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PHASE TRANSFORMATIONS ON SOLID SURFACES

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## PHASE TRANSFORMATIONS ON SOLID SURFACES

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Phase transformations with varying temperature are common in solids. The possibility of phase transformations on crystal surfaces appears to have not been given theoretical consideration although the binding energy of misfitting mono-layers has been examined.<sup>1</sup> It has been thought that a thermodynamically stable crystal surface must always be flat and exhibit the structure of the bulk solid. The purpose of this letter is to show that phase transformations can occur on surfaces because of the entropy associated with the phase transformations. Computations on the (100) faces of argon and silver show that they form surface structures which are thermodynamically stable in appropriate temperature regions and are different from the structure of the flat (100) "substrate" surface.

The treatment presented here is not general. The transformation to only one other possible structure has been considered. Unfortunately, present techniques require that each suggested structure be handled separately. The C(2X1) structure (Fig. 1) was chosen as an illustration since the LEED results in recent investigations have suggested that this structure is actually present.<sup>2</sup> The important contribution to the problem made by this note is that the configurational entropy of a non-registry surface makes possible a transition to a state of lower free energy.

A (100) surface of a fcc lattice may be viewed as a stack of square planes in which each successive layer is positioned so that its atoms

are above the holes of the plane below. This leads to a structure ABAB... The surface plane alone may be regarded as a square planar two dimensional lattice and has a (1X1) structure where the angle between the axes is  $90^\circ$ . A C(2X1) surface plane (Fig. 1) may be formed from the (1X1) by translating every other row of atoms one half an atomic distance in the surface plane. The surface structure so formed can be regarded as having a unit cell with two principle axes at  $90^\circ$ , one of which is equal to those of the (1X1) surface structure and the other twice as long, and having a centered atom in the cell; this is not a primitive cell for this structure as long as the plane is flat but is a convenient notation for describing the structure in terms of the normal (1X1) surface. The translation of a row of surface atoms greatly increases their overlap with the substrate atoms as the distance of the nearest substrate neighbors from the translated atoms is only .85 the normal bulk separation. As a result the translated atoms relax away from the surface plane in order to reduce their overlap with the substrate neighbors. This relaxation greatly reduces the energy of formation of the translated structure and results in a surface with a saw-tooth configuration (Fig. 2). Without relaxation, the energy of formation of the C(2X1) structure from the (1X1) is too great to allow formation of the C(2X1) below the melting point of the solid.

For argon and silver we have calculated the free energy of formation of the C(2X1) surface structure (Fig. 1) from the flat (1X1) structure of the (100) surface. We have found that at sufficiently high temperatures but below the melting point the C(2X1) structure is more stable than the (1X1). This phase transformation is possible because of the entropy change associated with the formation of the C(2X1) surface structure.

We assume that the crystal may be represented by a pair-wise additive two-body potential. Argon is represented by a Lennard-Jones 6-12 potential<sup>3</sup> and silver is represented by a Morse potential.<sup>4</sup> These potentials successfully predict some but not all the properties of solids and have been used previously to calculate relaxations of flat surfaces.<sup>5</sup> We have neglected all quantum effects and the kinetic energy of the atoms.

Since the  $P\Delta V$  term is so small, the free energy of formation of an arbitrary surface structure from the (1X1) structure may be written as

$$\Delta F = \Delta E - T (\Delta S_{\text{config}} + \Delta S_{\text{vib}})$$

where  $\Delta E$  is the difference in the binding energy of the two structures,  $\Delta S_{\text{config}}$  is the entropy difference arising from the configurational degeneracies of the two structures, and  $\Delta S_{\text{vib}}$  is the entropy change due to changes in the phonon spectrum of the surface atoms.

The C(2X1) is formed from the (1X1) structure by displacing every other row of surface atoms one half of an atomic distance in the surface plane (Fig. 1). The change in energy for this process,  $\Delta E_0$ , (Table I), is the difference in the binding energies of the (1X1) and C(2X1) structures in the surface plane. All energies were obtained by summation over 591 atoms which is sufficient to assure reliable results. The summations were made on a CDC 6600 computer. In computing the binding energy for the (1X1) structure we have considered the relaxations of the perfect (100) surface.<sup>5</sup> The atoms in the C(2X1) surface layer were allowed to relax perpendicularly to the surface plane. The displacements,  $\delta_1$ , (Table II and Fig. 2), which maximize the binding energy of the atoms in the "relaxed" C(2X1) structure were obtained. The difference between the maximized binding energy and the binding energy of the (1X1) structure

is then the energy of formation,  $\Delta E$  (Table I), of the new surface structure. Relaxation of the surface atoms perpendicularly to the surface plane greatly reduces the energy of formation of the C(2X1) structure.

