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ADSORPTION AND DIFFUSION ON THREE STRUCTURES OF THE (100) SURFACE OF A FACE CENTERED CUBIC CRYSTAL

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ABSTRACT

The energy of adsorption of argon atoms on the argon (100) surface is calculated for three possible structures of that surface, the normal (1x1) structure, and C(2x1) and C(5x1) structures. The adsorption energies are lower by 20% on the C(2x1) and C(5x1) structures than on the normal (1x1) structure. The adsorption site symmetry varies with structure as do the separations of the adsorption energy maxima.

Ad-atom diffusion barriers are calculated on all three structures. The energy barrier on the C(2x1) and C(5x1) structures is lower than that on the normal (1x1) structure by as much as 70%, depending on the direction of the diffusion.

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I. INTRODUCTION

Adsorption on solid surfaces has been studied experimentally for many years. Such studies yield some information about the nature of solid surfaces and can have considerable practical application in catalysis.

Recently, high speed computers have made possible very detailed calculations of the properties of solid surfaces. These theoretical surface investigations can be separated into two areas: the properties of the ideal equilibrium solid surface, and the interaction of ad-atoms and the properties of defects on solid surfaces. Several calculations have been made of the equilibrium spacing of the surface planes of molecular crystals[1,2,3] and of metals;[3] they relax outward from the crystal and the increase in the planar spacing of the surface layer can be as large as 12%. These calculations of surface relaxations also yield surface energies. Calculations of heats of adsorption have been made for a number of surface sites of various faces of cubic crystals.[4,5] In making such calculations, the adsorbed atom is allowed to relax perpendicularly to the surface to a potential energy minimum. In one such calculation,[4] the surface atoms near the adsorbed atom were also allowed to relax; this relaxation increased the calculated heat of adsorption by less than 0.3%. Calculations of adsorption potential diagrams have also yielded surface diffusion barriers.[5]

Low Energy Electron Diffraction (LEED) has been used to study clean solid surfaces and the interaction of gas atoms with the atoms in the surface. The LEED pattern is altered by adsorption of gas atoms.[6] As for clean surfaces, the interpretation of the new patterns is not as yet fully understood.

The authors have previously proposed a theory of surface phase transformations.[7] They have shown that, for a simple model of the argon (100) surface, it is possible for the surface atoms to rearrange from the normal (1×1) structure, Fig. 1, to a C(2×1) structure, Fig. 2, or a C(5×1) structure, Fig. 3, as well as a number of other structures. These phase transformations are possible without an accompanying rearrangement of the substrate. The transitions occur by shifting rows of surface atoms half an interatomic distance parallel to the surface. After the transition, the surface has a saw-tooth configuration as the shifted atoms are raised up from the surface plane, Fig. 2b. The authors have shown that this theory of surface phase transformations explains much LEED data for clean face-centered-cubic metals.[8]

In this paper, we examine the adsorption and diffusion of argon on the (1×1), C(2×1), and C(5×1) structures of the argon (100) surface. We show that the heat of adsorption of argon on the C(2×1) and C(5×1) structures is roughly 20% lower than the heat of adsorption on the (1×1) structure. The symmetries and separations of the adsorption sites are altered from those of the (1×1) structure. Ad-atom diffusion barriers on the C(2×1) and C(5×1) structures are up to 70% lower than on the (1×1) structure.

II. THE MODEL

We employ the following model of solid argon: (1) all quantum effects are neglected; (2) only the potential energy is considered; (3) the potential energy is pairwise additive; and (4) the atoms interact with a Lennard-Jones 6-12 potential

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

where r is the interatomic separation. We use the argon potential parameters obtained by Kihara[9] which give a solid binding energy of 2035 cal/mole and 0°K interatomic distance of 3.79 Å.

These assumptions are subject to several criticisms: (1) neglects zero-point motions and (2) restricts the strict validity of the calculations to 0°K. The assumption of pairwise additivity of the potential (3) is most subject to question. This assumption has been the subject of much discussion in the literature.[10,11,12] At this time, it is not certain whether many body forces do in fact play an important role in solid argon.[13] As the true potential functions in solids are not well known and many body forces are very difficult to include in calculations, the general practice is to neglect the many body forces in calculating atomic properties of solids. It is hoped that information gained in this way, while not necessarily exact for real solids, will yield insight into the behavior of the real world.

