

## Reliability of Low-Energy Electron Diffraction for Studies of Surface Order-Disorder Phenomena

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(Received 5 November 1985)

It is shown that a determination of critical exponents in surface phase transformations based on a kinematic analysis of LEED peak intensities is subject to errors caused by multiple scattering that are large enough to prevent a clear assignment to a known universality class. The multiple-scattering contribution arises from short-range fluctuations and has its maximum value at the transition temperature. The specific-heat exponent of the surface phase can be measured directly from the variation of the integral-order-beam intensity with temperature that is caused by the multiple scattering.

PACS numbers: 61.14.Hg, 61.14.Dc, 64.70.-p, 68.35.Rh

Low-energy electron diffraction (LEED) provides the most convenient and readily accessible tool for studying critical phenomena at crystal surfaces and has been used in several such investigations.<sup>1-6</sup> A major uncertainty in the interpretation of experiments in terms of critical exponents or order parameters is the influence of multiple scattering, which causes the diffraction to probe multisite correlations and not simply pair correlations as in x-ray or neutron diffraction. In the past this complication has been neglected, on the basis of arguments that near normal incidence, multiple-scattering processes in the overlayer are weak. We show here by explicit calculations of effective scattering amplitudes that this argument is not justified in general and that a kinematic analysis of peak intensities can lead to errors in the determination of critical exponents that are large enough to prevent a clear assignment of the experimental system to one of the known universality classes. We derive expressions that allow an assessment of the influence of multiple scattering and suggest methods to determine its magnitude and the diffraction conditions for which it is weak. We also show that multiple scattering is related to the specific-heat exponent of the overlayer phase.

In a second-order phase transition usually three critical exponents,  $\beta$ ,  $\gamma$ , and  $\nu$ , can be measured from diffraction data.<sup>7</sup> They describe the temperature dependences of the order parameter,  $M$ , the correlation length,  $\xi$ , and the amplitude,  $I_D$ , of the critical scattering at  $\mathbf{q} = 0$ , where  $\mathbf{q}$  is a momentum vector:

$$M \sim t^{2\beta}, \quad t < 0, \quad (1)$$

$$I_D(\mathbf{q} = 0, t) \sim |t|^{-\gamma}, \quad \xi \sim |t|^{-\nu},$$

where  $t = (T_c - T)/T_c$  is the reduced temperature. The correlation length,  $\xi$ , is defined by the exponential decay of the pair correlation function  $p(r)$ , for  $r \gg \xi$ : i.e.,  $p(r) \sim r^\theta \exp(-r/\xi)$ , where  $r$  is the separation between two scatterers, and  $\theta$  is an exponent that depends on the specific model and is dif-

ferent for the temperature regions  $T < T_c$ ,  $T > T_c$ , and  $T = T_c$ .<sup>8-10</sup> The order parameter,  $M$ , is given by the limit of pair correlations for large distances. In a LEED experiment the order parameter is measured from the intensity of the central peak (the Bragg intensity component) in a superlattice-beam profile. The fluctuations in order and the correlation length are measured from the amplitude and width of the diffuse intensity around this central peak (the critical-scattering component). The correlations that are probed by LEED contribute to the diffracted intensity not with their statistical weight but with a weight that also involves scattering amplitudes. The intensity of the diffuse scattering consequently reflects not only statistical fluctuations in order but also fluctuations in the scattering amplitudes. If multiple scattering is important the scattering amplitudes of atoms that are identical except for their positions in the structure can be quite different. It is this effect that leads to errors in the determination of critical exponents.

