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SURFACE VIBRATIONS OF CRYSTALS WITH CHEMISORBED ATOMS

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I. Introduction

It is now a well established fact that the adatom-adatom interaction is an important factor determining many aspects of thermodynamic and kinetic properties of crystal surfaces with chemisorbed species. It is most clearly demonstrated by the tendency of chemisorbed layers to form distinct phases which possess well defined two-dimensional periodicity and order /1/. Recently, a considerable attention has been given to experimental observations and calculation of superstructures of two-dimensional surface lattices with adsorbate and to transitions between different phases/2/. In these calculations the lattice gas approximation has been used which assumes the rigidity of underlying substrate/3-6/. This approximation was shown to describe satisfactorily the experimental results in many cases. On the other hand, the adsorbate-induced reconstruction, e.g., in the case of adsorbed hydrogen on tungsten (100) shows the necessity to involve both the adsorbate and substrate into the calculation /6/. The strong dependence of the properties of the adsorbed gas and of the substrate on the state of its counterpart leads to interesting effects also in kinetics where it is responsible, e.g., for an oscillatory behaviour of CO oxidation on Pt/7/.

The purpose of our paper is to calculate the influence of chemisorbed atoms with lateral interactions upon the vibrational spectra of surface substrate atoms and the effect of dynamical properties of the substrate on the thermodynamic properties of the adsorbed lattice gas.

In our calculations we use a simple model simulating properties of (100) crystal surfaces with chemisorbed atoms. We replace the surface substrate layer by a quadratic two-dimensional harmonic square lattice. In both the substrate and adsorbate we assume only nearest neighbour interactions. The method of calculation based on the Bogolubov variational principle and quasichemical, polynomial and mean field approximations for the lattice gas of adsorbed molecules was developed in detail in /8/.

II. Model Hamiltonian

The adsorbing surface of a solid is modeled by a mono-atomic two-dimensional lattice. Each adsorbed atom (adatom) is assumed to be strongly bound to one surface atom. In this case the system surface + adatoms can be described by the Hamiltonian

$$H = \sum \frac{p_i^2}{2(M+m_i)} + \frac{1}{2}\sum_{i\neq j}\phi(R_i - R_j) + V\sum_i n_i + \frac{1}{2}\sum_{i\neq j} J(R_i - R_j)\, n_i n_j \tag{1}$$

where M and m are the masses of the surface atoms and of the adatoms, respectively, p_i are their momenta. The interaction between the two surface atoms located at the lattice sites i, j is described by the potential $\phi(R_i - R_j)$ depending on the position vectors R_i, R_j. The potential $J(R_i - R_j)$ has the same meaning as $\phi(R_i - R_j)$ but in the system of adsorbed atoms. n_i =0,1 are the occupation number operators and V is the effective chemical potential of adatoms. These are considered in thermodynamical equilibrium with an ideal monoatomic gas of low pressure. Therefore, it is $V = -(\varepsilon + \mu_g)$ where ε has the meaning of the energy of adsorption and μ_g is the chemical potential

$$\mu_g = kT \ln\left[\frac{P}{(kT)^{\frac{5}{2}}}\left(\frac{2\pi\hbar^2}{m}\right)^{\frac{3}{2}}\right].$$

Here P is the pressure of the gas, m is the mass of gas atoms and T is temperature.

Now, using the Bogolubov variational method, we introduce the model Hamiltonian

$$H_{ph} = \sum_i \frac{p_i^2}{2M_0} + \frac{1}{2}\sum_{i\neq l} A^{\alpha\beta}_{il} X^{\alpha}_{il} X^{\beta}_{il} \tag{2}$$

$$R_i = \langle R_i \rangle + u_i \;; \qquad X^{\alpha}_{il} = u^{\alpha}_i - u^{\alpha}_l$$

