

Dominance of short-range-order effects in low-energy electron-diffraction intensity spectra

P. Hu, C. J. Barnes, and D. A. King

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom

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Using low-energy electron-diffraction (LEED) formalism, we demonstrate theoretically that LEED I - V spectra are characterized mainly by short-range order. We also show experimentally that diffuse LEED (DLEED) I - V spectra can be accurately measured from a disordered system using a video-LEED system even at very low coverage. These spectra demonstrate that experimental DLEED I - V spectra from disordered systems may be used to determine local structures. As an example, it is shown that experimental DLEED I - V spectra from K/Co {10 $\bar{1}$ 0} at potassium coverages of 0.07, 0.1, and 0.13 monolayer closely resemble calculated and experimental LEED I - V spectra for a well-ordered Co{10 $\bar{1}$ 0}- $c(2\times 2)$ -K superstructure, leading to the conclusion that at low coverages, potassium atoms are located in the fourfold-hollow sites and that there is no large bond-length change with coverage.

I. INTRODUCTION

Low-energy electron diffraction (LEED) has to date been used to determine the geometries of more than 500 surface structures, either clean or with adsorbed overlayers.^{1,2} Although the oldest and best established surface structural probe, LEED still attracts much interest due not only to advances in data collection and analysis techniques and improvements in accuracy, but also to some other challenging directions.³⁻⁵ Virtually all structures determined possess long-range order. Not until the recent development of diffuse LEED (DLEED) by Pendry and Saldin³ and its application⁶⁻⁹ was the technique extended to the study of systems with only short-range order.

Conventional LEED I - V analyses have to date only been applied to structural systems exhibiting long-range order, while DLEED is used to study systems with short-range order. In conventional LEED I - V calculations perfect order is assumed, and it is not surprising that well-ordered structures are always chosen for analysis. However, imperfectly ordered structures have been shown to have no serious consequences on I - V spectra.¹⁰ In a recent paper, Heinz, Starke, and Bothe¹¹ measured LEED I - V spectra from a system, O on Ni{100}, exhibiting only short-range order. Very recently, Starke *et al.*¹² reported a set of LEED I - V spectra from a disordered system, a monolayer of H₂O on Pt{111} using a new low-energy electron-diffraction detector. The results of Heinz, Starke, and Bothe¹¹ and Starke *et al.*¹² led to the suggestion that LEED I - V spectra measured from systems possessing short-range order only may be used to determine local structures. The theoretical basis of the technique has been qualitatively discussed by Van Hove.¹³

A convenient, accurate technique for determining surface structures exhibiting only short-range order is a useful addition to existing techniques, such as DLEED, surface-extended x-ray-absorption fine structure, and photoelectron diffraction. In order to examine the nature of the bonding between adsorbed alkali-metal atoms and

metal substrates, a knowledge of coverage-dependent bond lengths is required, and this provides an additional motivation for the present work.

We begin with a theoretical consideration of the subject, where the relationship between LEED I - V spectra and both long-range and short-range order is tackled. We demonstrate that LEED I - V spectra are characterized mainly by short-range order, and provide strong support for the idea that experimental DLEED I - V spectra from lattice-gas disordered systems, where adatoms are distributed randomly but each with an identical local environment, may be used to determine the local structure. Data are presented at several coverages for the system K/Co{10 $\bar{1}$ 0} which support these conclusions.

II. THEORETICAL CONSIDERATIONS

Order-disorder information is obtained by examination of a LEED pattern: the LEED spots are sharp and intense when the surface structure is well ordered, but diffuse when the surface structure is poorly ordered. This observation is used experimentally, for example, to study order-disorder phase transitions. This is usually achieved by fixing the incident electron beam energy and measuring the changes of beam profiles as a function of surface coverage or temperature. On the other hand, when a point in k space is fixed and the intensity variation with the incident electron beam energy is recorded, LEED I - V spectra are measured. The question we address here is the relationship between LEED I - V spectra and long-range order in the surface structure.