To calculate the influence of multiple scattering on diffraction from a structure consisting of domains and boundaries (and therefore having finite correlation lengths), it is convenient to define an effective scattering amplitude that relates the total outgoing flux from an atom with a specific environment to the incident beam.<sup>11,12</sup> Atoms in the centers of domains have environments different from those of atoms near domain boundaries and will have different effective scattering amplitudes. During a phase transition the density of domain boundaries changes and, hence, so do the effective scattering amplitudes. To demonstrate the magnitude of the variation in effective scattering amplitudes we have performed model calculations for two systems, Cu<sub>3</sub>Au(100), a surface on which a recent LEED study of the  $c(2 \times 2)$ -to- $(1 \times 1)$  order-disorder transition showed apparent strong multiple-scattering effects,<sup>4</sup> and the  $p(1 \times 2)$  overlayer of O on W(110), which was chosen to represent a typical chemisorption system. For both systems two layers, the superlattice

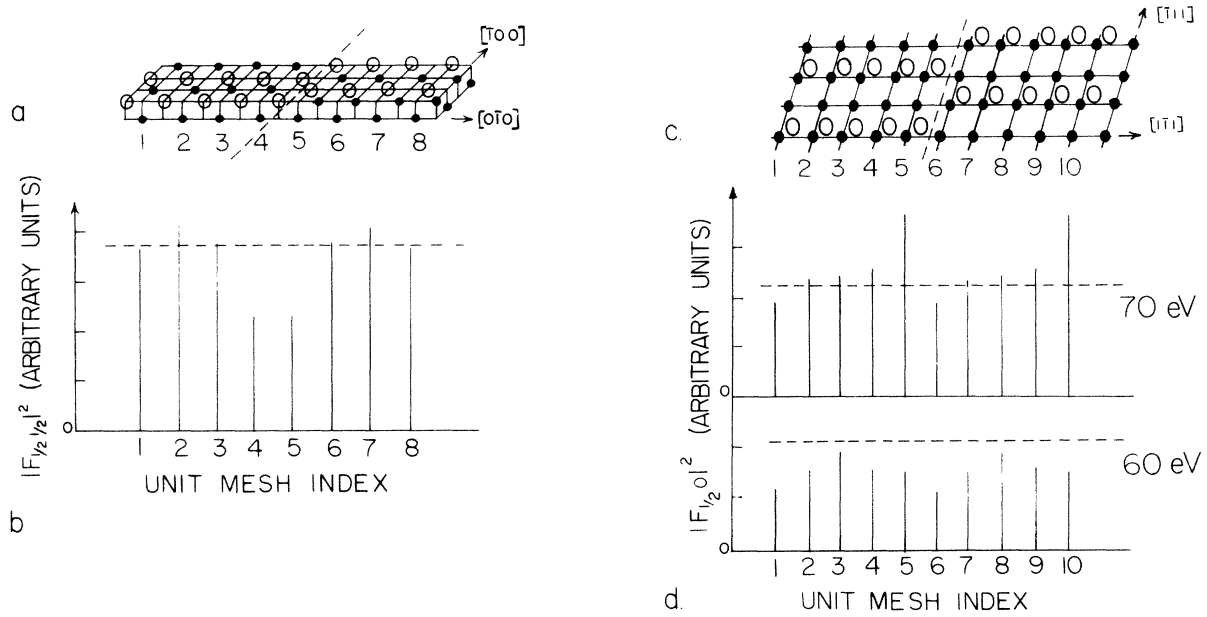


FIG. 1. Variation of effective scattering factors for unit meshes near an antiphase boundary. (a) Model of  $\text{Cu}_3\text{Au}(100)c(2 \times 2)$ . Filled circles, Cu atoms; open circles, Au atoms. (b) Effective scattering factors of the  $(\frac{1}{2}, \frac{1}{2})$  beam for the individual unit meshes shown in (a);  $E_p = 108$  eV, normal incidence. (c) Model of  $\text{W}(110)p(2 \times 1)\text{-O}$ . Filled circles, W; open circles, O. (d) Effective scattering factors of the  $(\frac{1}{2}, 0)$  beam at two energies for the individual unit meshes shown in (c). In (a) and (c) the antiphase boundary is marked by the dashed line. The dashed lines in (b) and (d) show the magnitudes of the scattering factors for the respective perfect lattices.

