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DEBYE-WALLER FACTOR FOR He/Pt(111)

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We report accurate measurements of the dependence of the specular reflectivity on surface temperature and on incident angle, for He scattering off Pt(111). The usual Debye-Waller formula with a Beeby correction fits the data, provided that the effective well depth is adjusted. We show that a full calculation of the Debye-Waller exponent also reproduces the data. The inelastic atom-surface interaction and the surface phonon spectrum used in the calculation are the ones that reproduce the time-of-flight data obtained in separate experiments. No further adjustable parameters are needed.

1. Introduction

The specular reflection coefficient I/I_0 of He atoms from clean smooth metal surfaces, when diffraction is negligible, is less than unity due to inelastic processes. In fact, $1 - I/I_0$ gives a direct measure of the integrated strength of the inelastic atom-surface coupling. The temperature dependence of I/I_0 and its dependence on incident angle should both be predicted directly by the theory, if the coupling is known. We report here some new data on the temperature dependence of I/I_0 that have been taken with particular care on the He/Pt(111) system for $25 < T < 700$ K and we compare these and earlier data [1,2] on angular dependence with theoretical results. For the calculations we use a simple model of inelastic coupling that correctly reproduces the intensity of single-phonon creation and annihilation processes inferred from the analysis of separate time-of-flight scattering data.

Some of us recently published [3] an analogous comparison with theory of older data obtained by Horne, Yerkes and Miller [4] for He/Ag(111). The

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present work, using more recent and carefully collected, data, represents a further testing of the same theory for a different system. The other system that has been studied in detail is He/Cu: data on specular and diffracted intensities have been collected by Lapujoulade et al. [5] and have been analyzed by these authors in collaboration with Jayanthi, Armand and Manson [6,7], using a model of inelastic scattering somewhat different from ours.

Basically, the questions addressed here and in the other papers just quoted concern the applicability of the simple formula

$$I/I_0 = e^{-2W}, \quad (1)$$

with

$$2W = \frac{3T_s (\hbar^2 \Delta k_z^2 + 8mD)}{Mk_B T_D^2}, \quad (2)$$

as a function of the surface temperature T_s and of the perpendicular momentum transfer Δk_z , for the appropriate values of the parameters D (the effective well depth) and T_D (the effective surface Debye temperature). M and m are the surface atom and He mass, respectively. If eq. (2) can be firmly established for well-characterized systems, it can then be used widely to analyze specular reflection and can be extended with some confidence to diffraction and to inelastic intensities.

An account of the experimental procedure and results is given in section 2 and the theoretical approach is described in section 3. Further details of the theory and general background discussion can be found in refs. [3,8], but for this calculation we have used exact, numerically computed matrix elements instead of the approximation used earlier. The conclusions are given in the final section: we can anticipate here that the data on He/Pt(111) generally support eq. (2) with the values of T_D and D given by theory; however, D is larger than the well depth of the He-surface potential and depends on incidence conditions, especially at small Δk_z .

2. Experimental

The correctness of eq. (2) can be verified experimentally by measuring the specular reflection of a thermal He beam either as a function of the perpendicular momentum transfer Δk_z , at constant surface temperature T_s , or as a function of T_s at constant Δk_z . Both types of experiments have been performed. They confirmed eq. (2) and led, within experimental uncertainty, to the same value for T_D , which is (accidentally) [3] close to the Debye temperature of bulk Pt. Note that the experiments have been performed in different molecular beam machines and with different Pt samples. The preparation of

the Pt(111) surface and cleaning procedures were, however, identical (see for details ref. [9]). The linear step density of both Pt(111) samples has been estimated to be less than 10^{-3} , corresponding to an average terrace width larger than 2000 Å.

2.1. I/I_0 versus Δk_z at constant T_s

These experiments have been performed in the apparatus described in some detail by Poelsema et al. [10]. Here we give only a few details pertinent to the present experiments. The He nozzle beam, generated at room temperature (He energy $E = 63$ meV) is collimated to 0.2° and modulated mechanically to improve signal to background discrimination. The quadrupole detector can be rotated on a goniometer in and out of the plane of incidence. The detector has been set at the largest distance from the sample (400 mm) in order to obtain the maximum detector angle resolution of 0.15° . All data have been taken in the pulse counting mode.