Utilizing the above model of solid argon, the authors have previously calculated the displacements of the first two layers of the argon (100)

surface, Fig. 1b.[3] These displacements are given as a percentage of the normal bulk planar spacing, Table I. The authors have also calculated the displacements of the surface layer atoms in the C(2×1) and C(5×1) structures, Fig. 2b.[7] For convenience, we call those atoms in rows which are shifted parallel to the surface shifted atoms; atoms in unshifted rows will be called unshifted atoms. The displacements of the atoms perpendicular to the surface and out of the normal surface plane are in Table II.

III. CALCULATIONS

The adsorbed atom is assumed to be located above a point (x,y) of the unit cell of a (100) surface. The distance of the ad-atom above the normal surface plane is δ. Then the heat of adsorption of the ad-atoms is

$$E(x,y,\delta) = - \sum_{\substack{\text{lattice}\\ \text{points}}} V(x_\ell - x,\ y_\ell - y,\ z_\ell + \delta)$$

where $(x_\ell,\ y_\ell,\ z_\ell)$ is a lattice point and V is the potential between two atoms having coordinates $(x_\ell,\ y_\ell,\ z_\ell)$ and $(x,\ y,\ -\delta)$.

The heat of adsorption $E(x,y,\delta)$ was maximized with respect to δ for fixed (x,y) by finding a δ such that

$$\frac{\partial E(x,y,\delta)}{\partial \delta} = 0 .$$

This maximization was carried out by a half interval technique on a CDC 6600 computer.

IV. RESULTS

We have calculated heats of adsorption of argon at a number of sites on (1×1), C(2×1), and C(5×1) structures of the argon (100) surface. The adsorbed atom was assumed to be an argon atom. The heats of adsorption are plotted in Figs. 4, 5, and 6. These figures are energy contour plots and show the general features of the surface. Energy contour plots for neon and krypton on argon are similar to these for argon on argon.

Tables III, IV, and V give the locations of all the adsorption energy maxima (adsorption sites) and the saddlepoints. The positions of the positions of interest are given in the coordinate system indicated in Figs. 4,5, and 6. Tables III, IV, and V also give the adsorption energies of the positions and their local symmetries. The notation for the symmetries is the standard crystallographic notation, C_n refers to n-fold rotational symmetry and σ_v refers to a vertical reflection plane.

The heat of adsorption for an argon at the maximum adsorption energy site on the (1×1) structure of the argon (100) surface, 1386 cal/mole, is not identical with that obtained by the authors in an earlier calculation,[4] 1367 cal/mole. In this calculation, the energies were calculated by summing over a crystal six planes thick; the earlier calculation summed over five planes. The value reported here is smaller than that reported by Goodman,[5] 1408 cal/mole (using our argon parameters); he summed over a much larger crystal.

There is only one possible adsorption site on the (1×1) structure and its adsorption energy is 1386 cal/mole and its symmetry is C_4. There are two sites on the C(2×1) structure with energies 1212 and 1164 cal/mole and symmetries C_3 and C_2. There are five sites on the C(5×1) with energies from

1207 to 1079 cal/mole and symmetries C_3, C_2, and σ_v. Thus, adsorption energy and site symmetry vary widely with structure on the (100) surface. The separation of the closest maxima on the (1×1) structure is 1.00 units (= 3.79 Å). The separation between closest maxima varies between .54 and 1.02 units on the C(2×1) structure and between .54 and 1.00 units on the C(5×1) structure.

From Table III, we see that the energy barrier for diffusion of argon ad-atoms on the (1×1) structure of the argon (100) face is 376 cal/mole. This agrees quite well with Goodman's 381 cal/mole.[4] We can obtain barriers for a variety of possible jumps on C(2×1) and C(5×1) structures from the data in Tables IV and V. Barriers for jumps on the C(2×1) and C(5×1) are contained in Tables VI and VII. The shifted atoms create a pipe for diffusion parallel to the shift; the barrier along this pipe is about 30% of the barrier for diffusion on the (1×1) structure. Diffusion perpendicular to the shift direction is complicated. The diffusing atom moves through a number of adsorption sites. The potential for motion of an argon ad-atom perpendicularly to the shift direction is shown in Fig. 7 for the C(2×1) structure. The total activation energy for diffusion across this complicated barrier is 320 cal/mole, which is also less than the energy barrier for diffusion of argon ad-atoms on the (1×1) structure.

