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SPRING COLLEGE IN CONDENSED MATTER
ON
"THE INTERACTION OF ATOMS & MOLECULES WITH SOLID SURFACES"
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DEFECTS ON SURFACES

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_ INTRODUCTION

Crystal : three-dimension periodic structure

Crystal plane: two-dimension periodic structure

The surface structure is characterrised by a unit mesh which is defined by two unit vectors.The plane structure is invariant with respect to a translation by a multiple of these unit vectors.

Defect: any perturbation which breaks the translational invariance

Origin of defects:

-Extrinsic: imperfect surface preparation,irradiation damage...

-Intrinsic: thermodynamic fluctuations

Defects are unavoidable on practical surfaces

Many of the practical properties of surfaces are due to their defects rather than to their basic structure ex:reactivity

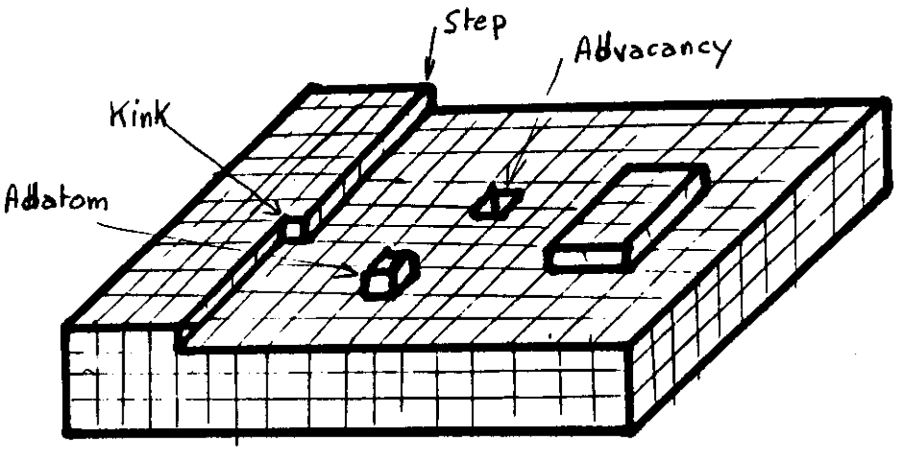
The defects can act as reactive centers in catalysis

Nature of defects:

-structural defects: misplaced atom or group of atoms or vacancy

-chemical defect: change in the chemical nature of some atoms without changing the geometry, ex:adsorbate.this case will not be considered here

Terrace,Step,Kink model:



atoms are represented by cubes

Points defects: adatoms, advacancies,kinks

Collectives defects: group of adatoms or advacancies,steps

plan of the course:

-experimental characterization of defects

-energetical properties of individual defects

-interaction between defects

-statistical thermodynamics of defects:the roughening transition

- -renormalization approach
- -SOS model

-roughening transition on step surfaces: theory and experiment

-dynamical aspects

2_EXPERIMENTAL CHARACTERIZATION OF SURFACE DEFECTS

Parameters to be measured:

- nature of the defect
- surface concentration
- statistiscal distribution

Direct methods:

- in the real space (microscopy at the atomic scale)
  - decoration techniques
  - field ion microscopy (FIM)
  - scanning tunnel microscopy (STM)

- in the reciprocal space (dffraction techniques)
  - LEED
  - X-ray diffraction at glancing angles
  - Helium beam diffraction (HBD)

Indirect methods:

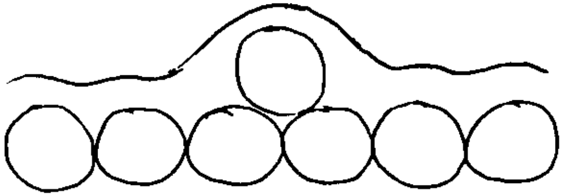
-any surface property which is dependant upon the presence of surface defects may be used to measure their concentration (ex: work function...).But calibration is needed

Measurements in the real and reciprocal space are very complimentary:

-in the real space the nature of defects is easily identified but statistical distribution estimate is tedious

-in the reciprocal space the statistical distribution is readily obtain but the nature of the defect is more difficult to extract

The most attractive complimentary methods are certainly STM and HBD.Both method measures the perturbation of the outer electron density due to the defect



limitation of STM: -duration of the scan which limits the measurements to frozen surfaces

-displacement of the defect(adatom) by the tip

Helium Beam Diffraction

HBD is not very sensitive to close packed structure (specular reflection) but is very sensitive to their defects:

- the specular peak is weakened and eventually broadened
- a diffuse incoherent scattering appears

Two class of defect structures:

- point defects distributed on the surface
- random steps delimiting domains on the surface

Helium diffraction on a non-corrugated surface with point defects [1],[2]

only one kind of defect

probability of the defect on site i: θ

joint probability of two defects on site i and j: P_{ij}

$P_{ii} = \theta$ and for sites very far apart $P^{\infty}_{ij} = \theta^2$

Correlation coefficient:

$$C_{ij} = \frac{P_{ij} - \theta^2}{\theta(1-\theta)} \qquad C_{ii} = 1 \qquad C^{\infty}_{ij} = 0$$

The diffraction pattern is made of two parts:

-a coherent part

δ-function located at the nodes of the" surface reciprocal lattice

$I_0 \approx 1 - 2\theta\,\mathrm{Im}F(Q)$ specular peak

$I_G \approx \theta^2 |F(Q)|^2$ diffraction peaks due to defects

-an incoherent part

$$dP/d\Omega \approx |F(Q)|^2 \theta(1-\theta) \sum \exp(-iQ(R_i - R_j))\, C_{ij}$$

F(Q) is a function which only depends upon the He-surface potential in the vicinity of the defect.For $\theta \ll 1$ it does not depend upon their distribution

Im(Q) is related to the cross-section for incoherent scattering [3]

$\Sigma_{defect} = A_{unit\ cell}\,\mathrm{Im}F(Q)$

Then:

$I_0 = 1 - 2\theta\,\Sigma_{defect}/A_{unit\ cell}$

this cross-section is quite large $\Sigma_{defect} \approx 100$ Å^2 for adatoms or advacancies

the information about statistical distribution is contained in the dffuse scattering term through the Fourier transform of the correlation cefficient C_{ij}

for a completely random distribution:

$C_{ij} = \delta_{ij}$ thus $dP/d\Omega = |F(Q)|^2 \theta(1-\theta)$

Helium scattering on a surface with domains limited by monoatomic steps [4,5,6]

The domains have the same structure as the original surface but they are shift by a multiple of a constant vector: $\vec{U}(\vec{R}, z)$

(R:parallel displacement, z:normal displacement)

Phase shift: $\Phi_i = d\,[\vec{Q}.\vec{R} + (k^z_i + k^z_f)\,z]$ d:integer

Domains are supposed to be large so that multiple scattering from one domain to another is neglected

Then the scattered intensity is:

$$I_{scatt} = F(\vec{Q}) \sum_c \sum_{c'} \exp(i\vec{Q}(\vec{R}_c - \vec{R}_{c'}))\langle \exp(i\,\Phi_i(d-d'))\rangle$$

summation over all unit cell

$F(\vec{Q})$: form factor which only depends upon the scattering of helium on the perfect surface

The distribution of domains is contain in the second term which is called the structure factor

the first cumulant expansion of $\langle \exp(i\,\Phi_i(d-d'))\rangle$ gives the so- called gaussian approximation:

$$\langle \exp(i\,\Phi_i(d-d'))\rangle \approx \exp(-\langle (d-d')^2\rangle(\Pi^2/4)(1-\cos\Phi_i))$$

two important cases:

- $_{f}\Phi_{l} = 2n\Pi$ «in-phase» scattering

then:

$$\langle \exp(i_{f}\Phi_{l}(d-d')) \rangle = 1$$

interferences between domains are constructive
disorder is not seen

same scattering pattern as for the perfect surface (δ-functions)

- $_{f}\Phi_{l} = (2n+1)\Pi$ «anti-phase» scattering

interferences are destructive
the effect of disorder is maximum

3_PHYSICS OF AN ISOLATED DEFECT

Free energy of creation of a defect:

$F_d = E_d - TS_d$ E_d: energy of creation
S_d: entropy » »

The initial and final state must be carefully defined

Energy of creation

Broken bond model

Z: number of nearest neighbours (fcc:Z=12,bcc:Z=8)

Energy per bond = $2E_c/Z$ (E_c:cohesive energy per atom)

E_d = Number of broken bonds associated with the defect

Example:-Pair adatom-advacancy on a fcc(100) surface

4 broken bonds

$E_d = 4\times2E_c/12 = 2E_c/3$

-Pair of kinks on a [110] step on a fcc(100) surface

1 broken bond

$E_d = E_c/6$ so for one kink $E_d = E_c/12$

The broken bond model is very crude and generally overestimates the energy. For transition metals a better estimate can be obtain from the band structure in the tight binding approximation [7]:

$$\text{band-width} \approx \sqrt{2^{nd}\text{ moment of the d-state density}}$$

$$\approx \sqrt{Z}$$

Thus for an atom with only Z_i neighbours:

$$E_{c\,i} = E_c\sqrt{Z_i/Z}$$

Table I gives some results for advacancies on fcc and bcc surfaces.