and one underlying  $(1 \times 1)$  layer, were assumed. For  $\text{Cu}_3\text{Au}$  a periodic array of antiphase boundaries separated by 7 overlayer lattice constants was assumed.<sup>13</sup> The model and the scattering factors for the individual unit meshes are shown in Fig. 1. The domains are chosen large enough to avoid the occurrence of multiple-scattering paths that see more than one domain boundary. The individual scattering amplitudes for all unit cells were calculated by use of the symmetrized version of the  $t$ -matrix method.<sup>14</sup> The atomic potentials and nonstructural parameters were the same as those used in previous LEED structure analyses.<sup>15</sup> Figure 1(b) shows the effective scattering factors for the model of  $\text{Cu}_3\text{Au}(100)\text{-}c(2 \times 2)$  shown in Fig. 1(a). Figure 1(d) shows scattering factors for O on  $\text{W}(110)$ , which were calculated for periodic antiphase boundaries separated by 5 overlayer lattice constants [Fig. 1(c)]. Results on both systems show that effective scattering factors of unit meshes near domain boundaries may differ substan-

tially from those of meshes in the perfect lattice and that the variation due to multiple scattering may be of the same order of magnitude as the scattering factors of meshes in the perfectly ordered structure. The lateral extent of this variation away from the domain wall may frequently be limited to one or two lattice constants but may in unfavorable cases be greater. Both the magnitude and extent depend on diffraction parameters and atomic scattering factors.

To calculate how the multiple scattering influences the determination of the order parameter and correlation length, we write the total diffracted intensity in terms of effective scattering amplitudes  $f_{i,n}(\mathbf{k}, \mathbf{k}')$ . The index  $i$  refers to the atom of type  $i$  (e.g., in the Ising model to atoms  $A$  and  $B$ ) and the index  $n = 1 - N_c$  refers to the atomic configuration of its environment. The total number  $N_c$  of different configurations depends on the attenuation length of the electron.  $\mathbf{k}$  and  $\mathbf{k}'$  are the wave vectors of the incoming and outgoing beams. The diffracted intensity at  $\mathbf{q}$  and reduced temperature  $t$  is then

$$I(\mathbf{q}, t) \sim N^2 |\bar{f}|^2 \delta(\mathbf{q}) + N \sum_r \sum_{i,j,m,n} \langle [f_{j,n}(\mathbf{r}) - \bar{f}] [f_{j,m}^*(0) - \bar{f}^*] \rangle e^{-i\mathbf{q} \cdot \mathbf{r}}, \tag{2}$$

where  $\bar{f} = \sum_{i,n} p_{i,n} f_{i,n}$  and  $\sum_n p_{i,n} = p_i$ ,  $\mathbf{q} = \mathbf{k} - \mathbf{k}' + \mathbf{g}$ ,  $\mathbf{g}$  is a reciprocal-lattice vector, and the arguments  $\mathbf{k}$  and  $\mathbf{k}'$  of the scattering amplitudes have been dropped. The probability  $p_i$  is the occupation number (or equivalently the coverage) for the  $i$ th sublattice. The probabilities,  $p_{i,n}$ , for the configurations describe the multisite correlations.

The influence of multiple scattering on the intensity of the Bragg scattering peak is seen by separating the contributions of boundary atoms:

$$f_{i,n} = f_{i,1} + \Delta f_{i,n}, \quad \bar{f} = \sum_i p_i f_{i,1} + \sum_{i=1}^2 \sum_{n=1}^{N_i} p_{i,n} \Delta f_{i,n} = \sum_i p_i f_{i,1} + \sum_i x_i(t) \bar{\Delta} f_i, \quad \bar{\Delta} f_i = \sum_n \Delta f_{i,n}, \quad (3)$$

where the  $f_{i,1}$  are the effective scattering amplitudes in the ordered structure for  $T < T_c$ ,  $\bar{\Delta} f_i$  is the average deviation from  $f_{i,1}$ , and  $x_i(t)$  is the fraction of atoms of type  $i$  near a boundary. This fraction is proportional to the total boundary length of the fluctuations. To a first approximation we assume that  $\bar{\Delta} f_i$  is constant during the ordering process. This approximation is, of course, only valid in a certain temperature range and not at  $T = T_c$ . The averages  $\bar{\Delta} f_i$  are defined differently below and above  $T_c$ .<sup>16</sup>