$$H_{ad} = V_0 \sum_i n_i + \frac{1}{2}\varkappa \sum_{i\neq l} n_i n_l$$

$$H = H_{ph} + H_{ad}$$

in which the surface atom variables and the adatom variables are separated. The dynamic of surface atoms is described by H_{ph}. Here, as is usual in the lattice dynamics, the potential energy is expanded around the equilibrium positions $\langle R_i \rangle$ and only first nonzero terms are considered. The adatoms are described by the Hamiltonian H_{ad} which can easily be transformed into the known Ising Hamiltonian. The variational parameters are determined by the minimum of the thermodynamical potential with respect to M_0, $A^{\alpha\beta}_{ij}$, V_0 and $\varkappa$. These conditions yield /8/

$$A^{\alpha\beta}_{ij} = \nabla^{\alpha}_{i} \nabla^{\beta}_{j} \langle \phi(R_i - R_j) \rangle_{ph} + \langle n_i n_j \rangle_{ad} \nabla^{\alpha}_{i} \nabla^{\beta}_{i} \cdot \langle J(R_i - R_j) \rangle_{ph}$$

$$\frac{1}{M_0} = \frac{1}{M} + \langle n_i \rangle_{ad} \left[\frac{1}{M+m} - \frac{1}{M} \right] = \frac{1}{M} \left[1 - \langle n_i \rangle_{ad} \frac{m}{M+m} \right] \tag{3}$$

$$\varkappa = \langle J(R_i - R_j) \rangle_{ph}$$

$$V_0 = V + \frac{1}{2} \langle P_i^2 \rangle_{ph} \left[\frac{1}{M+m} - \frac{1}{M} \right]$$

where $\langle \; \rangle_{ph}$, $\langle \; \rangle_{ad}$ denote the thermal averages with the Hamiltonian H_{ph} and H_{ad}. This means that now the lattice parameters (M_0, $A^{\alpha\beta}_{ij}$) and the adatom parameters (V_0, $\varkappa$) depend on temperature.

III. The frequency spectrum of a surface with adsorbed atoms

In accordance with the Bogolubov variational method we shall investigate two additive systems. Their coupling is included in the parameters $\varkappa$, $A^{\alpha\beta}_{ij}$, M_0 and V_0 defined by (3). In order to analyse the behaviour of the frequency spectrum, we have to specify the structure and the interactions between the surface atoms and between the adatoms, i.e. the potentials $\phi(R_i - R_j)$ and $J(R_i - R_j)$. We shall assume the simplest case when the surface has a structure of the simple square lattice with interactions (the central and noncentral) between nearest neighbours only. The adatoms interact with their nearest neighbours by central forces only. We assume further that the adatom-substrate interaction leads besides changes in the interaction constants and the masses of the surface atoms, to a change of the lattice parameters, but without changing the shape of the cell.

For this reason A in equations (2,3) is the force constant matrix of the simple square lattice. It is diagonal with two nonzero elements (A_1 - the central, A_2 - the noncentral). The frequencies of the surface vibrations are then given by the known relation /9/

$$\omega^2_{j=1}(q) = \frac{2}{M_0}\left[A_1(1-\cos q_1 A) + A_2(1-\cos q_2 a)\right] \tag{4}$$

and cyclic for the polarization $j = 2$, where a is the lattice parameter, q is the wave vector with components q_1 and q_2. The displacement correlation function is given by the formula

$$\langle (X^{\alpha}_{iz})^2\rangle_{ph} = \frac{\hbar}{2NM_0}\sum_{q,j}\frac{1-\cos q_1 a}{\omega_j(q)}\,\mathrm{cotgh}\,\frac{1}{2}\beta\hbar\omega_j(q)$$

$$\beta = (kT)^{-1}.$$

The correlation function may be found analytically only in the high temperature limit

$$\langle (X^{\alpha}_{iz})^2\rangle_{ph} = \frac{1}{\pi\beta A_1}\left[\mathrm{arctg}\sqrt{\frac{A_1}{A_2}} + \frac{A_1}{A_2}\,\mathrm{arctg}\sqrt{\frac{A_1}{A_2}}\right]. \tag{5}$$