Fig. 1 shows the dependence on $\cos^2 \theta_i$, i.e. the dependence on Δk_z^2 at fixed energy, of the specular peak height at a fixed target temperature of about $T_s = 450$ K. On the semilogarithmic plot, the data should fall on a straight line, if eqs. (1) and (2) are valid. The corresponding Debye temperature is $T_D = 231 \pm 2$ K and the effective well depth is $D = 12$ meV. The theoretical curves also plotted are discussed in the last section.

2.2. I/I_0 versus T_s at constant Δk_z and inelastic scattering data

This second type of experiment has been performed in the high resolution scattering apparatus described in detail by David et al. [11]. The apparatus

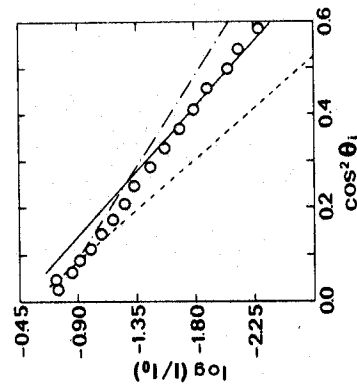


Fig. 1. Reflectivity at $T_s = 450$ K and $E_i = 63$ meV versus $\cos^2 \theta_i$. Circles: experimental results. Full line: theoretical results with the potential of eq. (12), using modified surface force constants (section 3.3). Dashed line: same as full line, but using bulk force constants. Dash-dotted line: same as full line, but with a potential containing only the repulsive part with Beeby corrections.

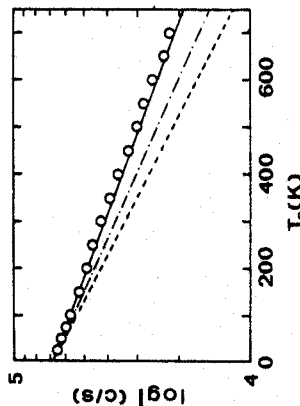


Fig. 2. Reflected intensity at $E_i = 18.9$ meV and $\theta_i = 45^\circ$ versus surface temperature. Same symbols as for fig. 1.

consists of a He nozzle beam source, an ultrahigh-vacuum target chamber, and a pseudorandom time-of-flight (PRTOF) detector line; the total scattering angle is fixed at 90° , i.e. $\theta_i = \theta_f = 45^\circ$. The angular spread of the incident beam and the angle subtended by the detector are both equal to 0.2° . The overall energy spread of the PRTOF spectrometer (including the energy spread of the beam, pseudorandom chopper and detector) is $\Delta E/E \approx 2.1\%$ for energies around 20 meV.

Fig. 2 shows the measured thermal attenuation of the specular peak height at constant Δk_z for the surface temperature range $25 < T_s < 700$ K in a semilogarithmic plot. No deviation from the behavior predicted by eq. (2) (a straight line) is observed in the entire temperature range. The resulting value for T_D is 232 ± 3 K assuming the same well depth of 12 meV.

With this experimental arrangement we have also measured the surface phonon dispersion of the clean Pt(111) [12]. Fig. 3 shows a typical He energy loss spectrum measured along the ΓK azimuth, with the incident beam angle and energy $\theta_i = 35^\circ$ and $E = 18.2$ meV, respectively. Also shown in fig. 3 is the theoretically calculated He energy loss spectrum (solid line) using the simple model for the inelastic coupling, which is discussed in the next section.

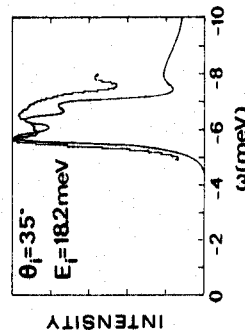


Fig. 3. He/Pt(111) energy loss spectrum measured along the ΓK direction with $\theta_i = 35^\circ$ and $E_i = 18.2$ meV. Histogram: experimental spectrum. Full line: theory.