Table I

face	bcc			fcc	
	Z_n	Z_{nn}	E_v/E_c	Z_n	E_v/E_c
(100)	0	2	-0.04	2	0.08
(110)	2	1	0.25	1	0.08
(111)	0	0	-0.04	3	0.24

Z_n: number of nearest neighbours

Z_{nn}:number of next nearest neighbours

Relaxation within the defect further decreases E_d but the effect is weak.

Entropy of creation [8]

It is due to the change in the vibration modes near the defect
Calculation is possible in the quasi-harmonic Einstein approximation

4-INTERACTIONS BETWEEN DEFECTS [9]

- Electronic interaction
- Elastic interaction
- Dipole interaction

Electronic interaction

-Direct interaction

similar to a chemical bond

very short range: a few Å

always attractive

-Indirect interaction through the substrate

oscillatory character

$\approx A(\cos(2k_f R)/R^{n})$ in the case of point defects

Elastic interaction

A defect induces a relaxation of the neighbouring atoms

its amplitude decreases as $1/R^2$

interaction between two point defects $\approx 1/R^3$

interaction between two steps $\approx 1/R^2$

the interaction is repulsive for two defects of the same kind but may be attractive or repulsive when they are different

Dipole interaction

very small exept in the case of ionic crystal

5 DEFECTS STATISTICS

Excess free energy due to defects:

$$F = \Sigma_i n_i F_i + \Sigma F_{int} - T\,S$$

n_i : number of defect of kind i
F_i : creation energy of defect i
F_{int} : interaction energy between defects
S: configurationnal entropy

If $F = 0$ at temperature T_r then the defects are spontaneously multiplied. This is called the roughening transition

Partition function:

$$Z = \Sigma \quad \exp(-E_c/kT)$$

E_c : energy of a configuration
Σ : sum over all configurations

$$F = -kT\ln(Z)$$

Probability of a configuration:

$$P_c = \exp(E_c/kT)/Z$$

The knowledge the defects statistics reduces to the calculation of Z. It is a very difficult problem even in simple case

Two approaches:

-Macroscopic: the solid is treated as a continuum

-Microscopic: SOS models

6-MACROSCOPIC APPROACH TO THE ROUGHENING TRANSITION [10]

η : surface free energy per unit area

When the surface is deformed by thermal fluctuations its energy increases proportionally to its increase of area

$$E = \int d\vec{R}\,(\eta\sqrt{(1+\mathrm{grad}(z^2))})$$

z fluctuations are expanded in a Fourier serie

$$z(\vec{R}) = \Sigma_k \eta z_k \exp(ikR) \quad \text{where: } \Sigma_k = (L^2/4\pi^2)\int_0^{\Lambda} 2\pi k\,dk$$

$\Lambda = a^{-1}$ a: lattice parameter in the z-direction

if $|\mathrm{grad}\ z| \ll 1$ then $E - E_0 = \Sigma_k \eta L^2 k^2 |z_k|^2/2$

at equilibrium every modes have an energy 1/2kT

Thus: $|z_k|^2 = T/\eta k^2 L^2$

and $z^2 = \Sigma_k |z_k|^2 = (T/2\Pi\eta)\int_0^{\Lambda} dk/k = (T/2\Pi\eta)\ln(\Lambda L)$

it can be shown also that:

$$\langle |z(\vec{R})-z(0)|^2\rangle = cte + (T/2\Pi\eta)\ \ln(\Lambda|R|)$$

Conclusion: a free surface is always rough

Localization of the surface on discrete lattice planes

periodic localization potential

$$E = \int d\vec{R}\,\eta\,\sqrt{(1-\mathrm{grad}(z^2))} \;+ V(1-\cos(2\Pi z/a))$$

partition function:

$$Z = \int dz_k\ \exp(E(z_k)/k_B T)$$

renormalization scheme: cut-off $\bar{\Lambda}$

for $\bar{\Lambda} < k < \Lambda$ $\quad Z = \exp(\bar{E}_k/k_B T)$

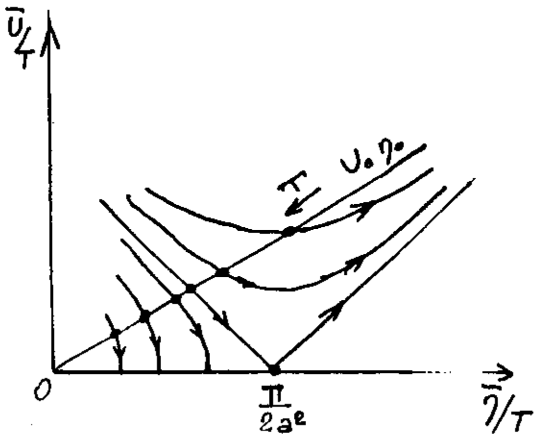
$\bar{E}_k$ depends upon the renormalized quantities $\bar{\eta}$ and $\bar{V}$

renormalization equations:

$$\left|\begin{array}{l} \dfrac{d\bar{U}}{dl} = \bar{U}\left(2-\dfrac{\Pi T}{a^2\bar{\eta}}\right) \\[2ex] \dfrac{d\bar{\eta}}{dl} = \dfrac{A(T)\bar{U}^2}{Ta^2} \end{array}\right.$$

$l = \ln\Lambda/\bar{\Lambda}$ $\qquad \bar{U} = \bar{V}/\bar{\Lambda}$

$A(T) \approx 0.2 - 0.4$



fixed point:

$$T=T_R \left|\begin{array}{l} \bar{U}=0 \\ \bar{\eta}=\Pi T_R/2a^2 \end{array}\right.$$

- For $T > T_R$ there is always a scale ξ above which $U \to \infty$

the surface is pinned on the periodic potential

- For $T \approx T_R$

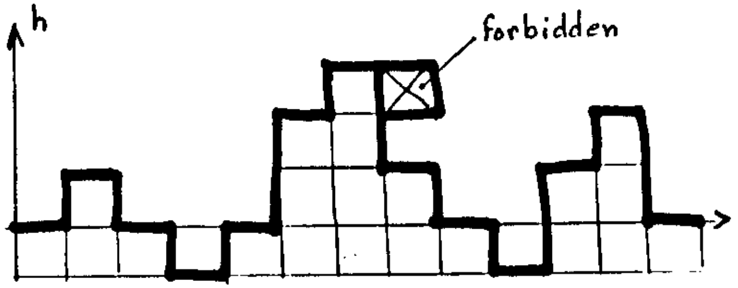
$$\xi \approx \exp(C/(T_R-T)^{1/2} \qquad F \approx \exp(-C/|T-T_R|^{1/2})$$

- For $t \geq T_R$ $\quad \bar{U}$ vanishes at any large scale

The surface behaves like a free sur face provided that η is replaced by its fully renormalized value $\bar{\eta}$

the singularity of ξ or F is very weak : all their derivatives vanishes at $T = T_R$. It is an infinite order transition.

7 _MICROSCOPIC APPROACH OF THE ROUGHENING TRANSITION:the SOS model [11]



J : interaction energy between two adjacent cubes

$$Z = \sum_{\{h_i\}} \exp(J/2k_B T)\sum_{i,\delta}|h_i - h_{i+\delta}|$$

$\{h_i\}$:configuration of columns heights

δ: neighbouring site to site i

Correlation function :

$$G(\rho) = \langle (h_i - h_0)^2\rangle \quad \text{with } \rho = |R_i - R_0|$$

The renormalization calculation is not so easy as previously since U is now infinite and the energy cannot be developped in power U. However it can be proved that the same conclusions hold ie. there is a roughening transition at T_R above which U still vanishes so that the correlation function $G(\rho)$ diverges logarithmically

This class of phase transition is called the Kosterlitz-Thouless transition

For the SOS model numerical calculations have shown that:

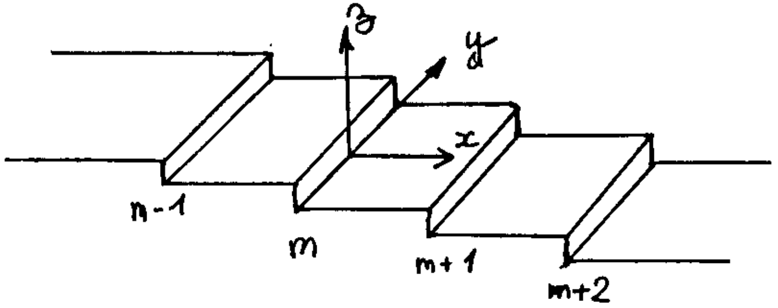
$$kT_R/J = 1.24$$

for usual crystals this fomula lead to the conlusion that the roughening temperature is higher than the melting point.