It is convenient to define the potentials $\phi(R_i - R_j)$ and $J(R_i - R_j)$ by means of the coefficients of their expansions. Then, as was shown in /8/, for our model of the surface and adatom system the first and third equation of (3) has the simple form

$$A_1 = B_1' + c\langle n_i n_j\rangle_{ad}$$

$$A_2 = B_2' \tag{6}$$

$$\varkappa = \langle J(R_i - R_j)\rangle_{ph} = J_0 - b\tilde{X}_0 + \frac{c}{2}\left[(\tilde{X}_0)^2 + \langle (X^{\alpha}_{iz})^2\rangle_{ph}\right]$$

when β_1 and β_2 are the nonzero elements of the force constant matrix, of the clean surface, or in other words, β_1 and β_2 are the second-order terms in the expansion of $\phi(R_i - R_j)$ about the equilibrium positions of the clean surface atoms (the first-order terms are identically zero); b and c are the first and second-order terms in a similar expansion for $J(R_i - R_j)$. The quantity $\tilde{X}_0$ expresses the change of the atomic equilibrium positions if gas atoms are adsorbed on the surface. As the atomic equilibrium positions $\langle R_i \rangle$ are determined by the boundary conditions which are represented by external isotropic pressure p acting in the surface plane from the force equilibrium condition for the surface atoms the following relation can be derived:

$$\tilde{X}_0 = \frac{-\frac{Vp}{a} + b\langle n_i n_j \rangle_{ad}}{\beta_1 + c\langle n_i n_j \rangle_{ad}} .$$

If we now express $\langle n_i \rangle_{ad}$ and $\langle n_i n_j \rangle_{ad}$ as functions of V_0 and $\varkappa$, then the close system of equations (3), (5), (6) may be solved and the surface atom frequencies (4) evaluated.

For $\langle n_i \rangle_{ad}$ and $\langle n_i n_j \rangle_{ad}$ the following approximations were used:

1) Molecular field approximation (MFA 1)

$$\langle n_i n_j \rangle_{ad} = \langle n_i \rangle_{ad}^2$$
$$\langle n_i \rangle_{ad} = \left[1 + \exp \beta(V_0 + 4\varkappa\langle n_i \rangle_{ad})\right]^{-1} \qquad (8)$$

for arbitrary neighbouring lattice sites i and j.

2) Molecular field approximation (MFA 2)

$$\langle n_i n_j \rangle_{ad} = \langle n_i \rangle_{ad} \langle n_j \rangle_{ad}$$
$$\langle n_i \rangle_{ad} = \left[1 + \exp \beta(V_0 + 4\varkappa\langle n_j \rangle_{ad})\right]^{-1} \qquad (9)$$

if the lattice is divided into two interpenetrating lattices described by $\langle n_i \rangle_{ad}$ and $\langle n_j \rangle_{ad}$ (a chessboard structure).

3) Quasichemical approximation

$$\langle n n \rangle_{ad} = \langle n \rangle_{ad} \frac{r - 1 + 2\langle n \rangle_{ad}}{r + 1} \tag{10}$$

$$\langle n \rangle_{ad} = \left[e^{-\beta(V_0 + 2\varkappa)} \left(\frac{r + 1 - 2\langle n \rangle_{ad}}{r - 1 + 2\langle n \rangle_{ad}} \right)^2 + 1 \right]^{-1}$$

$$r^2 = 1 - 4\langle n \rangle_{ad} \left(1 - \langle n \rangle_{ad}\right)\left(1 - e^{-\beta\varkappa}\right)$$

where for $\varkappa \geq 0$ it is $r \leq 1$.

4) Polynomial decoupling

$$\langle n n \rangle_{ad} = \sum_{k=0}^{4} C_4^k \langle n \rangle_{ad}^k \left(1 - \langle n \rangle_{ad}\right)^{4-k} \frac{k}{4} N_k \tag{11}$$

$$\langle n \rangle_{ad} = \sum_{k=0}^{4} C_4^k \langle n \rangle_{ad}^k N_k \left[1 - \langle n \rangle_{ad}\right]^{4-k}$$

$$N_k = \left[1 + \exp \beta(V_0 + k\varkappa)\right]^{-1}.$$

IV. Results and discussion

All our numerical calculations of the surface frequencies have been performed with the dimensionless quantities. The choice of the constant approximate corresponds to the chemisorption on the real crystal surface, where the resulting nearest neighbour interactions are mainly repulsive $(J_1 > 0)$ with few exceptions. We have put $J_0 = 0{,}15$, $\varepsilon = 2$, $ka = 0.11$, $c/B_2 = 1$, $B_1 a^2 = 8$, $B_1/B_2 = 3$, $vp = 0.03$. The mass ratio were taken either $M/m = 57.81$, or $M/m = 6$. The ratio of the masses $M/m = 57.81$ corresponds to hydrogen on crystal surface of N_i.