Saldin, Pendry, Van Hove, and Somorjai¹⁴ demonstrated theoretically that if disordered adsorbates are sufficiently far apart, the diffuse intensity can be separated into two parts: a structure factor that depends only on the nature of the long-range order and a form factor that includes the short-range structural information. However, the extension to high coverages has not been tackled quantitatively. Here, we use the "tree"-scattering schemes of Barton, Xu, and Van Hove,¹⁵ used in the theory of "near-field expansion in clusters," to deduce a

formalism which approaches the problem in a different way from that of Saldin *et al.*¹⁴

The incident electron wave is defined by a plane wave $e^{i\mathbf{k}_{in}\cdot\mathbf{r}}$ impinging on a surface from an electron gun. The incident wave can be scattered by one of the surface atoms, which is the "root" atom; the wave singly scattered by the "root" atom can be further scattered, forming a multiple-scattering "tree." As can be demonstrated,¹⁶ summing the multiple-scattering "trees" in the coherent area gives

$$\Psi_{\text{total}} = \sum_j \sum_s \Psi_{js} = \sum_{n=1}^N \sum_{m=1}^N e^{i(\mathbf{k}_{in}-k\hat{\mathbf{R}})\cdot(n\mathbf{u}+m\mathbf{v})} \times \sum_s e^{i(\mathbf{k}_{in}-k\hat{\mathbf{R}})\cdot\mathbf{w}_s} A_s, \quad (1)$$

where Ψ_{js} is a wave field from a scattering "tree" starting from the atom s in the unit cell j of the surface, \mathbf{k}_{in} is the wave vector of incident electrons, $\hat{\mathbf{R}}$ is the unit vector from the origin to the detector, \mathbf{u} and \mathbf{v} are the vectors of a unit cell, \mathbf{w}_s is the position of an atom relative to the unit cell origin. A_s is the summation of all the multiple scattering in the scattering "tree." This formalism includes multiple-scattering events and is exact. In the equation, the first term sums the scattered waves between different unit cells, and is related to the long-range order along the surface, while the second term sums the scattered waves within a unit cell, and is related to the short-range order. Therefore *the long-range and short-range order terms are formally separated.* The first two summations can be expressed as

$$\begin{aligned} & \sum_{n=1}^N \sum_{m=1}^N e^{i(\mathbf{k}_{in}-k\hat{\mathbf{R}})\cdot(n\mathbf{u}+m\mathbf{v})} \\ &= \sum_{n=1}^N e^{i(\mathbf{k}_{in}-k\hat{\mathbf{R}})\cdot n\mathbf{u}} \sum_{m=1}^N e^{i(\mathbf{k}_{in}-k\hat{\mathbf{R}})\cdot m\mathbf{v}} \\ &= \frac{1-e^{i\Delta\mathbf{k}\cdot\mathbf{u}N}}{1-e^{i\Delta\mathbf{k}\cdot\mathbf{u}}} \frac{1-e^{i\Delta\mathbf{k}\cdot\mathbf{v}N}}{1-e^{i\Delta\mathbf{k}\cdot\mathbf{v}}}, \end{aligned} \quad (2)$$

where $\mathbf{k}_{out} = k\hat{\mathbf{R}}$ and $\Delta\mathbf{k} = \mathbf{k}_{in} - \mathbf{k}_{out}$.

This is the very familiar structure factor.¹ When $\Delta\mathbf{k}$ is equal to a reciprocal-lattice vector, it gives N^2 , otherwise it is a very small number. Two important effects associated with the long-range order can be derived from the simple structure factor. (i) Long-range order certainly has a strong effect on intensities at different points in k space: for example, the $c(2\times 2)$ patterns are different from the $p(2\times 2)$ patterns due to differences in the long-range order. (ii) Well-ordered structures give rise to sharper patterns than poorly ordered structures. On the other hand, *the structure factor is energy independent.* Consequently, the structure factors are nothing but constant coefficients to the LEED I - V spectra. For an individual LEED I - V spectrum, the structure factor may affect the absolute intensities, but will not change the structural details of the spectrum.

Of course, the term A_s in Eq. (1) will contain "long-range order" information, because there will be some "long" branches along the surface in the multiple-scattering "tree." However, there are two arguments

which show that this is a very weak effect in the case of normal incidence. First, the longer "branches" of the multiple-scattering "tree" usually become weaker due to the rapid decay in amplitude with distance of multiply scattered waves. Second, the scattering of electrons by an atom is strongly anisotropic in the LEED energy range and has been termed "forward focusing" or "forward scattering"¹⁷⁻²⁰ in the medium-energy range. The angular distribution of the amplitudes of scattered electrons peaks increasingly in the forward direction as the electron energy is increased. The scattering amplitude corresponding to scattering along the surface at normal incidence is only a small fraction of that in the forward direction, particularly at high energies. Thus the scattering between adatoms along the surface is much weaker than the scattering between the adatoms and the substrate atoms at normal incidence. It should be noted that this approach can also be applied to diffuse LEED.¹⁶

III. THE DLEED I - V EXPERIMENT

LEED intensity measurements were carried out in a conventional UHV chamber operating at a base pressure of 5×10^{-11} Torr. The system was equipped with a four-grid rear-view LEED optics. LEED intensities were measured using a VG auto-LEED system. Using a Proxitronic CCD camera, which is very sensitive to low light levels, the incident beam current can be reduced. In addition, a good quality, high-resolution video cassette recorder was used, thus enabling LEED patterns over a 200-eV energy range to be recorded within several minutes for subsequent analyses or checks.