Thus it is expected that close-packed surfaces do not roughen before melting. However roughening is eventually possible on loosely packed surfaces like fcc(110) or vicinal surfaces.

8-THE ROUGHENING TRANSITION ON VICINAL SURFACES

A vicinal surface is a regular array of parallel monoatomic steps delimiting close-packed terraces

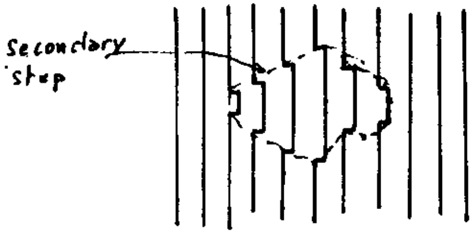


Note that the stability (or metastability) of such surfaces at low temperature implies that repulsive interactions between steps are present.

On such surfaces the lowest energy cost defect is the kink.

Pairs of kinks form detours.Surface energy is minimized if the detours are grouped into domains.The boundaries of such domains form what can be called secondary steps.

Vicinal surfaces can undergo a roughening transition through the multiplication of such secondary steps.



Macroscopic approach [12]

The surface is now anisotropic

Two surface tension: $\eta\eta'$

$$E = (1/2)\Sigma_q(\eta q_x^2+\eta' q_y^2)|u_q^2| + U\Sigma_{m,y}(1-\cos(2\Pi u_m(y))$$

$$u_m(y) = \Sigma\ u_q \exp(iq_x m+iq_y y)$$

$u_m(y)$: displacement of the m^{th} step at ordinate y

U: potential which localizes the steps at discrete lattice positions

The same renormalization procedure as before tells us that there is a roughening transition T_R such that:

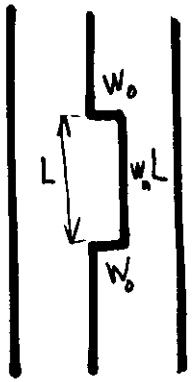
$$\sqrt{\eta\eta'} = \Pi T_R/2$$

Above T_R:

$$\langle(u_m(y)^2-u_m(0)^2)\rangle = (T/\sqrt{\eta\eta'})\ln(\rho)$$

$$\rho^2 = y^2(\eta'/\eta)^{1/2}+m^2(\eta/\eta')^{1/2}$$

Microscopic approach [12]



kink formation energy: W_0
step-step repulsion: $W_n L$

Identical to SOS model but here the columns lie flat along the terraces. The interaction is now isotropic:

W_0 along y, w_s along x, $W_0 >> w_s$

A rough estimate gives:

$$\eta' \approx w_s \qquad\qquad \eta \approx (T/2)\exp(W_0/k_B T)$$

Experimental evidence for step roughening

Helium Beam Diffraction on copper step surfaces:

Ni(113),Ni(115) [13,14]

Cu(113),Cu(115),Cu(1,1,11) [15,16,17]

Experimental observations:

-Anomalous behaviour of the thermal dependence of peak intensities

-Periodic broadening of the peak

-Peak profile is an anisotropic power law (exept for Cu(1,1,11))

the anisotropy increases with step distance

Results:

	T_R	W_0	w_s
Cu(113)	720 K	800 K	560 K
Cu(115)	380 K	≈800 K	120 K
Cu(1,1,11)	<<300 K (freezing)	?	≈ 6 K

Conclusion: The kink density on a step is always large at and above room temperature.

9_ THE DYNAMICS OF DEFECTS

The achievement of thermodynamical equilibrium suppose surface mobility. This is not the case at low temperature. Defects are always present in a frozen equilibrium at low T. Thus an ideal surface without any defects cannot occur in practice.

Experimental study by: _ Field Ion Microscopy [18]

_ Helium Beam Diffraction [19]

Example: HBD study of the mobility on Cu(115) a stepped surface.
The surface is roughened by ion bombardement. The annealing kinetics are followed by HBD.

Results:

-The surface is completely frozen for T<150 K

-The surface is always in equilibrium fot T>320 K

-Kinetics are followed in between

Apparent activation energy for migration ≈ 0.3 eV

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