The dimensionless surface atom frequency $\Omega^2 = M\omega^2 / B_1$, corres-ponding to the wave vector $q = (\pi/2a, 0)$ has been calculated in the approximations (8 - 11). Typical results are shown in Fig. 1-3, where Ω^2 is plotted as a function of T. Here the effect of gas pressure is also illustrated. It is evident that at the high tempe-rature the crystal surface is clean and the surface atoms vibrate with the frequencies which do not depend on the temperature.

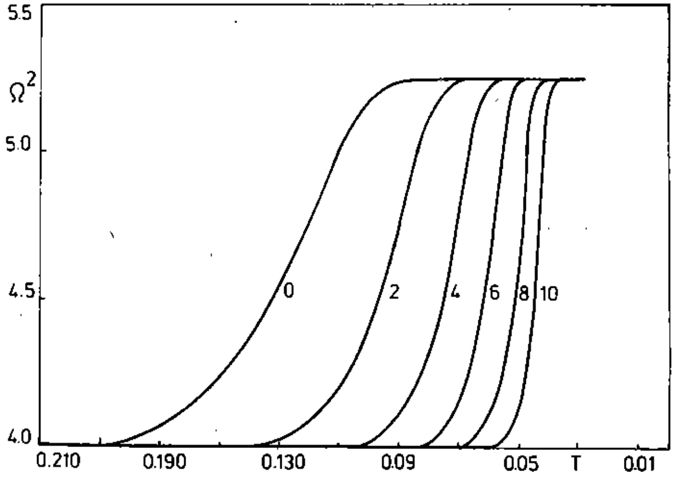

Fig. 1. The dimensionless surface atom frequency Ω^2 corresponding to the wave vector $q = (\frac{\pi}{2a}, 0)$ in the quasichemical approximation (10) as a function of temperature T and gas pressure $P = P_0 e^{-EX}$. The numbers at the curves mean the value of EX. The mass ratio of the surface atom to the gas atom is $M/m = 57.81$.

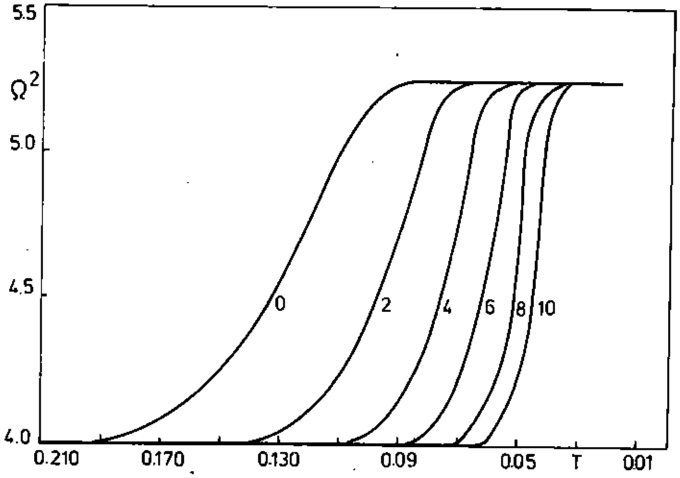

Fig. 2. The same as Fig. 1, but in the polynomial decoupling (11).

