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SURFACE PHASE TRANSFORMATIONS ON A MOLECULAR CRYSTAL

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ABSTRACT

Thermodynamic functions are calculated for surface structures on the (100) surface of a model argon crystal. It is shown that it is possible for a phase transformation to occur from the normal bulk-like structure to a new surface structure without an accompanying transformation of the bulk. This can occur below the experimental melting temperature of the solid.

Various properties of the phase transformation are considered including the dependence on the potential, the effect of impurities, and the effect of vacancies.

Excellent correlation with low energy electron diffraction data on metals is found.

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I. INTRODUCTION

Low energy electron diffraction (LEED) has been utilized in recent years to investigate the microscopic properties of solid surfaces.[1] A number of theories have been developed to account for the experimental observations. These theories have dealt with two basic areas of concern in explaining LEED data: the intensity of the diffraction peaks as a function of electron beam voltage, and the sudden appearance of additional diffraction spots corresponding to periodicities differing from those expected from the bulk structure.

McRae[2,3] has had considerable success explaining the intensity data using a multiple scattering model. Marcus and Jepsen[4] have recently done band structure calculations which also appear to agree qualitatively with existing intensity data. The initial attempts to explain the extra diffraction spots have not been so successful. These explanations were based on large concentrations of surface vacancies or surface impurities.

The unexpected periodicities in the LEED patterns indicate the possibility of stable arrangements of surface atoms with structures different from the bulk. The surface structures appear to form without any phase transformation of the substrate. It has been shown that the minimum potential energy configuration of alkali halide surfaces may not be flat and that the alkali and halide atoms may not lie in the same plane.[5] Feuchtwang[6] has shown that the minimum potential configuration of the surface of a monatomic crystal can exhibit a periodicity different from that of the bulk, provided that the interactions between the atoms satisfy certain conditions. The authors have also previously proposed,[7]

in a brief note, that the unexpected diffraction spots on the (100) surfaces of face-centered-cubic crystals are due to a rearrangement of the surface layer without any accompanying transformation of the substrate.*

The calculations presented in this paper are for argon represented by a Lennard-Jones potential. Argon was chosen for this study as its interactions may be reasonably represented by a pair-wise additive potential, though three-body-interactions are believed to be of importance. Experimental studies have been carried out primarily on metals. It is believed that conclusions based on argon may give some indication of what occurs in metals as the results of these calculations depend more on the general features of the potential than on the explicit form, i.e., Morse, Lennard-Jones, or others. Extensive calculations have been carried out previously on the relaxations of normal argon surfaces[8-10] and on the energy and configuration of argon surface defects.[11]

In this paper we examine the possibility of phase transformations on crystal surfaces without any transformation of the bulk. Thermodynamic variables are calculated in detail for the formation of one of many possible surface structures on the argon (100) surface; this structure is explicitly shown to be thermodynamically stable below the melting point of the solid. A second possible surface structure is examined and we show that it may also be thermodynamically stable below the melting point. We also examine the dependence of the thermodynamics of the transformation on the compressibility of the solid and on the presence of lattice defects. The temperature of formation of the transformed structure is sensitive to the presence of impurities. Surface vacancies can cause the transformed

* In that note, the possibility of such a transformation was incorrectly attributed to the configuration entropy of the transformed structure.

structure to revert to the normal bulk-like structure at high temperatures.

These conclusions are in accord with LEED observations on metals. The appearance of additional spots in LEED patterns has been observed to be very sensitive to the presence of impurity gases; the extra spots disappear at high temperatures.

We also examine qualitatively the possiblity of surface structures on (110) surfaces on face-centered-cubic crystals and again obtain reasonable agreement with experimental observations on metals.

The phase transformations which are examined in this paper can explain some, but not all, of the structures observed on metal surfaces. This theory does not account for the structures of very large periodicity such as observed on silicon.

II. THEORY

A. Thermodynamics

If a first order phase transformation occurs at a temperature T, then

$$\Delta F = \Delta H - T\Delta S = 0.$$

To find the transformation temperature, it is necessary to evaluate ΔH and ΔS. In this calculation, we assume that

$$\Delta H = \Delta E$$

which is an excellent approximation at the low pressures used in LEED experiments. We also assume that the only contributions to the energy are the potential energy of system and the zero-point energy

$$\Delta E = \Delta E_{potential} + \Delta E_{zero\text{-}point}.$$

The entropy term may be written as

$$\Delta S = \int \frac{\Delta Cp}{T}\, dT$$

$$= \int \frac{\Delta Cv}{T} + \int \Delta \frac{\alpha^2 v}{\kappa}\, dT$$

where α is the thermal expansion coefficient, κ is the compressibility and V is the volume.

For the transformations examined in this paper, $\Delta E_{potential}$, $\Delta E_{zero\text{-}point}$, ΔC_V, and $\Delta \frac{\alpha^2 v}{\kappa}$ are all positive. Hence, any neglect of $\Delta E_{zero\text{-}point}$ or the $\Delta \frac{\alpha^2 v}{\kappa}$ terms leads to a predicted value of the transformation temperature which is too high.

B. Model

The model adopted for the argon crystal is based on the following

assumptions: (1) only the potential energy of the crystal need be considered; (2) the total potential energy of the crystal is pairwise additive; (3) the atoms interact with a Lennard-Jones 6-12 potential having the form

$$V(r) = \frac{\beta}{r^{12}} - \frac{\alpha}{r^{6}}$$

and (4) the entropy and zero-point energy may be computed from an Einstein approximation.

