.

We used the following procedure to analyze the critical behavior of the corrected data. T_c was systematically varied between 640 and 740 K. For each choice of T_c, A_0 was chosen by a linear extrapolation between the nearest data points on each side of T_c. The data were then plotted on a $\ln[I(t)-A_0]$ vs $\ln|t|$ graph, and the longest straight-line portion on each side of T_c was determined by a linear least-squares fitting. Examples for T_c values of 680, 695, and 710 K are shown in Fig. 2. The best overall fit was taken to be that which most closely yielded $\alpha_+ = \alpha_-$ and had nearly equal correlation coefficients for $t > 0$ and $t < 0$.

The best fits were obtained for $692\text{ K} < T_c < 698$ K, and the average value of α_+ and α_- over this range of T_c was $\alpha = 0.02 \pm 0.05$. This result is in excellent agreement with the expected Ising value, $\alpha = 0$.

We also estimated the critical exponent $\nu = 1.1 \pm 0.1$ and $690\text{ K} < T_c < 700$ K from the measured increase in the FWHM of the $(0,-\frac{1}{2})$ beam in the range $0.02 < t < 0.07$. This result agrees with the Ising value $\nu = 1$ and gives added confidence in our results for α and T_c.

These results for α and ν rule out the possibility that the transition is first order. For the case of no coexistence region, the BER analysis would yield $\alpha = 1$ (Ref. 4), and the increase in FWHM would be abrupt. For the case of a coexistence region of width ΔT, the integrated intensity of the fractional order diffraction beam would decrease

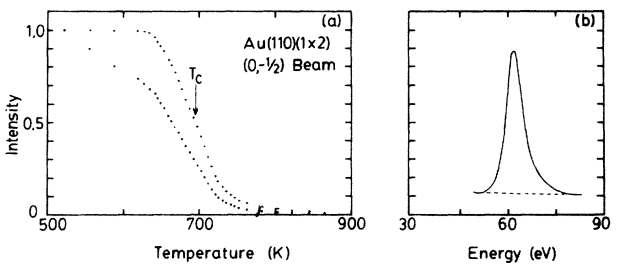

FIG. 1. (a) Measured intensity vs temperature before (0) and after (+) correction for the Debye-Waller factor. (b) $(0,-\frac{1}{2})$ diffraction beam profile at $T = 478$ K. The background correction used in the analysis is indicated by the dashed line.

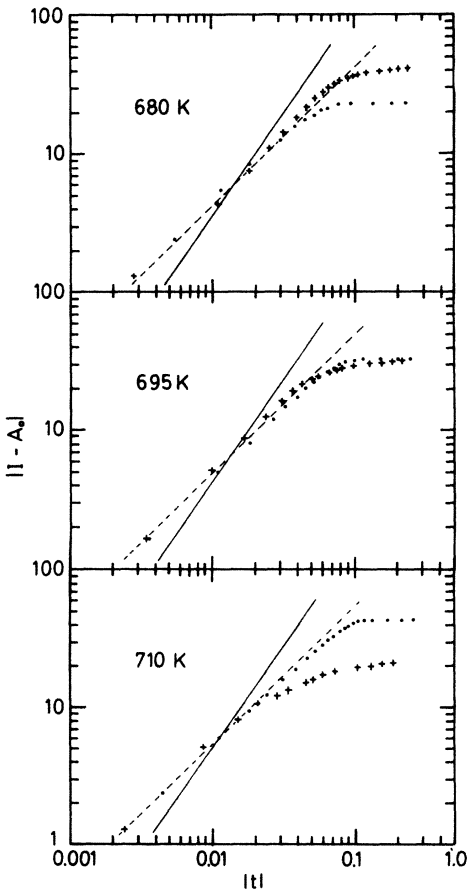

FIG. 2. Plots of corrected intensities vs reduced temperature. The dashed lines show the behavior expected for an Ising system with $\alpha = 0$ and the solid lines the behavior for a three-state Potts system with $\alpha = 0.33$.

linearly ($\alpha=0$) according to the lever rule. However, since disordered regions would nucleate and grow *within* the ordered (1×2) regions, atoms remaining in the (1×2) phase retain their original long-range correlations over most of the coexistence region. Thus, half-order beam FWHM's would remain constant over most of the mixed-phase region. A linear increase over the remainder of the region, as observed, would be accidental. Kinetic limitations due to nucleation and growth phenomena could also lead to hysteresis effects which were not observed.