The Co $\{10\bar{1}0\}$ crystal was mounted on a manipulator which can be tilted in two orthogonal planes. The crystal was initially cleaned by cycles of argon-ion bombardment and annealing. The crystal was then dosed with O_2 and heated to about 650 K to remove a residual small amount of carbon. Finally, the clean surface was obtained by a light argon-ion bombardment, followed by a brief anneal.²¹

Potassium adsorption was performed using a commercially available getter source, which was well outgassed before the measurements. The coverage of potassium on Co $\{10\bar{1}0\}$ was calibrated and is described in detail elsewhere.²² The crystal was cooled to 170 K for data acquisition.

All data reported here were measured at normal incidence. The criterion utilized for good normal incidence settings was a Pendry R factor less than 0.1 for symmetrically equivalent beams. The quality of data was further improved by averaging symmetrically equivalent beams. The DLEED I - V spectra were obtained using a similar method to that reported by Heinz, Starke, and Bothe¹¹ and Starke *et al.*¹² The procedure used was as follows. (i) DLEED I - V spectra were measured using the conventional LEED I - V method: the intensities at certain points in k space, for example at the $(\frac{1}{2}, \frac{1}{2})$ position, were measured while sweeping the beam energy. However, instead of tracking a moving beam as in conventional LEED, the track was controlled manually to measure the diffuse intensities in the DLEED I - V case. To check the reprodu-

cibility of the experimental data, several sets of DLEED I - V spectra for both the clean surface and different K coverages were measured on different days. Visual comparison of the data sets indicated that the DLEED I - V spectra were indistinguishable. Furthermore, an integrating mode was used in which the intensity is obtained by integrating the intensities within an electronic window. In contrast, for conventional LEED a background-subtracting mode is normally used in which the background is determined with respect to the edge of the electronic window and subtracted simultaneously. (ii) The minima in the DLEED I - V spectra were fitted with a polynomial background which was then subtracted. (iii) The spectra were normalized with respect to the primary beam current. (iv) The spectra were normalized by a factor $1/E$. As the electron energy increases, the relative area in k space decreases, thus making a window size correction necessary. The incident beam current was about $1 \mu\text{A}$. The intensities were measured at 2-eV intervals for the energy range from 50 to 180 eV. The collection time for each data point was 0.3 s. The signal-to-noise ratio in a single spectrum is about 15 at intensity peaks, and it can be considerably improved by averaging symmetrically equivalent beams. The spectra shown in the paper were smoothed by a three-point smoothing routine.

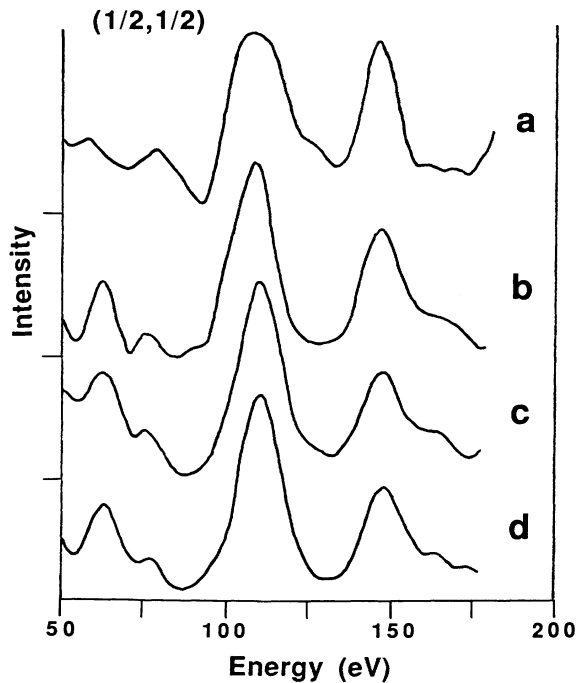


FIG. 1. Comparison between the DLEED I - V spectra from the clean surface and from three different potassium coverages on $\text{Co}\{10\bar{1}0\}$ at the $(\frac{1}{2}, \frac{1}{2})$ beam position. (a) The DLEED I - V spectrum from the clean $\text{Co}\{10\bar{1}0\}$ and at potassium coverages (b) 0.07, (c) 0.1, and (d) 0.13 monolayer. Each spectrum is rescaled and the zero lines are shifted. The maximum intensity in spectrum (a) from the clean surface is about half of those in spectra (b)–(d).