The assumptions made are subject to a number of serious criticisms. It is well known that the Einstein approximation gives incorrect values of the entropy. However, the Einstein heat capacity of a solid is lower than the true heat capacity or Debye heat capacity at low temperatures. Therefore, the Einstein model leads to too low values of the entropy in the bulk. Assuming that this under-estimate of the entropy would also occur on the surface, where it is believed that the heat capacity decreases as T^2 at low temperatures rather than as T^3 as in the bulk,[12] the Einstein approximation tends to under-estimate the entropy changes associated with the surface phase transformation. This error leads to calculated values of transition temperatures to high temperature phases which are higher than would be obtained in a better calculation.

The assumption of pair-wise additive forces is subject to much question. Jansen[13] has shown that consideration of three body forces can explain the stability of face-centered cubic crystals relative to hexagonal close packed crystals. However, Rossi and Danon[14] have indicated that inclusion of three body forces leads to a large error in

the heat vaporization. They attribute this to either neglected four body forces or to a poor potential function. Losee and Simmons[15] measured the energy of formation of a vacancy in solid krypton (which is much like argon for potential purposes). They found that consideration of two body forces only leads to a value of the energy of a vacancy which is roughly 25% higher than the experimental result. At this time, it appears that many body forces play an important role in the solid state, but it is not known how to deal with them. We have chosen to neglect the many-body forces rather than handle them incorrectly as the results of the calculations can be compared only qualitatively with experiment.

Several authors have shown that the Lennard-Jones 6-12 potential cannot account for all of the properties of solid or even gaseous argon. The potential is useful, however, and we use Kihara's[16] constants in the potential function which give a bulk inter-atomic distance of 3.79 Å and a bulk binding energy of 1.414×10^{-13} ergs/atom.

C. Calculations

The authors have previously calculated the displacements of the first two planes of the argon (100) surface from their bulk planar spacings,[10] Fig. 1. $\delta_1 = .02604$ and $\delta_2 = .00623$ with the normal bulk planar spacing taken as 1. This normal (100) surface has a (1X1) structure. The FCC crystal is a stack of square planar lattices arranged such that the atoms in each layer lie below the holes of the layer above. This leads to an ABAB... structure.

A C(2X1), Fig. 2, surface structure may be formed from the (1X1) structure, Fig. 1, by translating every other row of atoms of the (1X1) structure one-half an inter-atomic distance in the surface plane. The

surface structure so formed can be described as having a unit cell with axes at 90° to each other and one axis equal in length to those of the (1X1) cell and the other twice as long. The structure may be called C(2X1) because of the axis lengths and the centered atom which is not equivalent to the corner atoms.

The potential energy of formation of the C(2X1) structure from the (1X1) structure, $\Delta E_{potential}$, is the difference between the total potential energy of the crystal with the C(2X1) surface structure and with the (1X1) surface structure. As we have assumed that the potential is pairwise additive, all energy terms which do not involve a surface atom cancel out in the subtraction. The potential energy of formation of the C(2X1) structure is then

$$\Delta E_{potential} = \Delta E_{surface-surface}[C(2X1)] + E_{surface-bulk}[C(2X1)]$$

$$- E_{surface-surface}[C(1X1)] - E_{surface-bulk}[(1X1)]$$

where $E_{surface-surface}$ is the sum of the potential energies between all atoms in the surface and $E_{surface-bulk}$ is the sum of the potentials between the surface atoms and the bulk atoms. In calculating the energies, care must be taken to count each term only once. Thus

$$E_{surface-surface} = \frac{1}{2} \sum_{\substack{i,j \\ i \neq j \\ i,\, j \text{ surface atoms}}} V(r_{ij})$$

$$E_{surface-bulk} = \sum_{\substack{i,j \\ i \text{ a surface atom} \\ j \text{ a bulk atom}}} V(r_{ij})$$

r_{ij} is the distance between atoms i and j.

Initially, in forming the C(2X1) structure from the (1X1), we assume that C(2X1) structure preserves the surface planar spacings of the (1X1) structure. For this process $\Delta E_{potential}$ is given in Table I. All numerical values in this paper were obtained by summing over 360 atoms on a CDC 6600 computer.

After shifting every other row of surface atoms, the distance between the translated surface atoms and the nearest substrate atoms, Fig. 2, is only .85 times the normal bulk separation. The translated atoms relax outwards from the surface in order to reduce their overlap with the substrate atoms. This gives the C(2X1) structure a saw-tooth configuration. The energy of formation of the C(2X1) structure was minimized with respect to the relaxations Δ_1 and Δ_2 on a CDC 6600 computer by a half interval method. The values of Δ_1 and Δ_2 which minimized $\Delta E_{potential}$, the energy of formation of the C(2X1) structure with relaxation allowed, were Δ_1 = .18696 and Δ_2 = .00986, taking the normal planar spacing as 1. $\Delta E_{potential}$ is contained in Table I for the relaxed structure. Relaxation greatly reduces the energy of formation of the C(2X1) structure.

After allowing the C(2X1) structure to relax to a minimum potential energy configuration, the force constants were computed for the surface atoms and the atoms in the atoms in the first plane below the surface. These were then used to compute the change in entropy in forming the C(2X1) structure

and the change in zero-point energy. The entropy and zero-point energy were computed in the constant volume Einstein approximation. The entropy was computed at 80°K; the experimental melting point of argon is 84°K and its 0°K Debye temperature is 92°K. As was pointed out in the section on thermodynamics the Einstein constant volume entropy leads to calculated transformation temperatures which are too high.