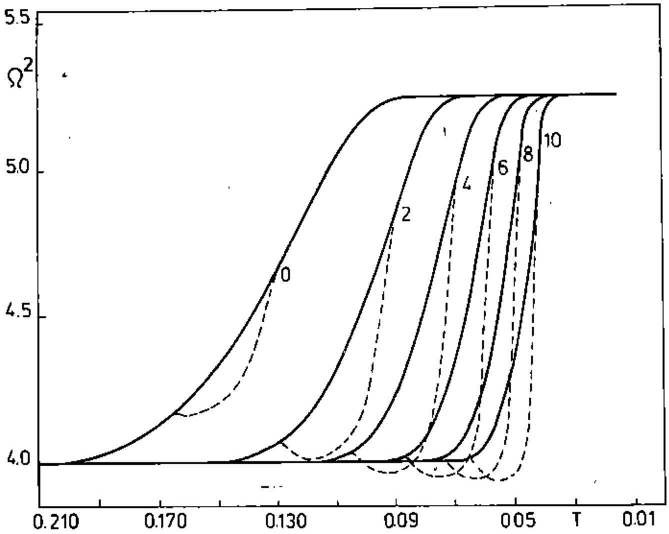

Fig. 3. The same as Fig. 2, but in the molecular field approximations. The solid lines correspond to MFA 1 (8), the dashed lines correspond to MFA 2 (9). MFA 2 differs from MFA 1 only in the middle part of the curves.

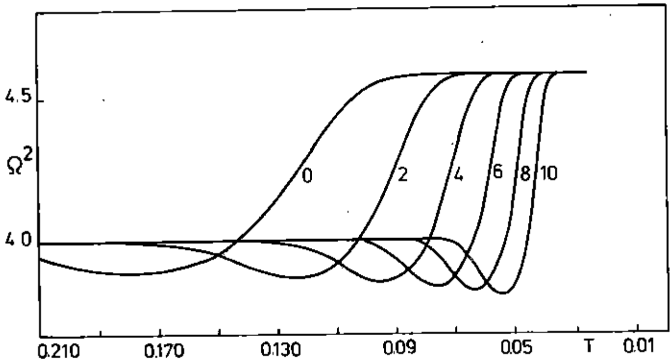

Fig. 4. The same as Fig. 1, but for the mass ratio M/m=6.

In our case the surface frequency Ω^2 is equal to 4. With decreasing the temperature, at constant gas pressure, gas atoms are adsorbed on the crystal surface and Ω^2 becomes a function of the temperature T. The maximal value of Ω^2 depends on the adatom mass and corresponds to the coverage $\theta = \langle n \rangle = 1$ when the monolayer of the gas atoms is adsorbed. It follows from (4) that the growing force constant raises the surface frequencies while the effect of the growing mass of atoms is opposite. In all the approximations, except MFA 2 (see below Figs. 7-8, where the functions θ and $\langle n n \rangle_{ad}$ are displayed), M_0 and A_1 are monotone increasing in magnitude if T decreases. For the mass ratio $M/m = 58.71$, that is for the light gas atom mass, the change of the mass of surface atoms has a small influence on the frequency curves and these are non-decreasing in the temperature region where $\langle n n \rangle_{ad}$ are small. Only in the approximation MFA 2, in which the correlations between neighbouring adatoms are overestimated (the dashed lines in Fig. 3), the effect of the mass can exceed the effect of the force constant and the surface frequency can decrease with decreasing temperature.

A different situation is for the heavy gas atoms, in our case it is $M/m = 6$. Here, the influence of the changing mass is also seen at small coverage, as it is illustrated in Figs. 4-6. All the curves start at $\Omega^2 = 4$ and then they decrease due to the increasing mass of surface atoms. The decrease of frequencies depends on the correlations between the adatoms. If these are neglected, i.e. if $\langle n n \rangle = \langle n \rangle^2$ (MFA 1), the frequency reaches the minimum at the coverage $\theta = 0.225$, as follows from (4). This minimum frequency is the same for all P (see Fig. 6).

Fig. 7 shows the typical behaviour of $\langle n \rangle$ and $\langle n n \rangle$ in the quasichemical approximation. The behaviour of these functions in the polynomial approximation is practically the same. For these approximations the relation

$$\langle n n \rangle \simeq \langle n \rangle^2 e^{-\beta \varkappa} \quad , \quad \varkappa > 0$$

is satisfied if the coverage is small.

The adsorption isotherms evaluated in the molecular field approximation are shown in Fig. 8. The dependence of θ versus T at fixed gas pressure has a similar character. It is known that our model of an adsorbing surface does not exhibit first order phase transitions if the nearest neighbour interaction is repulsive ($\varkappa > 0$). Our results agree with this prediction.