V. CONCLUSIONS

In this paper, we have examined adsorption of argon on three possible structures of the argon (100) surface, the normal (1×1) structure and C(2×1) and C(5×1) structures. The existence of such structures on metal surfaces was previously predicted by the authors and has been found to explain some previously incompletely understood LEED data.[8]

We have found then adsorption energies are roughly 20% lower on the C(2×1) and C(5×1) structures than on the (1×1) structure. The adsorption site on the (1×1) structure has C_4 symmetry, while the adsorption sites on the C(2×1) structure have C_3 and C_2 symmetry and the sites on the C(5×1) structure have C_3, C_2, and σ_v symmetry. The distance between adsorption sites on the C(2×1) and C(5×1) structures varies from 54% to 102% of the (1×1) adsorption site separation.

Diffusion barriers on the C(2×1) and C(5×1) structures are much lower than on the (1×1). They are reduced by up to 70% depending on the direction of motion.

These results obtained via a simplified model of argon may not be directly applicable to metals. However, they do suggest a number of chemical phenomena which may be observable on high temperature metal surfaces. Adsorption energies may decrease somewhat. Diffusion barriers may decrease. The predicted change in adsorption site symmetry and spacing may cause a drastic change in the catalytic behavior of the surface.

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Table I

The displacements, δ_i, of the first two layers of the argon (100) surface.

δ_1 (%)	δ_2 (%)
2.604	.589

Table II

Displacements, Δ, of the shifted and unshifted surface atoms of the C(2×1) and C(5×1) structures of the argon (100) surface. The displacements are perpendicular to the surface plane. They are given as a percentage of the normal bulk planar spacing away from the normal (1×1) surface plane.

Structure	Atom	Δ (%)
C(2×1)	Shifted	18.7
	Unshifted	1.0
C(5×1)	Shifted	18.7
	Unshifted	.7

Table III

Adsorption energy maxima and saddlepoint positions for argon on the (1×1) structure of the argon (100) surface. Only one member of each equivalent set is given.

Site type	Location	Adsorption Energy cal/mole	Symmetry
Max	(.50,.50)	1386	C_4
Saddle	(.50, 0)	1010	C_2

Table IV

Adsorption energy maxima and saddlepoint positions for argon on the C(2×1) structure of the argon (100) surface. Only one member of each equivalent set is given.

Site type	Location	Adsorption Energy (cal/mole)	Symmetry
Max	(.50,.27)	1212	C_3
Max	(0, .51)	1164	C_2
Saddle	(.50, 0)	1109	C_2
Saddle	(.27,.40)	1102	σ_v
Saddle	(0, 1.00)	892	C_2

Table V

Adsorption energy maxima and saddlepoint positions for argon on the C(5×1) structure of the argon (100) surface. Only one member of each equivalent set is given.

Site Type	Location	Adsorption Energy cal/mole	Symmetry
Max	(.50,.27)	1207	C_3
Max	(0, .51)	1160	C_2
Max	(.50, 1.71)	1137	σ_v
Max	(0, 1.51)	1132	C_2
Max	(.50, 2.50)	1079	C_2
Saddle	(.50, 0)	1109	C_2
Saddle	(.17, .40)	1099	C_3
Saddle	(0, 1.00)	882	C_2
Saddle	(.21, 1.59)	1057	σ_v
Saddle	(.50, 2.14)	931	σ_v
Saddle	(0, 2.50)	842	C_2

Table VI

Diffusion barriers for argon ad-atoms on the C(2×1) structure of the argon (100) surface. The barriers which must be crossed for diffusion perpendicular to the shift are marked $\perp$, that for diffusion parallel to the shift $\|$.

Initial Position	Final Position	Barrier Energy(cal/mole)	Type
(.50, .27)	(.50, -.27)	103	$\perp$
(.50, .27)	(0, .51)	110	$\perp$, $\|$
(0, .51)	(.50, .27)	52	$\perp$
(0, .51)	(0, 1.49)	272	$\perp$

Table VII

Diffusion barriers for argon ad-atoms on the C(5×1) structure of the argon (100) surface. The barriers which must be crossed for diffusion perpendicular to the shift are marked ⊥, that for diffusion parallel to the shift ‖.

Initial Position	Final Position	Barrier Energy(cal/mole)	Type
(.50, .27)	(.50, -.27)	98	⊥
(.50, .27)	(0, .51)	108	⊥, ‖
(0, .51)	(.50, .27)	61	⊥
(0, .51)	(0, 1.51)	278	⊥
(0, 1.51)	(0, .51)	252	⊥
(0, 1.51)	(.50, 1.71)	75	⊥
(.50, 1.71)	(0, 1.51)	80	⊥
(.50, 1.71)	(0, 1.51)	201	⊥
(.50, 2.50)	(.50, 1.71)	148	⊥
(.50, 2.50)	(-.50, 2.50)	237	

FIGURE CAPTIONS

Fig. 1 The (1×1) 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(2 1) structure of the (100) surface of a FCC crystal. The shaded circles represent 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 (1×1) surface displacements and Δ_i the extra displacement of the transformed structure.