ΔS_1 is the change in vibrational entropy of the surface layer and ΔS_2 is the change in entropy of the first layer below the surface. $\Delta E_{Z.P}$ is the total change in zero-point energy of the first and second layers. ΔS_1, ΔS_2, and $\Delta E_{Z.P.}$ are included in Table I. ΔS_1 was also computed using the Nernst-Lindemann approximation and was found to agree within 2% to the Einstein value. As can be seen from Table I, the second layer contributes 13% of the total entropy and the change in zero-point energy is significant when compared to $\Delta E_{potential}$, the change in potential energy in forming the C(2X1) structure.

The configuration entropy of a given structure is

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

where W is the configurational degeneracy of the structure. For the (1X1) structure W = 1 as there is only one possible configuration and $S_{config} = 0$. In forming the C(2X1) structure we could have shifted either of two sets of rows. Hence, there are two C(2X1) structures which differ only by a translation of the surface. Two more equivalent structures may be formed by rotating the surface 90°. Thus the C(2X1) structure has a configurational degeneracy of 4 and $S_{config} = k \ln 4$. For the formation of the C(2X1)

structure from the (1X1)

$$\Delta S_{config} = k \ln 4 = 2X10^{-17} \text{ ergs/deg}^{*}$$

ΔS_{config} is clearly negligible when compared with $\Delta S_1 + \Delta S_2$. Hence, $\Delta S = \Delta S_1 + \Delta S_2$. Later, we shall see that if we allow small domains having the C(2X1) structure rather than an infinite C(2X1) structure, the configurational entropy is no longer negligible.

There exist many possible structures like the C(2X1) structure which can be formed by shifting rows of atoms on the surface. The properties of each such structure must be computed separately. We chose to carry out detailed calculations on the C(2X1) structure as experimental work has indicated its presence. Some data on another possible structure will be presented in the next section.

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* In the earlier note[7] suggesting the possibility of a phase transformation to the C(2X1) structure, the authors incorrectly stated that

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

where n is the number of surface atoms per unit area. This error was pointed out by the authors in an erratum.[17]

III. RESULTS

In the preceding section we have calculated various thermodynamic quantities for the phase transformation from the (1X1) structure, Fig. 1, to the C(2X1) structure, Fig. 2, of the (100) surface of an argon crystal. Combining the various terms in Table I,

$$\Delta F = 4.83 - .0592\ T\ \text{ergs/cm}^2$$

for the formation of a C(2X1) structure from a (1X1) structure on the (100) surface of argon. Thermodynamically, the C(2X1) structure is stable with respect to the (1X1) if ΔF for the transformation from the (1X1) structure is negative. ΔF for this transformation is zero for $T = 81.5°K$. Accordingly, the C(2X1) structure is stable on the argon (100) surface at temperatures above 81.5°K. This temperature is below the experimental melting point of solid argon, 84°K; the melting temperature of the model of solid argon is not known.

We found that the perpendicular relaxation of the surface layer greatly reduces the energy of the transformation from the (1X1) to the C(2X1) structure. A more refined calculation of ΔE would consider the relaxations in at least the first plane below the surface. This would reduce ΔE and thereby reduce the transition temperature. We have also underestimated ΔS for the transformation. Thus, for this model of solid argon, 81.5°K is an upper limit for the transition temperature from the (1X1) to the C(2X1) structure of the (100) surface.

A. Domain Size

The discussion above was based on an infinite C(2X1) structure covering the entire surface of the crystal. Experimentally, it has been found that the new high temperature features in a LEED pattern must come from small domains of varying orientation on the surface of the single crystal. We have pointed out that

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

where W is the number of distinguishable configurations of the structure. If we assume that the C(2X1) structure is formed in uncorrelated domains having an average of N atoms per domain, then, for a unit area,

$$W = 4^{n/N}$$

where n is the number of atoms per unit area. The quantity 4 is the four possible configurations of each domain which is like the fourfold configurational degeneracy of the infinite C(2X1) structure. Accordingly

$$S_{config} = \frac{n}{N} k \ln 4$$

for the C(2X1) structure and

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

for its formation from the (1X1). This may be conveniently written as

$$\Delta S_{config} = \frac{1}{N} n k \ln 4 = \frac{1}{N} .1335 \text{ (ergs/cm}^2\text{/deg)}.$$

If we assume that the domains are sufficiently large that ΔE and ΔS are not altered appreciably from the values for an infinite structure, we may write

$$\Delta F = 4.83 - (.0592 + \frac{.1335}{N} T \text{ (ergs/cm}^2\text{)}$$

for the formation of a C(2X1) surface with an average domain of N atoms. It has been estimated that the domains seen in LEED experiments contain twenty to forty atoms.[18]

Table II contains transition temperatures from the (1X1) structure to the C(2X1) structure for various domain sizes. As can be seen in Table II, the formation of small domains in the C(2X1) structure can significantly lower the transition temperature from the (1X1) to the C(2X1) structure.

B. Variation in Potential

The calculations presented in this paper were carried out in order to get an indication of what happens on metal surfaces. Accordingly, we have done limited calculations on the phase transformation from the (1X1) to the C(2X1) structure with two potentials besides the Lennard-Jones 6-12, the 6-7 and 6-30. These potentials represent extremes in softness and hardness. The parameters for the 6-7 and 6-30 were chosen so as to give a bulk inter-atomic distance of 3.79 Å and bulk binding energy of 1.414×10^{-13} ergs/atom; these are the same as given by the 6-12 potential used in the other calculations presented in this paper.