IV. RESULTS AND DISCUSSION: K ON $\text{Co}\{10\bar{1}0\}$

A comparison between DLEED I - V spectra from the clean surface and from three different potassium coverages of 0.07, 0.1, and 0.13 monolayer on $\text{Co}\{10\bar{1}0\}$ at the $(\frac{1}{2}, \frac{1}{2})$ position is shown in Fig. 1 in which each spectrum is rescaled and the zero lines are shifted, indicating by the bars on the left-hand side of the figure. Despite the apparent visual similarities, there is a clear difference between the spectrum from the clean surface and the spectra with adsorbed potassium. Although two peaks at 110 and 148 eV in the clean surface spectrum can also be found in spectra with adsorbed potassium, the remaining peaks are at different energies and all peak shapes and relative intensities are different. In contrast, the main structures, i.e., the peak positions and relative intensities, in the spectra of different potassium coverages are very similar. To illustrate this quantitatively, we calculated Pendry R factors which are shown in Table I, comparing the 0.13-monolayer I - V spectrum with those from the other surfaces. Poor agreement with the clean surface demonstrates the point that the data from the K-covered surfaces contain new information.

To focus on the adsorbate structure, the diffuse intensities from the scattering between adsorbate and substrate

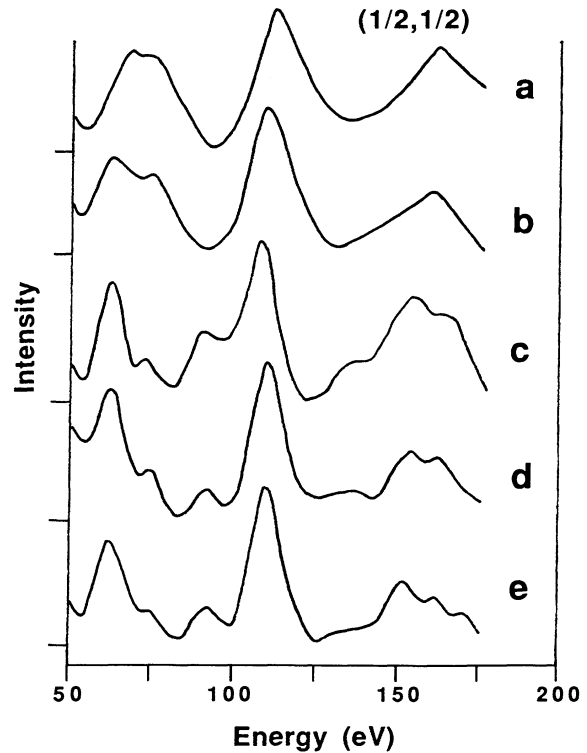


FIG. 2. Comparison between (a) the full dynamical calculated curve, (b) the experimentally measured conventional LEED I - V curve for $\text{Co}\{10\bar{1}0\}$ - $c(2 \times 2)$ -K at the $(\frac{1}{2}, \frac{1}{2})$ positions, and DLEED I - V curves from the three different potassium coverages of (c) 0.07, (d) 0.1, and (e) 0.13 monolayer at the same positions. The maximum intensity in spectrum (b) from ordered $c(2 \times 2)$ is several orders of magnitude larger than those in spectra (c)–(e).

TABLE I. Pendry R factors for comparisons of Fig. 1(d) with Figs. 1(a)–1(c).

Spectra	Clean surface (a)	0.07 monolayer (b)	0.1 monolayer (c)	0.13 monolayer (d)
R_p	0.55	0.21	0.16	0.00

can approximately be obtained by subtracting the intensities measured from the clean surface [Fig. 1(a)] from the intensities with the adsorbate [Figs. 1(b)–1(d)]; this device has been discussed and used in DLEED (Refs. 6–9 and 23–25) and DLEED I - V .¹¹ Figure 2 shows the DLEED I - V spectra for the three different potassium coverages after the subtraction. It is clear that the DLEED I - V curves obtained from these different potassium coverages are very similar. Comparison of these curves to the conventional LEED I - V curve from the $c(2 \times 2)$ potassium overlayer in the same positions in k space and a conventional, fully dynamically calculated curve indicates strong similarities. This leads to the conclusion that the local structures for the three different potassium coverages are very similar, and furthermore that they are also similar to the local structure of the $\text{Co}\{10\bar{1}0\}$ - $c(2 \times 2)$ -K, in which the potassium atoms were found to be located in fourfold-hollow sites.²² We can also exclude the possibility that there are large bond-length changes in the potassium coverage range of 0.07–0.13.