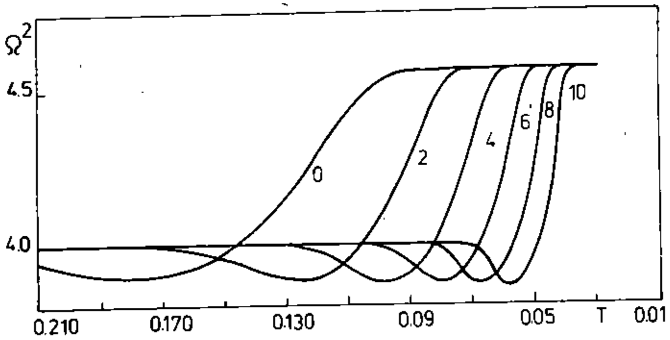

Fig. 5. The same as Fig. 2, but for the mass ratio M/m=6.

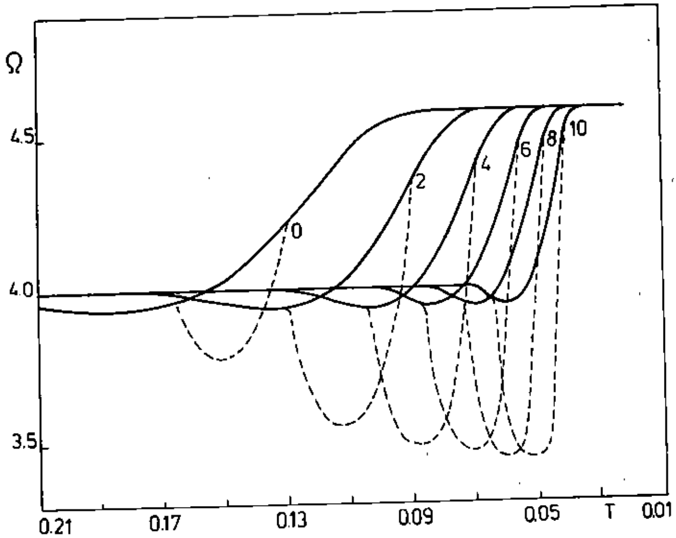

Fig. 6. The same as Fig. 3, but for the mass ratio M/m=6.

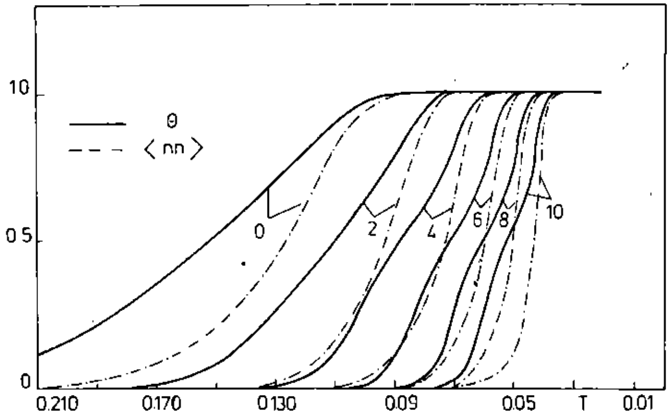

Fig. 7. The coverage (the solid lines) and the correlation function (the dot-and-dashed lines) as a function of temperature T for the mass ratio M/m=57.81. The calculation are performed in the quasichemical approximation (10).

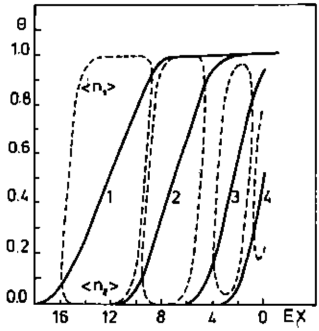

Fig. 8. The coverage as a function of gas pressure $P = P_0 e^{-EX}$ at fixed T (1 - T = 0.045, 2-T = 0.065, 3-T = 0.105, 4- T = 0.150). For each T the solid line corresponds to MFA 1 (8), the dashed lines correspond to MFA 2 (9). The mass ratio is M/m = 57.81.

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