With the 6-7 and 6-30 potentials, only $\Delta E_{potential}$, the energy of the transformation from the (1X1) to the C(2X1) structure with the surface layer relaxed and ΔS_1, the change in entropy of the first layer, were calculated. These are tabulated in Table III along with the corresponding data for the 6-12 potential. Neglecting all contributions to the free energy of transformation except ΔS_1 and $\Delta E_{potential}$, we can write

$$\Delta F' \cong \Delta E_1 - T\,\Delta S_1$$

T', the temperature at which $\Delta F'$ becomes equal to zero, is also tabulated in Table III. T' gives some indication of the temperature at which the phase transformation would be expected. Finally, we have included in Table III, the bulk compressibilities computed from each of the potentials.

As can be seen in Table III, both the entropy and energy of the transformation increase as the compressibility decreases. The net effect is that the transition temperature, T', increases sharply as the solid becomes more incompressible.

C. Impurities

We have examined the effect of a substitutional surface impurity on the transformations from the (1X1) to the C(2X1) structure. The impurities used were Ne and Kr. To represent the argon-impurity interactions, the Lennard-Jones 6-12 potential parameters of argon,[16] krypton,[19] and neon,[16] were modified as follows: If r_{AA} is the minimum potential separation and U_{AA} the depth of the potential well for two atoms of type A, then

$$r_{AB} = \frac{r_{AA} + r_{BB}}{2}$$

$$U_{AB} = (U_{AA}\, U_{BB})^{1/2}.$$

We may envision an impurity atom substituted for an argon in the (1X1) structure of the (100) surface. We then allow the surface to undergo a phase transformation to the C(2X1) structure. The impurity atom may lie in either a shifted or unshifted row. The presence of the impurity atom changes the energy and entropy of the phase transformation. Table IV contains the changes in the energy $\Delta(\Delta E)_{imp}$, and entropy, $\Delta(\Delta S)_{imp}$, due to the

presence of one impurity going into either the shifted or unshifted positions. In calculating ΔE_{imp} and ΔS_{imp} the impurity atom was allowed to relax perpendicularly to the crystal surface to a position of minimum potential energy in both the (1X1) and C(2X1) structures.

The change in free energy of the transformation, due to the impurity, is

$$\Delta(\Delta F)_{imp} = \Delta(\Delta E)_{imp} - T\Delta(\Delta S)_{imp}.$$

We can get an idea of the effect of the impurity by setting T equal to our calculated transition temperature, 81.5°K. At 81.5°K

$$\Delta(\Delta F)_K \text{ (shifted)} = 4.6\text{X}10^{-15} \text{ (ergs/krypton atom)}$$
$$\Delta(\Delta F)_K \text{ (unshifted)} = 3.1\text{X}10^{-15} \text{ (ergs/krypton atom)}$$
$$\Delta(\Delta F)_{Ne} \text{(shifted)} = -13.6\text{X}10^{-15} \text{ (ergs/neon atom)}$$
$$\Delta(\Delta F)_{Ne} \text{(unshifted)} = 9.3\text{X}10^{-15} \text{ (ergs/neon atom)}$$

Shifted and unshifted refer to whether the impurity atom is in a shifted or unshifted row.

The krypton atoms hinder the phase transformation by about the same amount going into either the shifted or unshifted positions. The neon atom greatly prefers to go into the shifted positions; going into the shifted position, the neon atom aids the transformation. Multiplying by the density of shifted sites, $3.48\text{X}10^{14}/\text{cm}^2$

$$\Delta(\Delta F)_{Ne} \text{(shifted)} = -5.2 \text{ (ergs/cm}^2\text{)*(concentration of Ne atoms in shifted position)}$$

at 81.5°K. A small concentration of surface neon impurity going into the up position could appreciably decrease the free energy and hence the temperature of the transformation from the (1X1) to the C(2X1) structure. This preference of the neon impurity could play a large role in determining

the surface structure formed, if more than one is possible, and also in determining the domains of the structure on an impure surface.

It is of interest to have an estimate of the (1X1) surface concentration of impurity atoms knowing the bulk concentration. This may be estimated by calculating the change in energy, ΔE, and entropy, ΔS, of a crystal when a bulk impurity atom is moved to the (100) surface and replaced, in the bulk, with an argon atom from the surface. ΔE and ΔS for this process are tabulated in Table V. We are interested in the surface concentration of impurity atoms at temperatures near the transition temperature, 81.5°K. The free energy change in exchanging a bulk impurity atom with a surface argon atom is

$$\Delta F = \Delta E - T\Delta S$$

where ΔE and ΔS are from Table IV. For a Kr impurity at 81.5°K

$$\Delta F = 1.9\text{X}10^{-14} \text{ ergs/atom}$$

and for the Ne impurity

$$\Delta F = -.7\text{X}10^{-14} \text{ ergs/atom.}$$

The realtive concentration of bulk and surface impurity atoms is given by

$$\frac{[\text{Surface}]}{[\text{Bulk}]} = e^{-\Delta F/kT}.$$

For Kr impurities at 81.5°K

$$\frac{[\text{Surface}]}{[\text{Bulk}]} \simeq 0.2.$$

For Ne impurities at 81.5°K

$$\frac{[\text{Surface}]}{[\text{Bulk}]} \simeq 2.$$

At equilibrium, at temperatures near the transition temperature of the clean perfect model argon surface, the concentration of surface imputities is very close to that of bulk impurities. In LEED experiments, very high purity crystals are used. Impurities such as neon on the argon surface can play an important role in the phase transformations only if they are present on the surface in large concentrations.

