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Helium-adsorbate cross section on highly corrugated substrates

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The interaction of He atoms with adsorbates placed on strongly corrugated substrates is investigated both theoretically and experimentally. An analysis of the scattering process within the transition matrix approach suggests that the normalized differential cross section, associated with the attenuation of coherent diffraction due to incoherent scattering in the presence of adsorbates, is expected to be largest for the most intense coherent diffraction peaks. For the adsorption of K on Cu(115), this trend is experimentally observed.

He scattering from weakly corrugated surfaces gives rise to specular scattering, which is often many orders of magnitudes more intense than diffraction for higher-order Bragg peaks. Thus, weakly corrugated surfaces are almost perfect mirrors for He atoms. The deposition of small amounts of adsorbates on the surface produces incoherent scattering, which leads, in turn, to a decrease of the coherently scattered diffraction peak intensity. In the limit of high adsorbate dilution, the attenuation of the relative specular peak height is a direct measure of the probability for incoherent scattering, and the relative specular peak intensity decreases linearly with adsorbate coverage.[1] Thus, one can define a total cross section for incoherent scattering from the flat surface through the expression

$$\Sigma_s^f = -\frac{1}{n}\frac{d(I/I_0)}{d\theta}\bigg|_{\theta=0}, \tag{1}$$

where n denotes the number of substrate atoms per unit area, and I/I_0 is the relative specular intensity at adsorbate coverage θ. For practical purposes, I_0 is often taken as the intensity of the specularly reflected beam of the surface prior to deposition of the adsorbate.

On the other hand, He diffraction from strongly corrugated surfaces gives rise to diffraction patterns which are characterized by a number of coherent diffraction peaks, whose intensities differ but are often of the same order of magnitude. Adsorbates on such a surface also produce incoherent scattering, and consequently, coherent diffraction is attenuated. From an experimental point of view, then, the question arises whether one can use the relative attenuation of any diffraction peak for the determination of the cross section. For this purpose, we introduce what we call in the following "the normalized differential cross section,"

$$\Sigma_G^c = -\frac{1}{n}\frac{d(I_G/I_{0G})}{d\theta}\bigg|_{\theta=0}. \tag{2}$$

Here, I_{0G} is the intensity of the Gth diffraction peak prior to adsorption. With this definition, the normalized differential cross section is identical to the total cross section [Eq. (1)], if one considers diffraction from a mirrorlike surface. However, in the case of diffraction from a corrugated surface the questions then arise, first, whether the normalized differential cross sections are the same for all diffraction peaks, and moreover, whether the value of the cross section for the specular peak is the same compared to the cross section in an otherwise identical but uncorrugated system.

Based on theoretical grounds, the answers are no. An examination of the theoretical expressions shows (i) that on the corrugated surface the normalized differential cross section will be largest for the most intense peaks, and (ii) that the total cross section of the adsorbate placed on a flat surface is larger than the specular peak cross section of the same adsorbate positioned on a corrugated surface of the same nature. We show here experimentally that the former expected trend is verified for the system K/Cu(115).

THEORETICAL EXPECTATIONS

In order to justify the above statements, it is necessary to look at the equations that give the reflection coefficients and the cross sections.[2,3] For simplicity, we discuss in the following at first the theoretical expectations in terms of the differential cross section only. The ratio of an intensity measured in a final state f, to the incident intensity, gives the reflection coefficient for transition from initial state i to the final state f. For the specular channel of a periodic surface, this quantity is given by

$$R_{si} = \left|1 - \frac{i\pi h_{si}}{p_i}\right|^2 = 1 + \frac{2\pi}{p_i}\,\mathrm{Im}(h_{si}) + \frac{\pi^2}{p_i^2}\,|h_{si}|^2, \tag{3}$$

where h_{si} is the T-matrix element for the transition from the initial to the final state, and p_i the dimensionless normal component of the incident wave vector.