V. CONCLUSIONS

Using the LEED formalism of Barton, Xu, and Van Hove,¹⁵ we have quantitatively demonstrated that instead of long-range order, LEED I - V spectra are dominated by short-range order in the surface plane, even at high ad-

sorbate coverages, leading to the suggestion that diffuse LEED I - V spectra can be used to determine the local structure of adsorbates on surfaces, particularly at low coverages. We have also shown that DLEED I - V spectra can be accurately measured using a video-LEED system even at very low coverage. Our experimental data from $\text{K}/\text{Co}\{10\bar{1}0\}$ at potassium coverages of 0.07, 0.1, and 0.13 monolayer closely resemble calculated and experimental data for the $\text{Co}\{10\bar{1}0\}$ - $c(2 \times 2)$ -K system at 0.5 monolayer, leading us to suggest that at low coverages, potassium adatoms are located in fourfold-hollow sites and that there is no large bond-length change with coverage between 0.07 and 0.13 monolayer.

Full dynamical calculations, for example cluster calculations, should be performed in order to obtain accurate analyses of surface structures. Nevertheless, from the present work and that of Heinz, Stark, and Bothe¹¹ and Starke *et al.*,¹² it is clear that DLEED I - V analysis is a powerful technique for the study of disordered surface structures.

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¹J. B. Pendry, *Low Energy Electron Diffraction* (Academic, London, 1974).

²M. A. Van Hove and S. Y. Tong, *Surface Crystallography by LEED* (Springer-Verlag, Berlin, 1979).

³J. B. Pendry and D. K. Saldin, *Surf. Sci.* **145**, 33 (1984).

⁴P. J. Rous and J. B. Pendry, *Surf. Sci.* **219**, 355 (1989); **219**, 373 (1989).

⁵J. B. Pendry, K. Heinz, and W. Oed, *Phys. Rev. Lett.* **61**, 2953 (1988).

⁶K. Heinz, D. K. Saldin, and J. B. Pendry, *Phys. Rev. Lett.* **55**, 2312 (1985).

⁷K. Heinz, K. Müller, W. Popp, and H. Lindner, *Surf. Sci.* **173**, 366 (1986).

⁸U. Starke, P. L. de Andres, D. K. Saldin, K. Heinz, and J. B. Pendry, *Phys. Rev. B* **38**, 12 277 (1988).

⁹P. Piercy, P. A. Heimann, G. Michalk, and D. Menzel, *Surf. Sci.* **219**, 189 (1989).

¹⁰W. S. Yang, F. Jona, and P. M. Marcus, *Phys. Rev. B* **27**, 1394 (1983).

¹¹K. Heinz, U. Starke, and F. Bothe, *Surf. Sci.* **243**, L70 (1991).

¹²U. Starke, K. Heinz, N. Materer, A. Wander, M. Michl, R. Döll, M. A. Van Hove, and G. A. Somorjai, *J. Vac. Sci. Tech-*

nol. (to be published).

¹³M. A. Van Hove, in *Chemistry and Physics of Solid Surface VII*, edited by R. Vanselow and R. F. Howe (Springer-Verlag, Berlin, 1988), p. 513.

¹⁴D. K. Saldin, J. B. Pendry, M. A. Van Hove, and G. A. Somorjai, *Phys. Rev. B* **31**, 1216 (1985).

¹⁵J. J. Barton, M.-L. Xu, and M. A. Van Hove, *Phys. Rev. B* **37**, 10 475 (1988).

¹⁶P. Hu and D. A. King (unpublished).

¹⁷W. E. Egelhoff, Jr., *Phys. Rev. B* **30**, 1052 (1984).

¹⁸H. C. Poon and S. Y. Tong, *Phys. Rev. B* **30**, 6211 (1984).

¹⁹P. J. Orders and C. S. Fadley, *Phys. Rev. B* **27**, 781 (1983).

²⁰W. E. Egelhoff, Jr., *Solid State Mater. Sci.* **16**, 213 (1990).

²¹M. Lindroos, C. J. Barnes, P. Hu, and D. A. King, *Chem. Phys. Lett.* **173**, 92 (1990).

²²C. J. Barnes, P. Hu, M. Lindroos, and D. A. King, *Surf. Sci.* **251/252**, 561 (1991).

²³U. Starke, P. Bayer, H. Hloch, and K. Heinz, *Surf. Sci.* **216**, 325 (1989).

²⁴H. Ibach and S. Lehwald, *Surf. Sci.* **176**, 629 (1986).

²⁵P. L. de Andres, P. J. Rous, and J. B. Pendry, *Surf. Sci.* **193**, 1 (1988).