D. Surface Vacancies

The authors have previously examined the concentration of surface vacancies on the argon (100) surface.[11] At temperatures near the melting point, .3% of the surface sites are vacant. If a vacancy is created at a site in a shifted row of atoms in the C(2x1) structure, the entire row of atoms collapses back into the (1x1) unshifted locations. One atom, adjacent to a vacancy in its row, collapses into the hole and leaves a hole in its former location. This hole then propagates down the row until the entire row has collapsed. Thus the formation of surface vacancies tends to collapse the C(2x1) structure back to the (1x1) structure. The shifted row with the vacancy was found to collapse even if a large krypton impurity was located adjacent to vacancy and in its row.

E. Other Surface Structures

A number of surface structures similar to the C(2x1) can be envisioned. We have examined in detail the properties of only the C(2x1). However, we have also carried out limited calculations on a C(5x1) structure, as a LEED pattern corresponding to this structure has been observed. The C(5x1) structure was formed by shifting two of every five rows; it takes its name from the size of the unit cell and the centered atoms (Fig. 3). The surface atoms were allowed to relax perpendicularly to

the surface and the energy, $\Delta E_{potential}$, and entropy ΔS_1, of formation of the relaxed C(5x1) structure were calculated using a 6-12 potential. ΔS_1 is the entropy change of the surface layer. $\Delta E_{potential}$ and ΔS_1 are tabulated in Table VI for the C(5x1) structure. Corresponding values are given for the C(2x1) structure for comparison. The temperatures T', for the transformations to the C(5x1) and C(2x1) structures from the (1x1) are also given in Table VI. In calculating T', only ΔE_1 and ΔS_1 were considered.

As can be seen from Table VI, the transition temperatures to the C(5x1) and C(2x1) structures are nearly equal. This near equality would presumably hold if further terms in the free energy of the C(5x1) were considered.

One can conceive of many possible structures obtained by shifting surface atom rows. A C(4x1) may be obtained by shifting every fourth row or C(3x1) from every third row. When a smaller fraction of the rows is shifted both the energy and entropy of the transformation are decreased. Like the C(5x1), these other structures may also be stable relative to the (1x1) at about the same temperature as the C(2x1).

IV. CORRELATION WITH LEED DATA FOR METALS

The calculations presented in this paper were made for an inexact model of argon. The properties of solid argon are, of course, different in many ways from those of metals. However, calculations on a limited model can be useful in understanding the properties of more complicated materials. As will be shown in this section, the calculated properties of the model of the solid argon surface correlate well with some of the experimental properties of metal surfaces.

We have found that it is possible to form a variety of C(nxl) surface structures on the (100) face of the face-centered-cubic argon crystal. Because of the symmetry of the (100) surface (square), these structures can all have two different orientations at 90° to each other. This is observed for all C(nxl) LEED patterns on (100) metal surfaces.[20]

The theory developed in the previous section indicates that surface defects can be very important in surface phase transformations. This may explain why very careful treatment of the surface is required in order to produce LEED patterns other than (1xl). The expected sensitivity of structure to impurities may determine which of several possible surface structures is observed. On the nickel (110) surface, only a (1xl) pattern is observed except in the presence of oxygen.[1] (2xl) structures are observed on the (110) and (100) surfaces of copper after exposure to oxygen.[21]

The formation of shifted row surface structures is a normal first order phase transformation. There is no reason to expect that it should not be reversible. LEED experiments have shown that once an (nxl) pattern is formed, it disappears on cooling and reappears on heating,[22] just as though an ordinary reversible phase change occurs.

We have found that formation of surface vacancies will cause our shifted row structures to revert to (1x1). Experimentally, (nx1) structures disappear as the temperature is raised.[22]

According to the theory developed above, a number of possible surface structures are quite similar in free energy. Impurities may determine which structure is formed. Somorjai[22] has found that either a (5x1) or a (2x1) LEED pattern can be observed from a (100) platinum surface in the same temperature region. He found that prolonged heating of the (2x1) pattern surface caused the (2x1) pattern to disappear and a (5x1) to appear. After the (5x1) structure was formed, the (2x1) could not be regenerated.

The shifted row surface structures arise from movements in the surface layer of atoms only. No rearrangement of the bulk occurs. This is in accord with the findings of Palmberg[23] on epitaxially grown single crystals; deposition of a mono-layer of silver on gold destroyed the gold surface structure and deposition of three mono-layers of gold on silver caused the appearance of a gold structure.

If we examine the appearance of (110) face of a FCC crystal, Fig. 4a, we see that it is possible to form distinct (nx1) structures in two different fashions. These arise from shifting the rows along different axes, Figs. 4b and 4c. A shift along the long axis, Fig. 4b, brings the shifted atoms appreciably closer to the substrate atoms. A shift along the short axis, Fig. 4c, causes less crowding. It should be easier to have a phase transformation involving shifts along the shorter axis than along the longer axis. Thus, we would expect it to be possible to form (nx1) structures on (110) surfaces having only one of two conceivable orientations.

Lyon[24] has, in fact, observed (2x1) and (3x1) structures on the (110) surface of platinum where only one orientation of the structure existed at a time. The patterns corresponding to shifts along our long axis were easily removed. The structures corresponding to shifts along the short axis were found to be quite stable. This is in accord with our expectation that the one structure should be more stable than the other.

The theory presented in this paper accounts for many of the properties of the structures observed by LEED. There is one piece of experimental data (for (nx1) structures) for which it does not account. The extra spots of the (5x1) structure on the gold and platinum (100) surface (that is, spots on the (5x1) LEED pattern which are not present in the (1x1) pattern) are not single spots. They are slightly split.[22,25] Our model does not account for this splitting. It is possible that a careful calculation of LEED patterns based on our (5x1) structure model and considering multiple scattering effects would give rise to these pairs.