With similar definition for h_{Gi} and p_G, the reflection coefficient for a higher-order diffraction channel G is given by

$$R_{Gi} = \frac{\pi^2}{p_i p_G}\,|h_{Gi}|^2. \tag{4}$$

When an adsorbate is placed on a periodic surface, the reflection coefficients are given, to first-order perturbation, by

$$R_{si}^{c+a} = R_{si} + \frac{2\pi}{p_i}\,\theta\,\mathrm{Im}(\tilde{T}_{si}) + \frac{\pi^2}{p_i^2}\,\theta 2\,\mathrm{Re}(h_{si}^{*}\tilde{T}_{si}) + \frac{\pi^2}{p_i^2}\,\theta^2|\tilde{T}_{si}|^2, \tag{5}$$

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for the specular beam on a corrugated surface and by

$$R_{Gi}^{c+a}=R_{Gi}+\frac{\pi^2}{p_i p_G}\,[2\,\theta\ \mathrm{Re}(h_{Gi}^*\tilde{T}_{Gi})+\theta^2|\tilde{T}_{Gi}|^2], \tag{6}$$

for a higher-order diffraction peak. In these expressions, $\tilde{T}_{si}$ is the matrix element for scattering from one single adsorbate placed on the corrugated surface and includes the contribution of multiple scattering between the adsorbate and the uncovered corrugated surface to the reflection coefficient.

The negative derivative of these expressions with respect to θ gives the differential cross section. The sum of all these quantities is equal to the total cross section. One gets, respectively, for the specular and nonspecular diffracted beams,

$$\Sigma_s^c=-\frac{2\pi}{p_i}\left[\mathrm{Im}(\tilde{T}_{si})+\frac{\pi}{p_i}\,\mathrm{Re}(h_{si}^*\tilde{T}_{si})\right], \tag{7}$$

$$\Sigma_G^c=-\frac{\pi^2}{p_i p_G}\,2\ \mathrm{Re}(h_{Gi}^*\tilde{T}_{Gi}). \tag{8}$$

A particular case is that of scattering from a flat surface. Then $R_{si}^f=1$ (elastic scattering considered only); that is to say, $h_{si}=0$ and

$$R_{si}^{f+a}=1+\frac{2\pi}{p_i}\,\theta\ \mathrm{Im}(T_{si})+\frac{\pi^2}{p_i^2}\,\theta^2|T_{si}|^2, \tag{9}$$

$$\Sigma_s^f=-\frac{2\pi}{p_i}\,\mathrm{Im}(T_{si}), \tag{10}$$

where T_{si} is the matrix element for scattering from an adsorbate placed on the flat surface. It includes the contribution of multiple scattering occurring in this process.

In general one cannot obtain analytical expressions for the imaginary and real parts, or the phase, of any T-matrix element. We can only get their values in a numerical calculation. This is the reason why we cannot demonstrate our statement rigorously. One can only expect that they are true, by looking at the mathematical properties of these equations.

We assume now that the reflection coefficient is less than 1, which means that the intensity of the specular or a higher-order diffracted beam is less than the incident one. Then, one gets from Eq. (3),

$$-\frac{p_i}{\pi}\leqslant\ \mathrm{Re}(h_{si})\leqslant\frac{p_i}{\pi}, \tag{11}$$

$$\frac{p_i}{\pi}\,(-1-a)\leqslant\ \mathrm{Im}(h_{si})\leqslant\frac{p_i}{\pi}\,(-1+a), \tag{12}$$

with

$$a=\left(1-\frac{\pi^2}{p_i^2}\,[\mathrm{Re}(h_{si})]^2\right)^{1/2}, \tag{13}$$

which shows that $\mathrm{Im}(h_{si})$ is always negative. This is generally true and this property is confirmed by numerical calculations.[2] Equation (9) confirms this statement: because the reflection coefficient should decrease with coverage, $\mathrm{Im}(T_{si})$ should always be negative. Therefore the cross section given by Eq. (10) is positive. The same argument applied to Eq. (5) shows that

$$\mathrm{Im}(\tilde{T}_{si})+\frac{\pi}{p_i}\,\mathrm{Re}(h_{si}^*\tilde{T}_{si})<0. \tag{14}$$

While $\mathrm{Im}(\tilde{T}_{si})$ is certainly negative, one cannot say anything about the sign of the real part. Therefore the reflection coefficient for a given diffraction beam with adsorbate on the surface [Eq. (6)] may be greater or smaller than that of the clean surface. However, the corresponding differential cross sections will have the same sign.

We now compare Σ_s^f to Σ_s^c, that is,

$$|\mathrm{Im}(T_{si})|$$

and

$$\left|\mathrm{Im}(\tilde{T}_{si})+\frac{\pi}{p_i}\,[(\mathrm{Re}h_{si})(\mathrm{Re}\tilde{T}_{si})+(\mathrm{Im}h_{si})(\mathrm{Im}\tilde{T}_{si})]\right|. \tag{15}$$

In the last expression the product of the two imaginary parts is positive as the imaginary part of each matrix element is negative. This term yields a decrease of the absolute value of the cross section and, on the whole, that on the uncorrugated surface will be probably the largest. Thus, due to enhanced multiple scattering, the decrease in coherently scattered intensity under the same kinematical conditions will be smaller on the corrugated surface than compared to the flat surface, and consequently, the differential cross section deduced for specular diffraction on the corrugated surface will be smaller than the total cross section for the flat surface.