A small value of α might also result if $t_{\min}$ approaches $t_{\max}$ due to small L values.[12] However, as discussed below, our measured T_c provides evidence that finite-size regions on our crystal are substantially larger than the 20 substrate spacings obtained for the crystal used in Ref. 1. Thus, we believe it unlikely that finite-size rounding has a significant influence on our results other than limiting $|t_{\min}|$ for fits of α.

Good fits for α were obtained for

$$0.004 \lesssim t \lesssim 0.035.$$

The diameter of finite-size regions, as estimated from Eq. (3) with ξ_0 about one lattice spacing, is therefore about 250 Au(110) lattice spacings along [1$\bar{1}$0] or about 100 nm. This result indicates that the substrate was of very good quality, and that its contribution to the measured beam FWHM is negligible compared to the instrumental broadening. The value of α is not very sensitive to $t_{\max}$ as is also pointed out by BER. This lack of sensitivity to $t_{\max}$ may explain the overlap of the independently determined t ranges over which linear fits were obtained for α and ν. Identical results for α are obtained if the fitting region is restricted to the $t_{\max}$ given in Eq. (4).

We note that the analysis described above does not determine the linear term $A_1 t$ in Eq. (2). This is necessitated by the fact that α is zero in the Ising case, so that the critical singularity is also linear in $|t|$. The results of BER suggest that ignoring A_1 causes the value of α extracted from the analysis to be too large. Although our analysis does not enable the coefficients $B_\pm$ to be extracted, inspection of Fig. 2 shows that $(A_1+B_+)/(A_1+B_-)$ is nearly unity. A more sophisticated fitting procedure is not warranted given the accuracy of the data.

The critical temperature of 695 ± 3 K is substantially larger than the 650 ± 1.5 K obtained by Campuzano *et al.*[1] This difference is consistent with that expected from finite-size effects. The effective critical temperature T_e is expected to vary with the scale L of finite-size regions approximately as[13]

$$T_c - T_e \equiv \Delta T \simeq a L^{-\nu} T_c \ ,$$

where a is a constant and L is measured in lattice spacings [0.408 nm along the [1$\bar{1}$0] direction for Au(110)].

Landau[14] has determined a for the case of a finite simple Ising model with free boundary conditions using Monte Carlo simulations and finds $a = 1.25 \pm 0.04$, verifying an earlier result of Ferdinand and Fisher[13] who also present general arguments that a should be of order unity independent of the details of the Hamiltonians. Assuming that our measured T_c is close to that for an ideal surface and taking $T_e = 650$ K from Campuzano *et al.*[1] yields $L \simeq 20$ lattice spacings. This is in excellent agreement with the mean-size estimated for ordered (1×2) regions on the Au crystal used by Campuzano *et al.*[1] Their data show that the full width at half maximum of the fractional-order diffraction beam is about 0.05 of the spacing between integral order beams, which also corresponds to ordered regions about 20 substrate lattice spacings wide.

In conclusion, we have measured the specific-heat exponent for Au(110)(1×2) using the method of integrated intensities proposed by Bartelt *et al.*[4] The resulting $\alpha = 0.02 \pm 0.05$ is in excellent agreement with the predicted value. This result also illustrates that the method greatly increases the utility of LEED as a technique to study critical phenomena. We have also presented evidence for a dependence of the effective critical temperature on finite-size effects consistent with theoretical predictions.

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