We consider a phase transition in an antiferromagnetic Ising model with two atoms,  $A$  and  $B$ . We obtain for the peak intensities<sup>17</sup>

$$I_p\left(\left(\frac{1}{2}, \frac{1}{2}\right), t\right) \sim M^2 N^2 |f_A - f_B|^2 \left| 1 + x(t) \frac{\bar{\Delta} f_A - \bar{\Delta} f_B}{f_A - f_B} \right|^2, \quad (4)$$

$$I_p\left((0, 0), t\right) \sim N^2 |f_A + f_B|^2 \left| 1 + x(t) \frac{\bar{\Delta} f_A + \bar{\Delta} f_B}{f_A + f_B} \right|^2,$$

where  $M$  is the long-range order parameter,  $N$  is the total number of atoms, and  $\bar{\Delta} f_A$  and  $\bar{\Delta} f_B$  are as defined above. Equation (4) shows that the intensities of the integral-order beams as well as the half-order beams vary with temperature. The temperature dependence of the fraction of atoms in boundaries behaves like the derivative of the free energy and is therefore related to the specific-heat exponent,  $\alpha$ , of the overlayer<sup>18</sup>:

$$x(t) \sim a + b^\pm |t|^{1-\alpha} + c^\pm |t|, \quad (5)$$

where the plus and minus signs apply for  $t > 0$  and  $t < 0$ , respectively.<sup>19</sup> We obtain for the critical behavior of the peak intensities of integral and half-order beams

$$I_p\left(\left(\frac{1}{2}, \frac{1}{2}\right), t\right) \sim t^{2\beta} |A_1^\pm(\mathbf{k}, \mathbf{k}') + B_1^\pm(\mathbf{k}, \mathbf{k}')| |t|^{1-\alpha} + C_1^\pm(\mathbf{k}, \mathbf{k}') |t|^2, \quad (6)$$

$$I_p\left((0, 0), t\right) \sim |A_2^\pm(\mathbf{k}, \mathbf{k}') + B_2^\pm(\mathbf{k}, \mathbf{k}')| |t|^{1-\alpha} + C_2^\pm(\mathbf{k}, \mathbf{k}') |t|^2.$$

The intensity variation of the integral-order beams with temperature is due purely to the influence of multiple scattering. A measurement of this variation allows a determination of the specific-heat anomaly during a phase transition. The factors  $A(\mathbf{k}, \mathbf{k}')$ ,  $B(\mathbf{k}, \mathbf{k}')$ , and  $C(\mathbf{k}, \mathbf{k}')$  are complex numbers that are proportional to the relative variation of effective scattering amplitudes. They may vanish at specific diffraction conditions but have in general the same order of magnitude as the single scattering, as shown in the examples in Fig. 1. The multiple-scattering contribution is different below and above the transition temperature and changes its sign, which causes a continuous increase or decrease of the intensities of the integral-order beams. Its influence is maximum at  $T_c$ . This behavior is illustrated schematically in Fig. 2. It has recently been observed for  $\text{Cu}_3\text{Au}(100)$ .<sup>4</sup> Specifically for  $\text{Cu}_3\text{Au}(100)$  we find a decrease of the  $(0,0)$ -beam intensity at 108 eV, in agreement with observation.<sup>4</sup> The magnitude of this decrease is also in rough agreement with experiment.<sup>4</sup> Equation (6) can also explain the observation that the peak intensities of neither the  $(\frac{1}{2}, \frac{1}{2})$  nor the  $(0,0)$  beam gave a straight line on a  $\log I_p$ -vs- $\log t$  plot,<sup>4</sup> as would be expected if a universal exponent  $\beta$  were measured.