The configurational entropy per unit area of a particular structure is given by

$$S_{\text{config}} = n k \ln W$$

where  $W$  is the configurational degeneracy of the structure and  $n$  is the number of surface atoms per unit area. For some very simple types of structures  $W$  may be readily obtained by simply counting the number of equivalent but distinguishable configurations. Examination of the C(2X1) structure (Fig. 1) shows that there are alternating non-equivalent rows of atoms. Therefore there are two equivalent, distinguishable, structures which differ from each other only by a translation of the surface structure. Two more equivalent, distinguishable, structures may be obtained by a  $90^\circ$  rotation of the initial structures. Thus the C(2X1) structure has a degeneracy of four and

$$S_{\text{config}} = n k \ln 4$$

for the C(2X1) structure. The flat (1X1) structure has only one possible configuration, that which is shown, and accordingly,

$$\begin{aligned} S_{\text{config}} &= n k \ln 1 \\ &= 0 \end{aligned}$$

Therefore the change in configurational entropy in going from the (1X1) structure to the C(2X1) is

$$\Delta S_{\text{config}} = n k \ln 4$$

The increase in configurational entropy makes possible the formation of the



C(2X1) surface structure from the (1X1) at sufficiently high temperature.  $\Delta S_{\text{vib}}$  was computed in the high temperature Einstein approximation.  $\Delta S_{\text{config}}$  and  $\Delta S_{\text{vib}}$  are included in Table I.  $\Delta S_{\text{vib}}$  is small compared to  $\Delta S_{\text{config}}$  and so the errors introduced by the Einstein approximation do not alter the qualitative conclusions of these calculations.

Combining the terms in Table I, the free energy of formation of the C(2X1) structure from the (1X1) structure on the (100) surface of argon is given by

$$\Delta F = 6.94 - .1835 T \text{ (ergs/cm}^2\text{)} \quad .$$

For silver

$$\Delta F = 180.8 - .2844 T \text{ (ergs/cm}^2\text{)} \quad .$$

For argon at temperatures in excess of 37.8°K and for silver at greater than 636°K,  $\Delta F$  is negative for the formation of the C(2X1) structure. Argon and silver are both face-centered-cubic solids and are described by qualitatively different two body potentials. One would expect that other solids characterized by other potentials could also exhibit similar surface phase transformations. It is also likely that argon and silver surfaces have other structures also of lower free energy than the normal flat surface in appropriate temperature regions. The possibility of the existence of surface structures should be considered in the interpretation of diffraction patterns observed by low energy electron diffraction (LEED).

#### Acknowledgements

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Table I. Thermodynamic data for the phase transformation from the (1X1) surface structure to the C(2X1) structure.

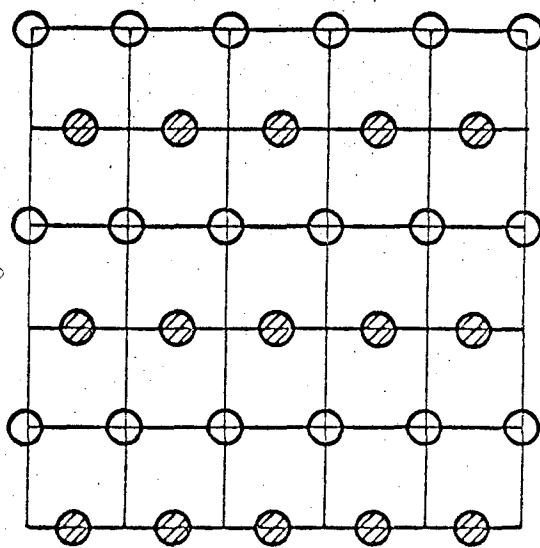
	$\Delta E_o$ (erg/cm <sup>2</sup> )	$\Delta E$ (ergs/cm <sup>2</sup> )	$\Delta S_{conf}$ (ergs/cm <sup>2</sup> deg)	$\Delta S_{vib}$ (ergs/cm <sup>2</sup> deg)
Argon	38.70	6.94	.1335	.0511
Silver	859.9	180.8	.2462	.0382

Table II. The distortions  $\delta_1$  and  $\delta_2$  of the C(2X1) structure for argon and silver are given as percentages of the normal bulk (100) planar spacing.

	$\delta_1$ (%)	$\delta_2$ (%)
Argon	21.27	3.55
Silver	20.95	6.96

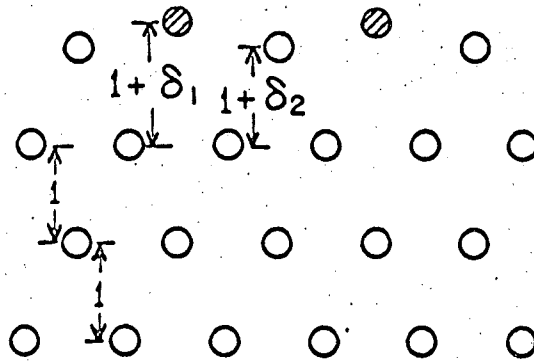
REFERENCES

1. H. H. Schmidt and G. Jura, J. Phys. Chem. Solids, 16, 60 (1960).
2. H. B. Lyon, A. M. Mattera and G. A. Somorjai, Symposium on the Fundamentals of Gas Surface Interactions, San Diego, California, December 14-16, 1966.
3. T. Kihara, J. Phys. Soc. Japan, 3, 265 (1948).
4. L. A. Girifalco and V. G. Weizer, Phys. Rev. 114, 687 (1959).
5. J. J. Burton and G. Jura, J. Phys. Chem. (in press).



XBL 672-573

Fig. 1 The intersections of the lines are the normal surface sites of the (1X1) structure. The circles are the atoms of the C(2X1) structure where the shaded atoms have been shifted from the normal sites.



XBL671 - 322

Fig. 2 The vertical displacements of the surface atoms from their planar positions in the C(2X1) structure. The shaded circles are the shifted atoms.

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