V. CONCLUSIONS

In this paper we have examined the thermodynamics of the formation of C(2x1) and C(5x1) structures from the normal (1x1) structure of the argon (100) surface. The C(2x1) structure is stable relative to the (1x1) at temperature below the experimental melting point of solid argon. The C(5x1) structure is stable at about the same temperature as the C(2x1).

Large concentrations of surface impurities can significantly effect the free energy of formation of the C(2x1) structure. It is possible that surface impurities play a large role in determining which of several free energetically similar surface structures is formed in a given experiment.

A vacancy in a shifted row of the C(2x1) structure causes the row to collapse back to the unshifted position. This could cause the entire C(2x1) structure to collapse to the (1x1) structure at sufficiently high temperatures.

These conclusions are in excellent accord with experimental LEED studies.

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Table I. Thermodynamic data for the phase transformation from the (1x1) structure to the C(2x1) structure of the (100) surface. $\Delta E_{potential}$ (unrelaxed) is the energy of formation of the C(2x1) structure without relaxation. $\Delta E_{potential}$ (relaxed) is the energy of formation of the C(2x1) structure when the surface atoms are allowed to relax. ΔS_1 is the change in entropy of the surface layer in forming the C(2x1) structure and ΔS_2 is the change in entropy of the first layer below the surface $\Delta E_{Z.P.}$ is the change in zero point energy of the first and second layers.

$\Delta E_{potential}$ (unrelaxed)	38.	$(ergs/cm^2)$*
$\Delta E_{potential}$ (relaxed)	6.37	$(ergs/cm^2)$*
ΔS_1	.0510	$(ergs/cm^2/deg)$*
ΔS_2	.0082	$(ergs/cm^2/deg)$
$\Delta E_{Z.P.}$	-1.54	$(ergs/cm^-)$

*This value is slightly different from that reported previously as we have considered the normal displacements of the first and second planes in forming the C(2x1) structure.

Table II. The transition temperatures, T from the (1x1) structure of the argon (100) surface to the C(2x1) structure for various average domain sizes, N.

N (atoms)	T (°K)
∞	81.5
80	79.5
40	77.5
20	73.5
10	66.5

Table III. Thermodynamic data for the phase transformation from the (1x1) to the C(2x1) structure of the argon (100) surface for three Lennard-Jones potentials. $\Delta E_{potential}$ is the energy of formation of the C(2x1) structure when the surface atoms are allowed to relax. ΔS_1 is the change in entropy of the surface layer in forming the C(2x1) structure. T' is the temperature at which the C(2x1) structure becomes stable. κ is the bulk compressibility.

Potential	$\Delta E_{potential}$ (ergs/cm^2)	ΔS_1 (ergs/cm^2/deg)	T'(°K)	κ (cm^2/dyne)
6-7	2.61	.0314	83	5.8×10^{-11}
6-12	6.37	.0510	125	3.4×10^{-11}
6-30	11.63	.0651	178	1.4×10^{-11}

Table IV. The change in potential energy, $\Delta(\Delta E)_{imp}$ and entropy, $\Delta(\Delta S)_{imp}$ of the transformation form the (1x1) to the C(2x1) structure of the argon (100) surface due to a substitutional impurity going in either the shifted or unshifted row of the C(2x1) structure.

Impurity	Position	$\Delta(\Delta E)_{imp}$ (ergs/impurity atom)	$\Delta(\Delta S)_{imp}$ (ergs/deg/impurity atom)
Kr	Shifted	-3.9×10^{-15}	-1.04×10^{-16}
Kr	Unshifted	-9.6×10^{-15}	$-.80\times10^{-16}$
Ne	Shifted	-2.6×10^{-15}	1.34×10^{-16}
Ne	Unshifted	10.4×10^{-15}	$-.13\times10^{-16}$

Table V. The change in potential energy, ΔE, and entropy, ΔS on a moving bulk impurity atom to the (100) surface of argon and returning a surface argon atoms to the bulk.

Impurity	ΔE (ergs/impurity atom)	ΔS(ergs/deg/impurity atom)
Kr	2.6×10^{-14}	$.87 \times 10^{-16}$
Ne	-5.2×10^{-14}	-5.5×10^{-16}

Table VI. Thermodynamic data on the formation of C(5x1) and C(2x1) structures from the (1x1) structure of the argon (100) surface. ΔE potential is the change in energy with the surface layer allowed to relax and ΔS_1 is the change in entropy of the surface layer. T' is the temperature of the transformation from the (1x1) structure, considering only ΔE potential and ΔS_1.

Structure	ΔE potential (ergs/cm^2)	ΔS_1(ergs/cm^2/deg)	T' (°K)
C(5x1)	5.11	.0399	128
C(2x1)	6.37	.0510	125

FIGURE CAPTIONS

Fig. 1 The (1x1) structure of the (100) surface of a fcc crystal. (a) Top view: the intersections of the lines are the normal surface sites and the atoms are circles. The unit cell is indicated with heavy lines and the atoms in the second layer with pluses. (b) Side view: the relaxations, δ_i, of the first two planes. The normal planar spacing is 1.

Fig. 2 The C(2x1) structure of the (100) surface of a fcc crystal. The shaded circles are shifted atoms. (a) Top view: the intersections of the lines are the normal surface sites. The unit cell is indicated by heavy lines. Unshifted atoms are open circles and second layer atoms are pluses. (b) Side view: atoms in unshifted positions are open circles. δ_i are the normal (1x1) surface displacements and Δ_i the extra displacement of the transformed structure.