To determine the influence of multiple scattering on

the diffuse intensity, we separate the fluctuations in order from the fluctuations occurring in the effective scattering amplitudes brought about by multiple scattering. We obtain for the peak value of the diffuse

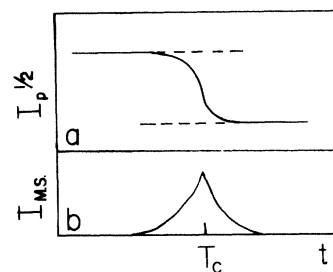


FIG. 2. Schematic representation of multiple-scattering correction for the peak intensities of integral-order beams. (a) Decay of the square root of the peak intensity,  $I_p((0,0),t)$  from Eq. (6), with temperature. In the kinematic limit there would be no intensity decay. (b) Multiple-scattering contribution. The maximum effect occurs at  $T_c$ . The multiple-scattering contribution is not necessarily symmetric around  $T_c$ . The same effect occurs in superlattice beams in addition to the intensity decay due to the order-disorder transition.

intensity<sup>20</sup>

$$I_D(\mathbf{q}=0, t) \sim |t|^{-\gamma} |A_1^\pm(\mathbf{k}, \mathbf{k}') + B_1^\pm(\mathbf{k}, \mathbf{k}')|t|^{1-\alpha} + C_1^\pm(\mathbf{k}, \mathbf{k}')|t|^2 + D^\pm(\mathbf{k}, \mathbf{k}')t^{-\alpha} + \text{const.} \quad (7)$$

Equation (7) shows that the peak intensity of the diffuse scattering has two different multiple-scattering corrections. The divergence  $|t|^{-\gamma}$  is enhanced or diminished by a cusplike function that arises from the fact that the average scattering amplitudes change with temperature. This factor is the same as for the central peak discussed above. In addition to that correction term there is a second contribution that exhibits a divergence like the specific heat. It arises from fluctuations in the effective scattering amplitudes and is therefore proportional to free-energy fluctuations. The factor  $D^\pm(\mathbf{k}, \mathbf{k}')$  has the same order of magnitude as the first correction term and vanishes only when all individual multiple-scattering contributions become negligibly small. One concludes that  $\gamma$  cannot be reliably obtained from a kinematic analysis.

In summary, we have shown that the peak intensities of the central peak and the critical scattering have multiple-scattering corrections that can be related to the specific-heat exponent. The total intensity—the sum of integrated critical scattering and the central peak—is not conserved as a function of temperature if multiple scattering is considered. In fact, the total intensity can be used to test whether multiple-scattering effects are important at the chosen diffraction conditions. When it is important, it can modify the values of the critical exponents that are extracted from the data sufficiently to shift assignment from one universality class to another. The description given above is valid only for a range of temperatures. Far away from the critical point the power-law approximation is not valid. Directly at the transition temperature the assumption made in Eq. (3) that the  $\overline{\Delta f}$ 's are temperature independent is not valid, because the correlation functions decay differently with distance at  $T_c$  from the way they do above or below  $T_c$ . Between these limits, it should be possible to analyze the critical behavior quantitatively.

Our conclusions thus cast doubt on the reliability of previous determinations of critical phenomena in overlayers that have been evaluated within the kinematic approximation. Although multiple scattering makes the analysis of the experimental phase-transition data more complicated, it also offers new perspectives. Because kinematic diffraction probes only the pair correlations, the existence of interactions between further neighbors must be deduced indirectly. If the calculations for the effective scattering amplitudes can be made quantitative, the measurement of multisite correlations becomes possible from an analysis of the

diffracted intensity during a phase transition.

This research was supported by the U.S. Office of Naval Research Chemistry Program.

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<sup>16</sup>For  $T > T_c$  the fluctuations are ordered regions within areas of uncorrelated occupation. Then  $\overline{\Delta f}_i$  is defined as the deviation from the mean value of the high-temperature limit. This is only of importance for the integral-order beams because the mean value  $\bar{f}$  vanishes for the superlattice beams.

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<sup>19</sup>In the Ising model  $|t|^{1-\alpha}$  is replaced by  $|t| \ln |t|$ .

<sup>20</sup>Details will be presented elsewhere.