Fig. 3 The C(5×1) structure of the (100) surface 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 heat of adsorption of an argon atom on the (1×1) structure of the argon (100) surface. The heaviest lines are the boundaries of the unit cell. The circles are the surface atoms and the plus a second layer atom. Energy contours are given in calories per mole. Reference coordinates are indicated.

Fig. 5 The heat of adsorption of an argon atom on the C(2×1) structure of the argon (100) surface. The heaviest lines are boundaries of the unit cell. The open circles are the unshifted atoms and the shaded circle a shifted atom. The pluses are second layer atoms. Energy contours are given in calories per mole. Reference coordinates are indicated.

Fig. 6 The heat of adsorption of an argon atom on the C(5×1) structure of the argon (100) surface. The heaviest lines are boundaries of the unit cell. The open circles are the unshifted atoms and the shaded circles shifted atoms. The pluses are second layer atoms. Energy contours are given in calories per mole. Reference coordinates are indicated.

Fig. 7 The barrier for diffusion of an argon ad-atom perpendicularly to the shift direction on the C(2×1) structure of an argon (100) surface. Energies are in calories per mole. Position is in terms of the reference coordinates in Fig. 5.

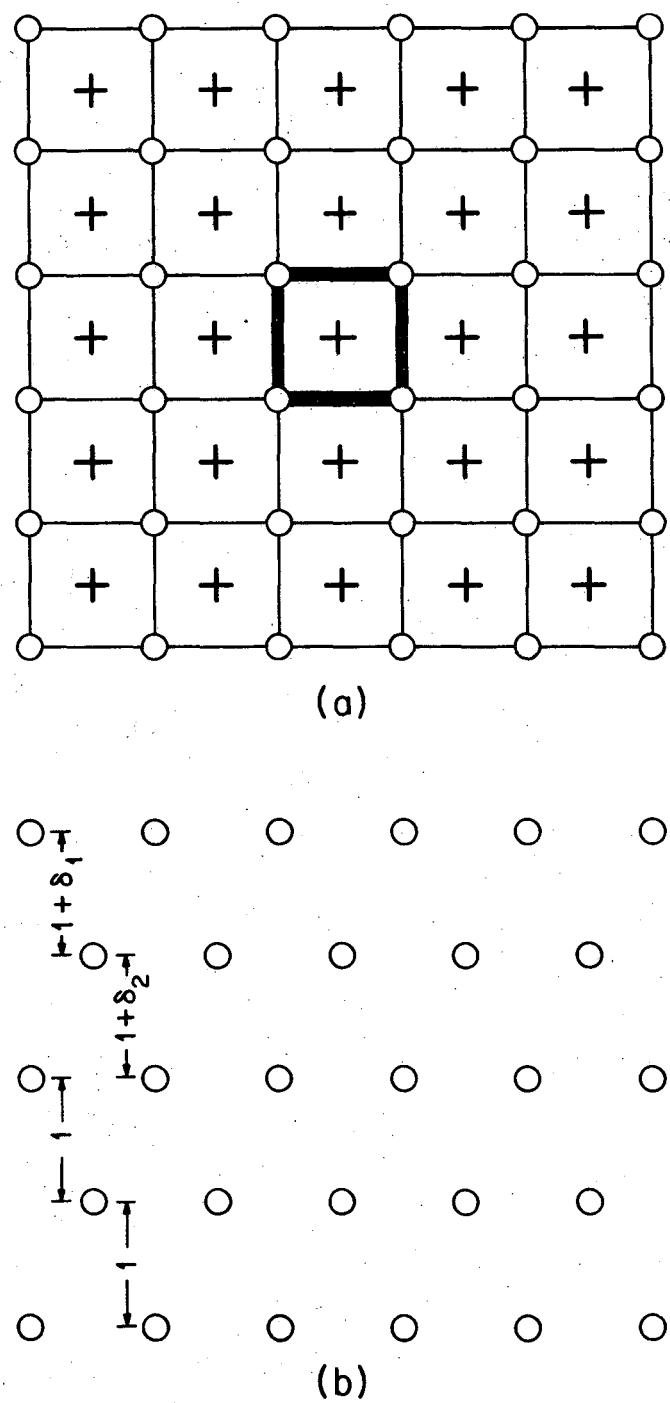

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Fig. 1

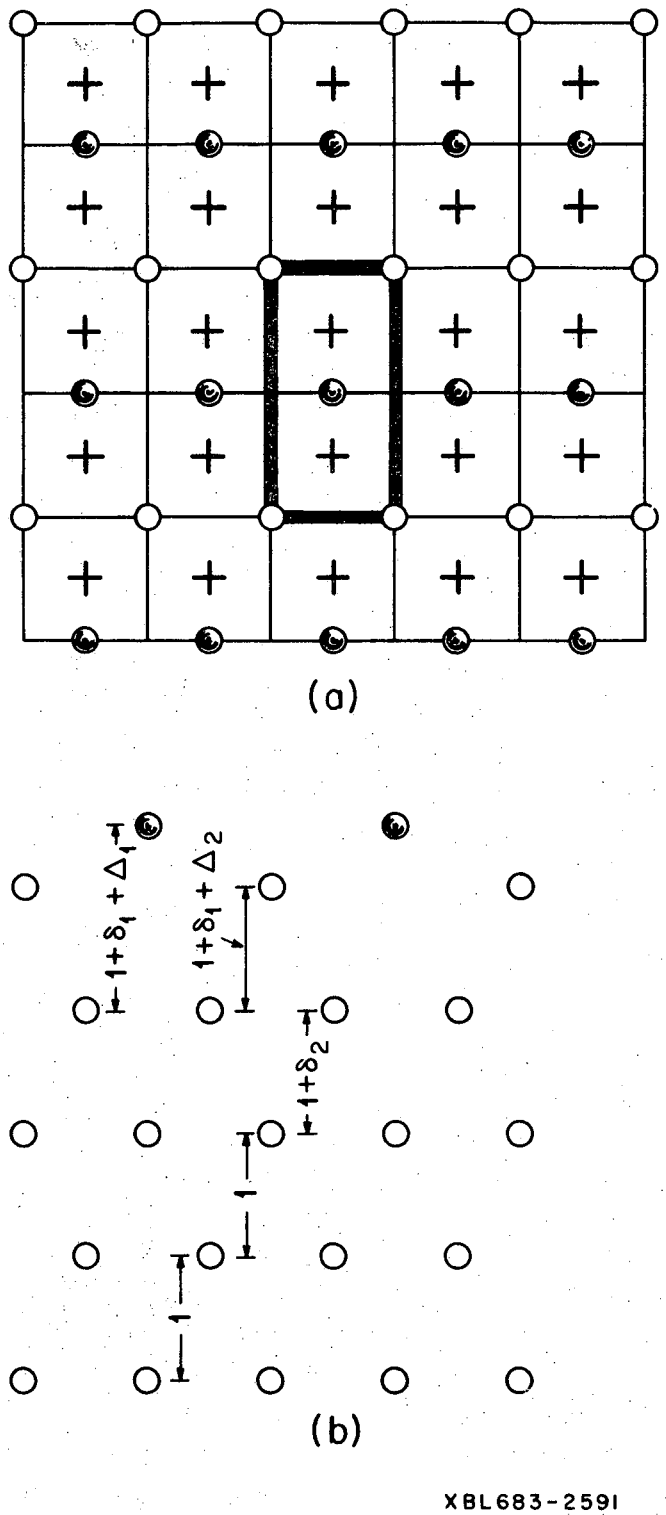

Fig. 2

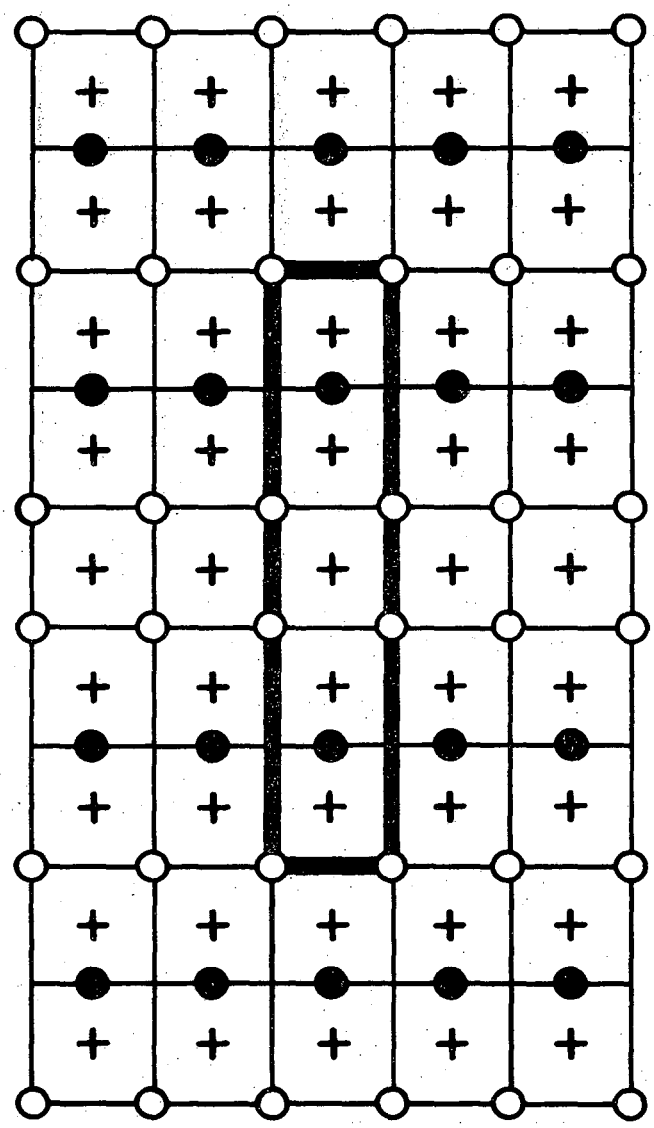

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Fig. 3

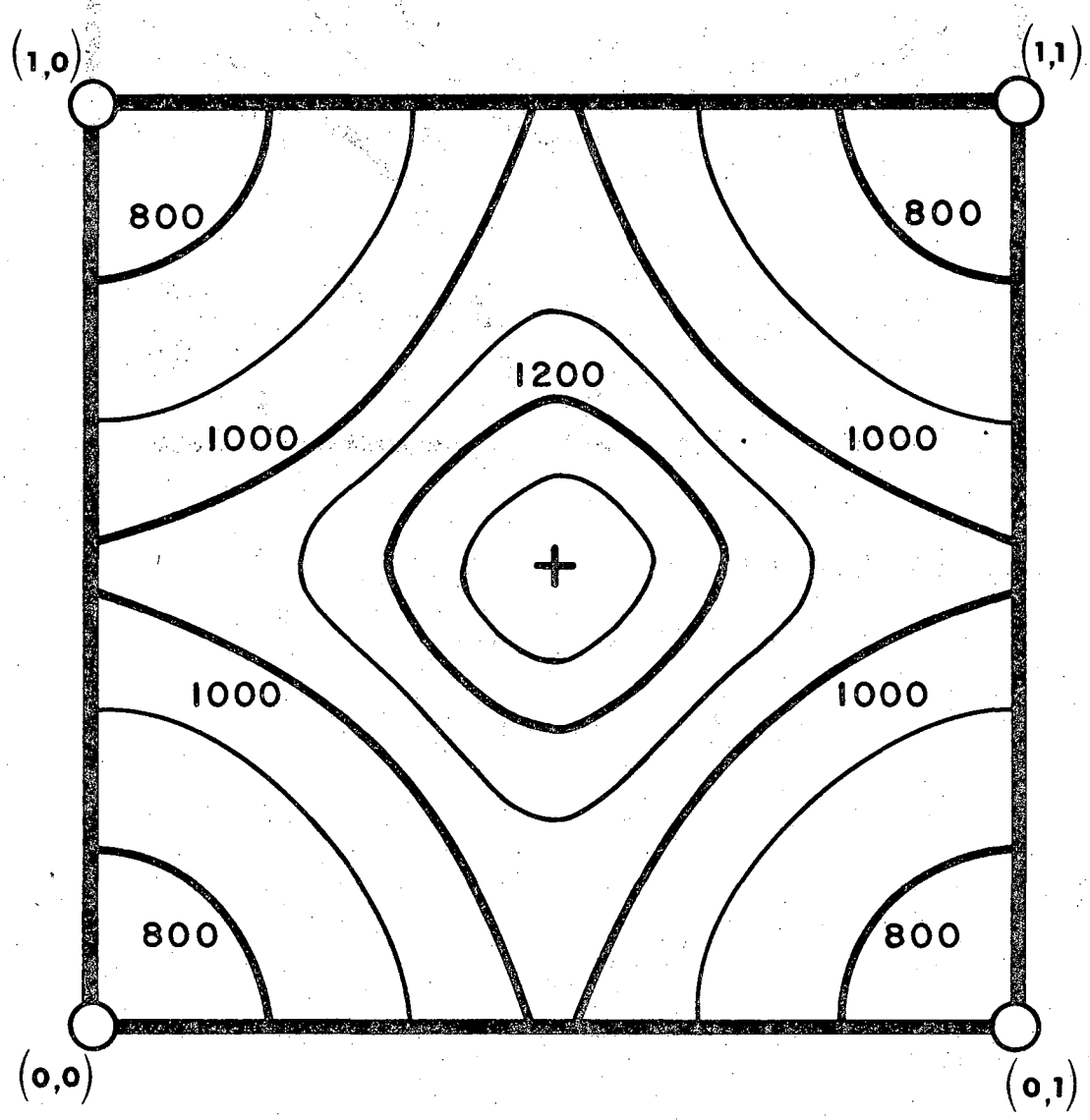

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Fig. 4

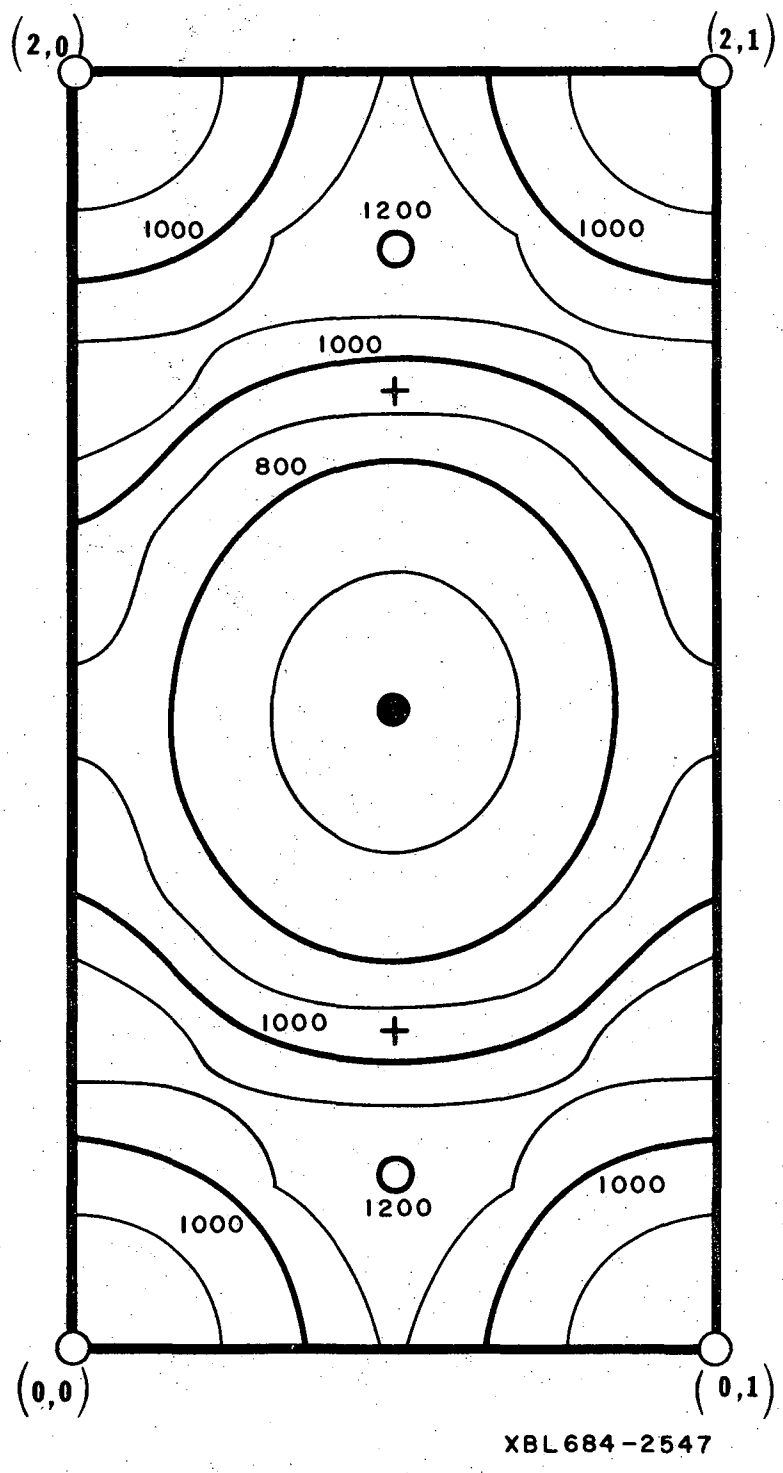
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Fig. 5