In spite of the richness of the phonon spectrum in this direction of the surface Brillouin zone (Rayleigh wave, pseudo Rayleigh wave as well as a longitudinal resonance are present) the intensities of the different single phonon excitations are well described by our simple inelastic coupling model. This model also fits quite satisfactorily the inelastic scattering data of Harten et al. for the same He/Pt(111) system [13].

3. Theory

In the distorted wave Born approximation (DWBA), the specular intensity is given by $I/I_0 = 1 - 2W$, where $2W$ is found in eq. (2.3) of ref. [3] (we shall not redefine all the symbols here):

$$2W = \frac{m^2}{2\hbar^3 N M k_{iz}} \sum_{\mathbf{Q}, r} \frac{\text{Re}(k_{iz})}{|k_{iz}|^2} \frac{n(\omega_r(\mathbf{Q}))}{\omega_r(\mathbf{Q})} \times \left| \int d\mathbf{z} \chi(k_{iz}, \mathbf{z}) \nabla \cdot \mathbf{U}_{\mathbf{Q}, r}(\mathbf{z}) \chi(k_{iz}, \mathbf{z}) \right|^2. \quad (3)$$

The replacement of $1 - 2W$ with $\exp(-2W)$ is partially justified by a semiclassical argument [14] and by the higher order calculations of Armand et al. [7] for He/Cu(111) (the deviations from an exponential that are found by these authors would not be appreciable in the temperature range $25 < T_s < 700$ K that we consider here). The crucial quantities in eq. (3) are the phonon frequencies $\omega_r(\mathbf{Q})$, the polarization vectors $\mathbf{e}(z)_r$ corresponding to the $(\mathbf{Q}, r)$ normal coordinate, and the matrix elements of the dynamical potential $U_{\mathbf{Q}, r}(\mathbf{z})$ given by:

$$U_{\mathbf{Q}, r}(\mathbf{z}) = \sum_{\mathbf{z}'} \mathbf{e}(\mathbf{z}')_r V_{\mathbf{Q}}(\mathbf{z} - \mathbf{z}'), \quad (4)$$

where $V_{\mathbf{Q}}(\mathbf{z} - \mathbf{z}')$ is the two dimensional (2D) Fourier transform of the interaction potential between the He atom and the atom plane at $\mathbf{z} = \mathbf{z}'$.

3.1. The potential

We consider the atom-surface interaction potential as the sum of a van der Waals attraction V_{vdW} and a repulsive part V_R .

The repulsive interaction in the effective medium approximation [15] can be written as:

$$V_R(r) = \alpha \sum_i \rho_s(r - r_i), \quad (5)$$

where [2] $\alpha = 176 \text{ eV } a_0^3$ ($a_0 = \text{Bohr radius}$) and the atomic charges ρ_s are constructed from the atomic wavefunctions of McLean and McLean [16] that

correspond to the minimum of the total energy of the free atom. The atomic positions r_i have been assumed to be those of the unrelaxed surface and the origin is chosen so that $z_i = 0$ for the surface atoms.

The attractive interaction due to the van der Waals forces is approximated as a sum of two-body interactions:

$$V_{\text{vdw}}(\mathbf{r}) = -c_6 \sum_i \frac{f_6(\beta|\mathbf{r}-\mathbf{r}_i|)}{(\mathbf{r}-\mathbf{r}_i)^6}. \quad (6)$$

The function f_6 eliminates the divergence at $|\mathbf{r}-\mathbf{r}_i| = 0$ and can be approximated by [17]:

$$f_6(x) = 1 - \sum_{k=0}^6 \frac{x^k}{k!} e^{-x}. \quad (7)$$

The parameter β is related to the repulsive potential and will be discussed later on.