Fig. 3 The C(5x1) structure of the (100) face of a fcc crystal. The intersections of the lines are the normal surface sites. The unshifted atoms are open circles and the shifted atoms shaded circles. The second layer atoms are pluses. The unit cell is shown by heavy lines.

Fig. 4 The (110) surface of a fcc crystal. The intersections of the lines are the normal surface sites. The unshifted surface atoms are open circles. Second layer atoms are pluses. The unit cell is shown with heavy lines. (a) The (1x1) structure. (b) A C(2x1) structure with shaded atoms shifted along the long axis. (c) A C(2x1) structure with shaded atoms shifted along the short axis.

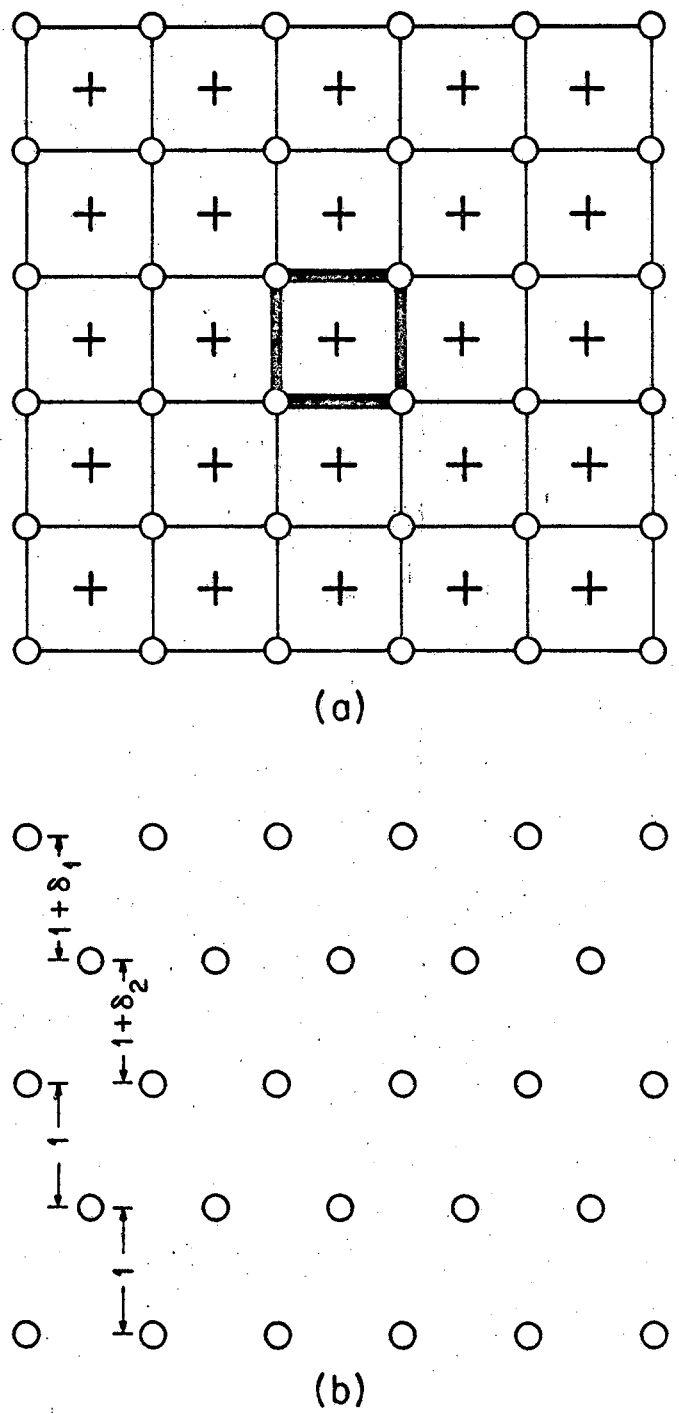

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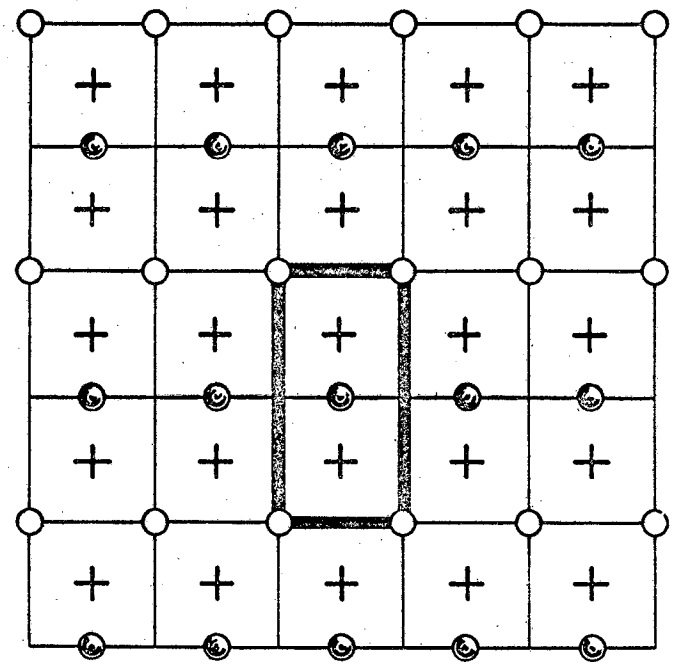
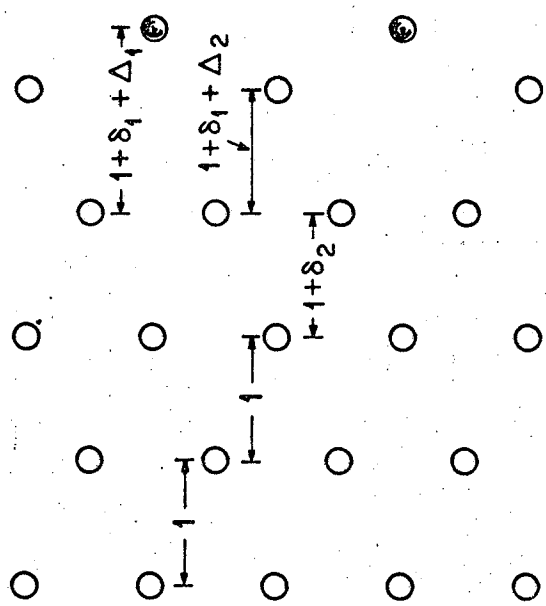
Fig. 1