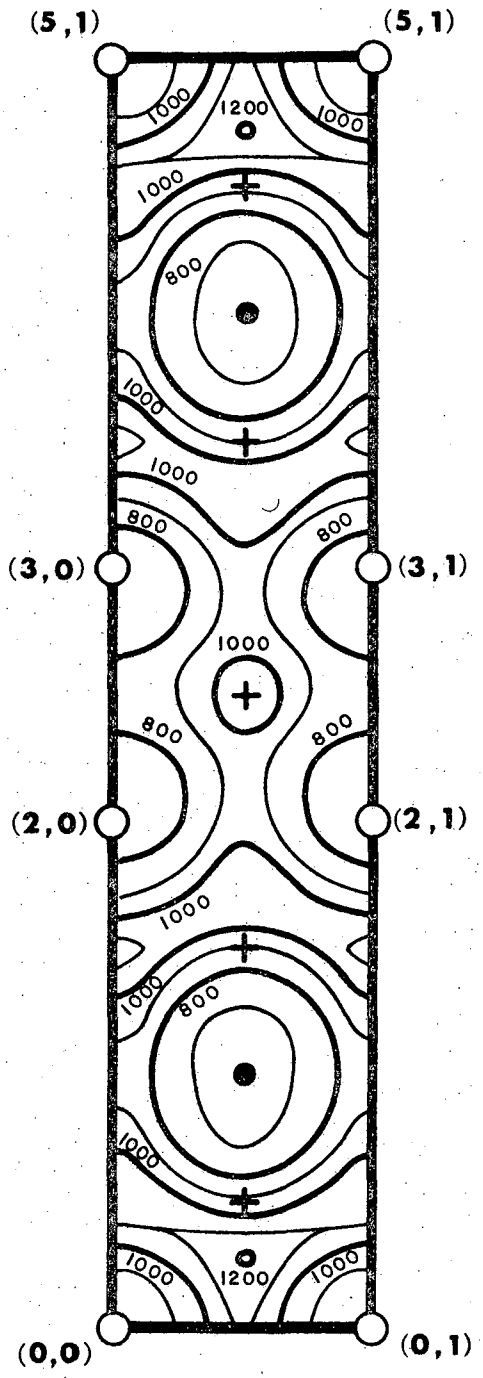

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Fig. 6

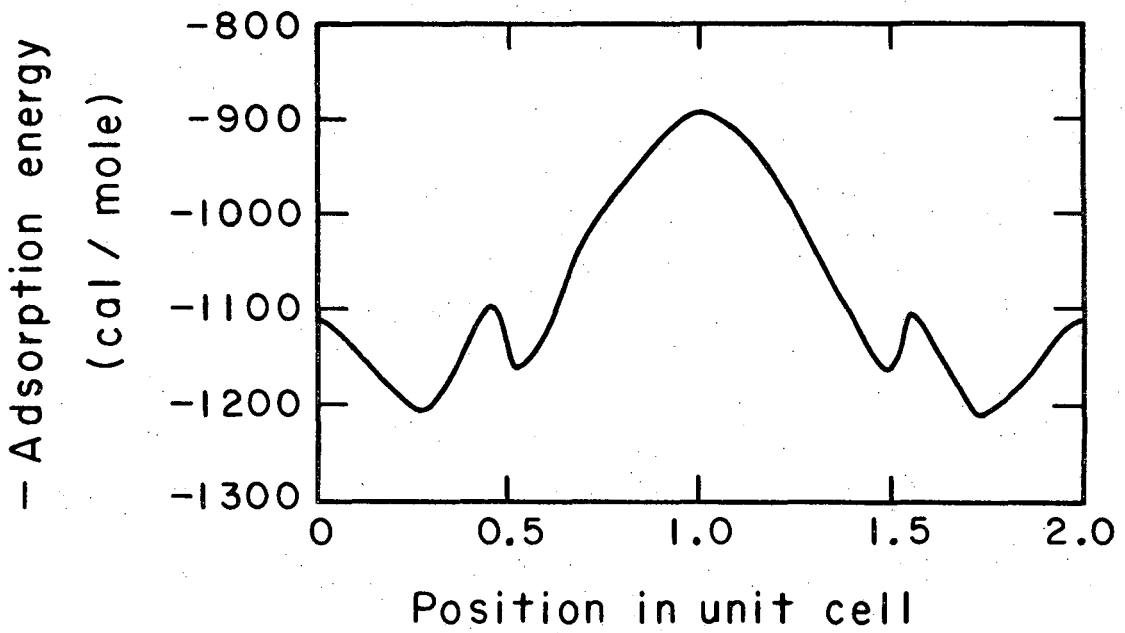

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Fig. 7

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