At large distances from the surface this term reduces to the usual expression:

$$V_{\text{vdw}}(z) = -c_3/(z-d/2)^3, \quad (8)$$

where d is the interplanar spacing, z is the distance from the top surface layer of atoms, and $c_3 = \pi c_6/6\Omega_0$ (Ω_0 is the atomic volume). At small distances eq. (6) takes into account the corrugation, in the attractive potential, produced by the surface atoms. In the calculations we take $c_6 = 408.45 \text{ eV } \text{\AA}^6$ which is 25% larger than the value quoted by Zaremba [18]. We found it necessary to increase the value of c_6 in order to reproduce the physisorption well derived by Kleiman and Landman [19] and to explain the decay of the inelastic scattering intensities [13]. A large value of c_6 is also justified by the neglect of higher order terms in the expansion of the van der Waals interaction in terms of the interatomic distances.

The total potential V is then given by:

$$V(\mathbf{R}, z) = \alpha \sum_i \rho_a(\mathbf{r}-\mathbf{r}_i) - c_6 \sum_i \frac{f_6}{(\mathbf{r}-\mathbf{r}_i)^6}, \quad (9)$$

where we have put $\mathbf{r} = (\mathbf{R}, z)$. We evaluate $V(\mathbf{R}, z)$ by taking a cluster of 289 atoms per plane and 15 planes, which ensures a good convergence of the attractive part.

According to eqs. (3) and (4) we should separate out the contribution of each atomic plane to $V(\mathbf{R}, z)$, compute the 2D Fourier transforms $V_0(z, z_i)$, evaluate their matrix elements, and then sum over Q in the first Brillouin zone in order to determine $2W$. Since this is very cumbersome, we simplify the calculation without affecting the accuracy of the results by fitting a simple analytic form to $V(\mathbf{R}, z)$ as follows.

For a given perpendicular energy E_z , the effective surface corrugation $z_i(\mathbf{R}, E_z)$ is determined by the classical turning points of the He atom:

$$E_z = V(\mathbf{R}, z_i(\mathbf{R}, E_z)). \quad (10)$$

In the quantum mechanical treatment the scattering processes that count most occur in regions of $\mathbf{r}$ space where z is close to z_i . For this reason our model potential should reproduce accurately the corrugation evaluated with the potential of eq. (9). We find that a good approximation to $V(\mathbf{R}, z)$ in the energy range $E_z = 5-40 \text{ meV}$ used in the experiments is given by:

$$V(\mathbf{R}, z) = U_0 \sum_{\mathbf{r}_i} \exp(-\beta z_i) \exp(-Q_c^2 |\mathbf{R} - \mathbf{r}_i|^2/2) - \frac{c_3 f_3(\beta(z-d/2))}{(z-d/2)^3}, \quad (11)$$

where f_3 is defined similarly to f_6 . The parameters U_0 and β are determined by using eq. (10) and requiring that eq. (9) and eq. (11) give the same average turning point $\bar{z}_i$ and the same derivative of $\bar{z}_i$ with respect to E_z . The factorized form of the repulsive term in eq. (11) is justified by the fact that $\nabla_i V(\mathbf{R}, z)$ with respect to the atomic position $\mathbf{r}_i$, evaluated numerically from eq. (9), is proportional to the Gaussian $\exp(-Q_c^2 |\mathbf{R} - \mathbf{r}_i|^2/2)$, as shown in ref. [20]. The corrugation effects due to the van der Waals interaction are largely included in the repulsive part. From the numerical values of $\nabla_i V(\mathbf{R}, z)$ at $z = z_i$, Q_c^2 can be determined with a least-squares fit. The values obtained in this way for $E_z = 10 \text{ meV}$ are $U_0 = 12.51 \text{ eV}$, $\beta = 1.83 \text{ \AA}^{-1}$, and $Q_c^2 = 0.9 \text{ \AA}^{-2}$. We note that the energy dependence of β , U_0 and Q_c is weak in the range of energies $E_z = 5-40 \text{ meV}$. For this reason we neglect it in the present calculations. We found that the corrugation obtained with the model potential reproduces to within 1% the corrugation derived from the cluster calculation.