The differential cross section for a diffraction channel on the corrugated surface is given by Eq. (8). In order to compare the differential cross section for two different diffraction peaks, we have to look at the real parts,[4]

$$|h_{Gi}||\tilde{T}_{Gi}|\cos(\varphi-\alpha), \tag{16}$$

which is the product of the modulus of the matrix element multiplied by the cosine of their phase differences. We know that the modulus of h_{Gi} is larger for the more intense diffraction peak [Eq. (4)]. One can expect that the same holds also for the modulus of $\tilde{T}_{Gi}$. Under this assumption, and if the phase differences for the two beams are comparable, it follows that the coherently diffracted beam with larger intensity will show a stronger attenuation in intensity at a given adsorbate coverage; thus the differential cross section associated with this diffraction channel will be larger than that for less intense ones.

In order to make contact with experiment, we consider now the normalized differential cross sections, which are equal to the differential cross sections Σ_s^c,Σ_G^c divided by R_{si} and R_{Gi}, respectively. Consequently, the kinematical factors disappear. Using the form (16) one gets

$$\Sigma_G^c=-\frac{|\tilde{T}_{Gi}|}{|h_{Gi}|}\,\cos(\varphi-\alpha). \tag{17}$$

Under the above assumption, if the modulus of $\tilde{T}_{Gi}$ decreases more rapidly than the modulus of h_{Gi}, by going from higher intensity peaks to the lower ones, the normalized differential cross section will be the largest for the largest peak intensities. Again this can be expected because the $\tilde{T}$-matrix elements contain all the multiple scattering between corrugated

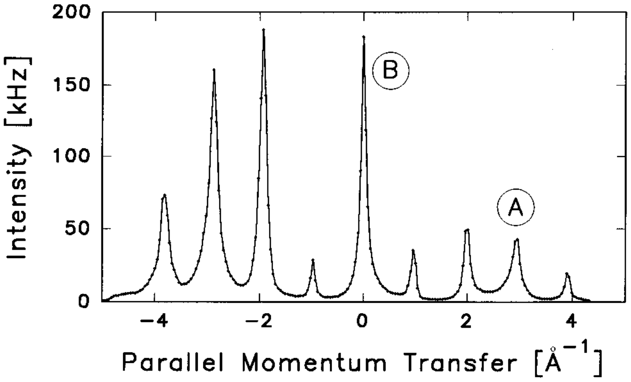

FIG. 1. He diffraction pattern from Cu(115). The scattering plane is perpendicular to the average step direction, the incident wave vector is $k_i=10.8$ Å^{-1}, and the angle between source and detector is 104°. Under these kinematical conditions, nine coherent diffraction channels are open, with maximum intensity variation of about a factor 10.

surface and corrugated surface with adsorbate. Note that the test on this last expectation, using the normalized differential cross sections, is more severe than that just using the unnormalized ones.

EXPERIMENT

We now confront these theoretical expectations with the cross sections determined for each coherent diffraction peak of the Cu(115) surface under adsorption of small amounts of K. This system has been chosen, since alkali-metal atoms interact repulsively[5] at low coverage, so that island formation is inhibited even at temperatures for which the adsorbate is mobile. Moreover, He diffraction from the clean Cu(115) surface perpendicular to the average step direction is characterized by the appearance of numerous diffraction peaks with significant variations in intensity (Fig. 1), which indicates that the He surface potential is highly corrugated in this direction.

Usually, the cross section for incoherent scattering is determined by monitoring the intensity attenuation of a selected diffraction peak with coverage. For the present purpose, we are interested in the attenuation of each of the diffraction peaks in Fig. 1. Since the expected effect might be small, the major difficulty is to assure an identical incident K flux for the experiments on different diffraction peaks. Therefore, we proceed for the determination of the normalized differential cross section (or rather the slope of the initial attenuation in intensity; we do not give here absolute values for the cross section, since the K coverage is not accurately independently known) for each diffraction peak as follows. Starting from the clean surface, we have continuously measured full angular distributions during deposition of K at low flux. This procedure has the advantage that the error in the determination of the cross section due to possible variations of the incident K flux is minimized. Moreover, one can easily check that the half widths of the coherent diffraction peaks do not change, which is a prerequisite for the use of peak amplitudes only. We found in the coverage range of this experiment that the half widths stay constant for all peaks within 6%.