(a)



(b)

XBL683-2591

Fig. 2

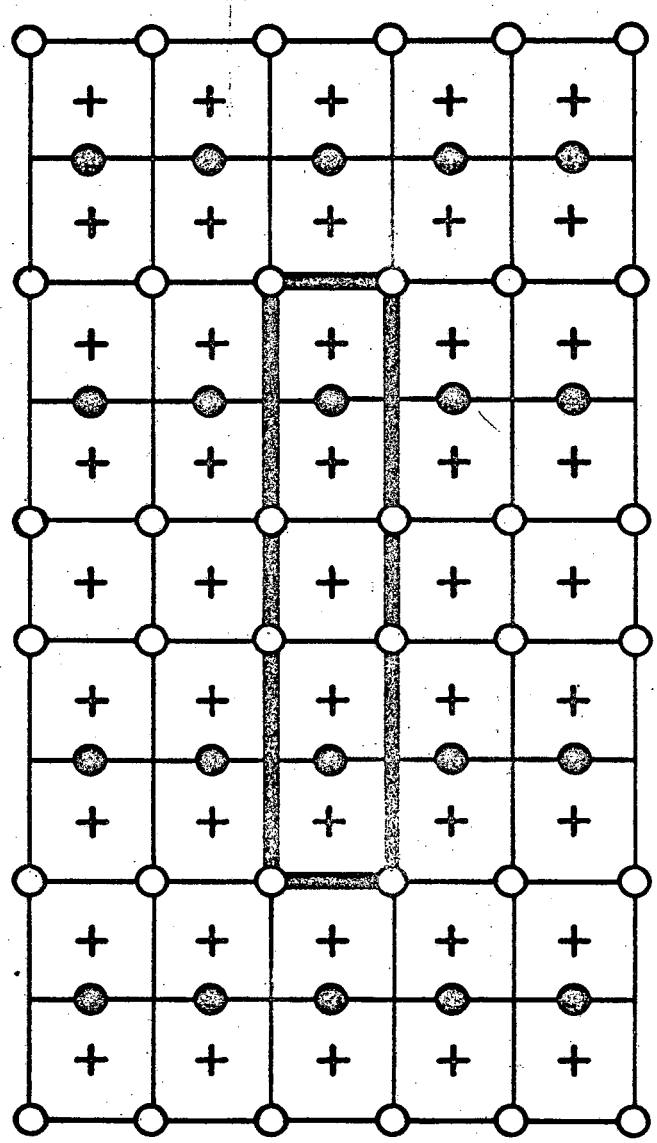


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Fig. 3

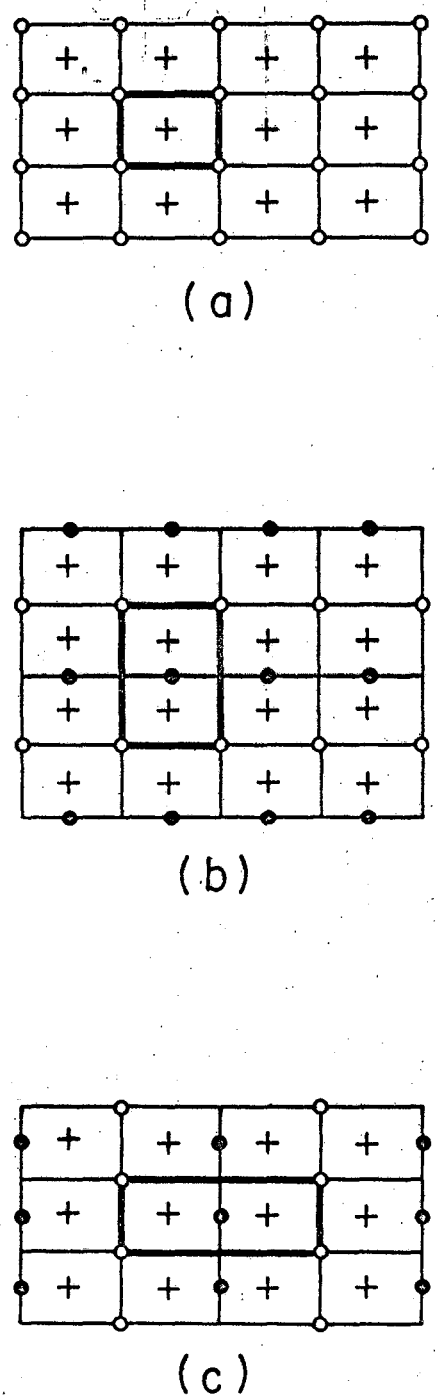

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Fig. 4

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