The laterally averaged potential calculated with the model potential of eq. (11) is reported in fig. 4. The difference with the laterally averaged total potential of eq. (9) is less than 0.1 meV and cannot be seen from fig. 4. In this figure is also reported the laterally averaged repulsive part of $V(\mathbf{R}, z)$. The major effect due to the inclusion of the attractive part is to shift to the left the classical turning point of the repulsive potential and to increase the cut-off parameter Q_c .

3.2. Matrix elements

In computing the dynamical atom-surface potential, we make the usual assumption that the long-range van der Waals interactions tend to cancel out when the sum over z_i is performed in eq. (4). We are then left with the repulsive interaction, which comes almost entirely from the top atom layer

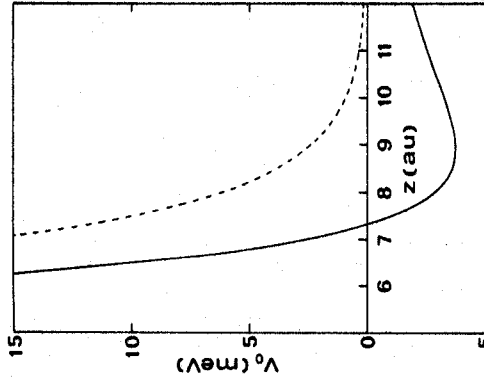


Fig. 4. The interaction potential for He/Pt(111).

($z_l = 0$). In effect then we need only the 2D Fourier transform of the repulsive part of the model potential (11), which is easily found analytically and gives

$$U_{Q,z}(z) = e(0|Q) \frac{2\pi U_0}{Q_c^2 A_c} e^{-\beta z} e^{-Q^2/2Q_c^2}. \quad (12)$$

The Gaussian factor which enters in $U_{Q,z}(z)$ is the lateral cut-off function which reduces the scattering intensity of the events with large momentum transfer. As discussed already in ref. [3], it accounts for the dynamical correlation of the motion of neighboring atoms and explains the Armand effect. It is also responsible for the fact that the effective surface Debye temperature T_D in eq. (2) is higher than the true surface Debye temperature, and in this case is (accidentally) about the same as the bulk Debye temperature.

With the model potential of eq. (12) the matrix elements that we need in order to evaluate the Debye-Waller exponent $2W$ are all obtainable from:

$$M(k_{iz}, k_{iz}) = \frac{2\pi\beta U_0}{Q_c^2 A_c} \langle \chi(k_{iz}, z) | e^{-\beta z} | \chi(k_{iz}, z) \rangle, \quad (13)$$

where the eigenfunctions $\chi(k_z, z)$ satisfy the Schrödinger equation:

$$\left[-\frac{d^2}{dz^2} + 2mV_0(z)/\hbar^2 \right] \chi(k_z, z) = k_z^2 \chi(k_z, z). \quad (14)$$

These eigenfunctions are normalized in such a way that the asymptotic limit ($z \rightarrow \infty$):

$$\chi(k_z, z) = 2 \sin(k_z z + \delta) \quad (15)$$

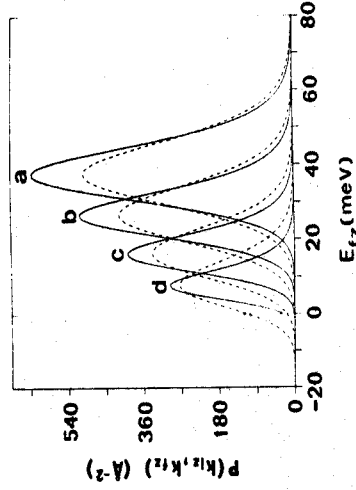


Fig. 5. Normalized squares of the matrix elements (see text). Full lines: numerical calculation using the full potential for an energy $E_i = 63$ meV and incident angles θ_i of: (a) 40° , (b) 50° , (c) 60° , and (d) 70° . Dashed lines: same calculation but for a repulsive potential with Beeby corrections. In this case the maxima occur at $\theta_i = \theta_l$.