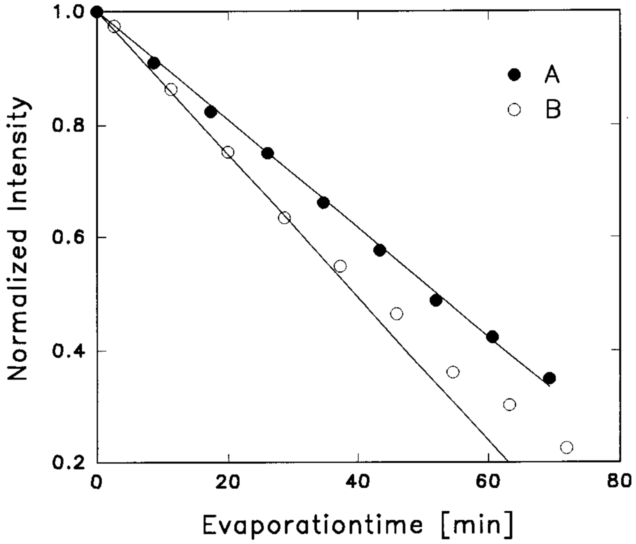

FIG. 2. Normalized (peak) intensity variation of the coherent diffraction channels labeled *A* and *B* in Fig. 1 with time under identical impinging K flux. The difference in slope and thus normalized differential cross section is about 30% for these two peaks, whose initial absolute intensities differ by about a factor 4.

Figure 2 shows the result of this experiment for selected diffraction peaks labeled *A* and *B* in Fig. 1. The slopes differ by about 30%, and the absolute value of the slope of peak *B* is larger, which implies that the differential cross section for the intense peak is indeed larger. In Fig. 3 we show a compilation of the slopes deduced from the initial decay in intensity for all diffraction peaks in Fig. 1. At least a tendency towards the theoretical expectation is indeed reflected in our data. However, this experimental result has to be discussed with respect to the following source of uncertainty. Generally, the cross section could show an intrinsic angular depen-

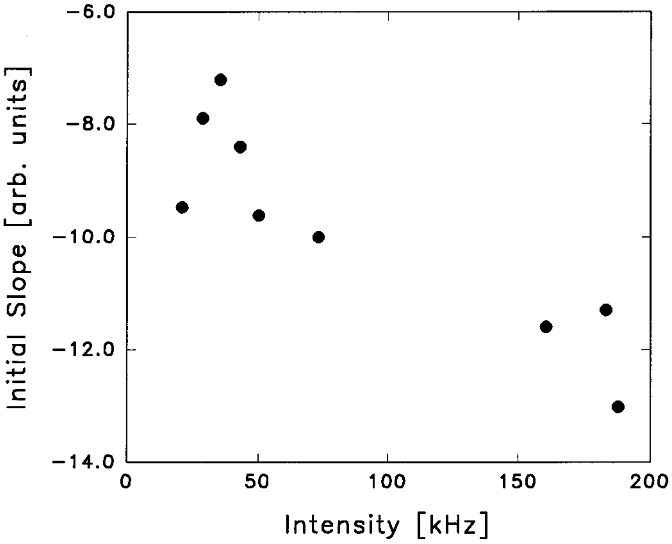

FIG. 3. Compilation of the initial slopes deduced from the attenuation of each diffraction peak in Fig. 1 due to K adsorption vs initial absolute peak intensity. The trend towards larger slopes and thus larger normalized differential cross sections for the most intense peaks is observed.

dence due to an anisotropic scattering potential.[6] Indeed, on the basis of the present data set, such an effect cannot be completely ruled out, but the fact that diffraction peaks with low intensity for both positive and negative parallel momentum transfer show a small cross section suggests that an intrinsic angular dependence of the cross section does not produce the observed phenomenon.

In conclusion, the normalized differential cross section for adsorbates positioned on strongly corrugated substrates has been investigated both theoretically and experimentally. Theory suggests that due to multiple scattering effects, the normalized differential cross section is largest for the most intense coherent diffraction peaks. This trend is observed experimentally for the He-K/Cu(115) system. Of course, further experimental work is necessary in order to establish whether this is a general phenomenon. Moreover, it would be useful to have an independent calibration of the K coverage in order to determine absolute values for the normalized differential cross section. This would allow for a direct comparison of the values deduced here for the corrugated surface with the total cross section of a corresponding mirrorlike surface, e.g., Cu(001).[7]

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