corresponds to an incident current $\hbar k_z/m$. To determine the phase shift δ and the eigenfunctions χ in the whole range of z , we use the predictor-corrector method of Numerov. To achieve good convergence [21] we integrate up to $z_{\max} = 250 a_0$ and we take an integration grid of $N = 3000$ equal steps. The predicted value in the point z_{j+1} is iterated in the procedure until there is no change (in the first 6 decimal figures) in the value of $\chi(j+1)$. Five iterations are sufficient to ensure this convergence. The matrix elements are then evaluated by a numerical integration.

The squares of the matrix elements for $Q = 0$, divided by the incident flux and by the final density of states, $P(k_{iz}, k_{iz}) = m^2 |M|^2 / \hbar^4 k_{iz} k_{fz}$, are presented in fig. 5 as a function of the final energy E_{fz} for various scattering geometries corresponding to $E_i = 63$ meV. We note that at high energy E_{fz} the maximum occurs at $E_{fz} = E_{iz}$ while it is shifted to the right at smaller values of E_{fz} . For comparison we have also evaluated the matrix elements corresponding to a pure repulsive potential with Beeby's corrections [22] to account for the acceleration produced by the attractive well, so that the effective initial and final momenta of the beam are:

$$k_z(D) = \sqrt{(2m/\hbar^2)(E_z + D)}. \quad (16)$$

For this potential the matrix elements M have an analytical expression [8] given by:

$$M(k_{iz}, k_{fz}) = 2\hbar^2 k_{iz} k_{fz} S(k_{iz}, k_{fz})/m, \quad (17)$$

with $S(k_{iz}, k_{fz}) = 1$. The square of the matrix elements must be normalized to

the true incident flux $k_{i,z}$ which is outside the attractive well and to the true interval of final momentum $dk_{f,z}$. With this normalization P is given by:

$$P(k_{f,z}, k_{i,z}) = 4k_{f,z}(D)k_{i,z}(D)S^2(k_{f,z}(D), k_{i,z}(D)). \quad (18)$$

The results obtained from eq. (18) are presented as dash-dotted lines in figs. 1 and 2. The calculations have been performed with $\beta = 1.0 \text{ a}_0^{-1}$ and $D = 28 \text{ meV}$. This value of D has been chosen to obtain an overall agreement with the exact calculation of P . Notice that for $E_{f,z} = E_{i,z} = 0$ the value of P in eq. (18) is $P = 8mD/\hbar^2$ which is not very different from the corresponding value that one obtains from the exact calculation.

3.3. Surface phonons

In the evaluation of eq. (3) and eq. (4), in order to find the surface eigenmodes $e(0)_\mu^Q$ and eigenvalues $\omega_\mu(Q)$, we will use the lattice dynamical model that we have used [13] in the study of inelastic scattering from the Pt(111) surface. Here we summarize briefly the method.

The surface is treated by considering a slab of $N = 90$ atomic planes by using a force constant parametrization scheme for the bulk. To account for the charge modification occurring in the surface region we have considered the surface force constants as free parameters to be fitted to the measured time-of-flight spectra. As discussed more fully in ref. [13], we find that the central nearest neighbors force constant between surface atoms must be weakened by 60% with respect to its bulk value in order to reproduce the observed modes that are present in addition to the Rayleigh wave, namely the pseudo Rayleigh wave and the longitudinal resonance. The accuracy of the model is proved by comparing the evaluated reflection coefficients with the experimental TOF spectra. Fig. 3 gives an example of the accuracy obtained with our phonon parametrization. As one can see the energy position of the three peaks is within 3% of the experimental values and the relative height of peaks is also accurately reproduced. In the calculations we have used the model potential of eq. (11).

4. Numerical results and conclusions

The calculations have been performed by using a slab of $N = 30$ planes and the integration over the 2D Brillouin zone in eq. (3) has been done with 45 special points chosen by the Baldereschi method (see ref. [3] for details). As in the case of Ag, we found that this choice gives an accuracy in the results to better than 5%. This was tested by varying both N (from 18 to 60) and the number of special points (from 18 to 135).

The full lines drawn in fig. 1 and in fig. 2 represent the result of the calculations with the model potential of eq. (11) and with the phonons computed by softening the surface forces to fit the inelastic data. The agreement with the experimental data is quite satisfactory.

To investigate the importance of an accurate description of the surface dynamics we also evaluated $2W$ by considering the phonon model in which the surface force constants are taken to be those of the bulk. The dashed lines in figs. 1 and 2 represent such a calculation. The disagreement obtained in this case proves indeed that the detailed features of the surface phonon density of states play a considerable role in the evaluation of $2W$.

The dash-dotted lines in figs. 1 and 2 refer to the calculation with the best phonon spectrum and with a potential containing only the repulsive part (matrix elements given by eq. (18)). As one can see from figs. 1 and 2, the use of a repulsive potential with Beeby corrections can give a reasonable agreement for both sets of experimental data only by taking an unreasonably large value of D (28 meV). To improve the agreement with the experimental data of fig. 1 one should increase the value of D while for the data presented in fig. 2 one should decrease D . Actually, the simple hard-wall model in the eikonal approximation, eq. (2), fits both sets of data with a more reasonable value of D (12 meV): this is not surprising, however, because in using eq. (2) T_D is treated as an additional adjustable parameter.

In conclusion both an accurate description of the surface lattice dynamics of the crystal and a realistic He-Pt(111) potential are required to interpret the experimental data presented here. The simple formula, eq. (2), describes as well as the full calculation does the dependence of the reflected intensity on the surface temperature T_s and the incidence angle, but the parameters D and T_D cannot be identified with the true well depth and surface Debye temperature, respectively. The true well depth, as inferred from our calculations, is about 4 meV (see fig. 4), while the best fit of eq. (1) to the data gives $D = 12 \text{ meV}$; the true surface Debye temperature (which we have not computed exactly) is expected to be about $T_{DB}/\sqrt{2}$, where T_{DB} is the bulk Debye temperature of Pt, while the best fit of eq. (1) to the data gives $T_D = 231 \text{ K}$, about equal to $T_{DB} = 240 \text{ K}$.

Acknowledgments

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PERIODIC PERTURBATIONS OF THE OSCILLATORY CO OXIDATION ON Pt(110)

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The catalytic oxidation of CO on a Pt(110) surface at low pressures operated under conditions (P_{CO} , T) of isothermal, self-sustained kinetic oscillations was subject to periodic perturbations of the oxygen partial pressure with variable frequency and (small) amplitude. The large variety of the effects observed in the response of the system is classified according to the principles of the bifurcation theory for periodically perturbed chemical systems: Besides harmonic resonance, nine bands of subharmonic or superharmonic entrainment could be identified. Quasi-periodic oscillations were obtained between the entrainment bands and showed the effect of frequency pulling. Upon approaching an entrainment edge markedly prolonged relaxation behavior (critical slowing down) was observed. The qualitative differences to previous findings with Pt(100) can be traced back to differences in the mechanisms dominating spatial self-organization.

1. Introduction

If a chemical reaction is operated under continuous, steady-state flow conditions its rate is determined by the concentrations of the molecules involved in the reaction and by adjustable parameters such as flow rate and temperature. These state variables are in general connected through a system of coupled, non-linear differential equations which can under certain conditions give rise to self-sustained temporal oscillations of the reaction rate, even if all the control parameters are kept constant. If for such a situation one of the said parameters is periodically modulated with frequency ν_p and amplitude A , a series of new phenomena may occur which have already been extensively investigated with homogeneous chemical reactions, both in theory and experiment [1-11]. Similar features could be observed in several studies with heterogeneous reactions, which, however, largely suffered from irregular oscillatory behavior of the autonomous (i.e. non-perturbed) system [12-15]. This holds even for the low-pressure catalytic oxidation of CO on a well-defined

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