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ABSTRACT

It is possible for the normal (1x1) structure of the argon (100) surface to transform to a C(2x1) structure below the melting point of the solid. This transformation occurs without any accompanying transformation of the bulk.

The transformation temperature is very sensitive to the presence of impurities. Vacancies can cause the new structure to disappear at high temperatures.

LEED data for metals are examined and are found to correlate quite well with the theory based on argon.

The transformed structures should differ substantially from the normal structures in studies of surface vibration frequencies, ad-atom diffusion, and catalysis.

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I. INTRODUCTION

A number of theories have been proposed to explain the Low Energy Electron Diffraction (LEED) patterns observed from the surfaces of metals. There are two basic areas of concern in understanding LEED data. Theories have been advanced to account for the variation of the spot intensities as a function of the voltage of the electron beam. These theories have been based primarily on either the kinematic model used in x-ray diffraction work or on multiple scattering; McRae[1,2] has had considerable success in explaining and predicting experimental intensity results using multiple scattering. The second area of concern has been the explanation of LEED patterns which have periodicities not corresponding to the periodicity of the substrate. Explanations of this phenomenon have been based on large concentrations of surface vacancies,[3] on surface impurities,[4,5] and on rumpled surface layers.[6] This paper will attempt to explain the origin of certain types of LEED patterns having unexpected periodicities.

In this paper we review briefly some LEED data (Sec. II), summarize a theory of the authors' on phase transformations on solid surfaces (Sec. III) and apply this theory to the interpretation of LEED data (Sec. IV). Finally, we examine some predicted properties of the transformed surfaces and indicate some possible experiments to confirm the authors' theory. We show that the transformed surface structures should have catalytic properties, ad-atom surface diffusion coefficients, and surface vibrational frequencies which differ greatly from those of the normal surface.

II. SUMMARY OF LEED DATA

An excellent review article[7] has been written on LEED and the reader is referred to it for general information on the technique. In this section, we summarize those LEED results which are pertinent to this paper.

If a back diffraction experiment is done from a two-dimensional lattice, the observed diffraction pattern is expected to exhibit the symmetry of the space reciprocal to the lattice. Low energy electrons are believed to not penetrate many layers into a crystal surface. The diffraction patterns are hence expected to exhibit a symmetry reciprocal to that of the cut plane of the crystal. The diffraction pattern having the expected symmetry is known as a (1×1) pattern, using the notation of Wood;[8] this means that the repeat distance of the diffraction pattern is equal to that expected from the surface net in both principle axis directions. A diffraction pattern with a repeat distance of 1/n in one direction and 1/m in the other is known as (n×m); this pattern has extra spots not expected from the bulk structure.

LEED experiments have been carried out on a number of FCC metals. Observed LEED patterns for various metallic crystal faces are tabulated in Table I along with the temperature regions in which these patterns form. The data presented in Table I are for nominally clean surfaces. Additional structures have been observed in the presence of high impurity concentrations. LEED patterns classifiable as (n×1) have not been observed on the (111) surface of FCC metals except, of course, the expected (1×1) pattern. We have not included the so-called ring structures in

Table I; they are not related to the theory presented in this paper and have been extensively discussed by Somorjai.[9]

There are several interesting properties of the surface structures observed by LEED which are relevant to our future discussion.

1. The (n×1) and (n×m) structures often require careful surface preparation, ion bombardment, and annealing before they can be observed.

2. Two (n×1) patterns can coexist, perpendicular to each other on a (100) surface.

3. Once an (n×1) structure is formed the solid may be cooled below its temperature region of stability and the pattern disappears.[9] Subsequent reheating causes the pattern to reappear.

4. Two or more different LEED patterns may be formed on the same face of a particular metal in the same temperature range.

5. The (n×1) structures disappear at temperatures well below the melting point of the solid.[9]

6. The formation of surface structures on copper,[11] nickel,[7] and platinum,[10] have been found to be sensitive to the presence of gases in the system.

7. (5×1) LEED patterns are found on the (100) surface of epitaxially grown gold crystals, indicating that surface structures can be formed on the pure metal.[12]

8. Deposition of three mono-layers of gold on a (1×1) structure of a silver (100) surface cause formation of a (5×1) gold pattern.[12]

9. Deposition of a mono-layer of silver on a (5×1) structure of a gold (100) surface caused the LEED pattern to revert to (1×1).[12]

III. THEORY

A satisfactory theory of surface structure must explain the experimental observations cited above. The theory presented in this section will be shown in Sec. IV to explain most of these data.

The authors have previously examined the possibility of a rearrangement of the argon (100) surface without a change in the structure of the bulk crystal.[13] The argon lattice was represented by a set of point atoms interacting by a pair-wise additive Lennard-Jones 6-12 potentials. Only the potential energy of the lattice was considered. The Einstein approximation was used for calculating entropies and zero-point energies. In making calculations on the properties of the argon surface, the relaxations of the ideally flat (100) argon surface were considered.[14]

This model has certain obvious disadvantages. Kinetic effects and many-body forces are neglected. The Lennard-Jones 6-12 potential predicts that the hexagonal-close-packed structure should be the stable structure of argon, whereas experimentally, face-centered-cubic is observed. These problems are discussed in the earlier publication.[13]

Though this model is not an exact representation of solid argon, it is believed to be useful for gaining insight into the real world. As will be seen, this study of argon can also yield some valuable ideas about metals, which are distinctly different from solid argon.

Using the model described above, the authors showed that it is thermodynamically possible for the normal (1×1) structure, Fig. 1, of the argon (100) surface to undergo a phase transition to a C(2×1) structure, Fig. 2a, without any corresponding transformation of the bulk.

We call this structure C(2×1) as it has a unit cell of normal length in one direction and twice as long as normal in the other direction; the "C" refers to the centered surface atom in the unit cell. In this transformation, every other row of the (1×1) structure is translated one-half an atomic distance parallel to the surface, Fig. 1 and 2a. The translating atoms relax perpendicularly outwards from the surface plane so that the C(2×1) structure has a saw tooth appearance, Fig. 2b. The C(2×1) structure is thermodynamically stable with respect to the (1×1) structure at 81.5°K, which temperature is below the melting point of argon, 84°K. The transformation can occur because the potential energy of the C(2×1) is not too much higher than that of the (1×1) and the C(2×1) structure's zero point energy is lower than that of the (1×1) structure while its entropy is higher.

The authors examined the effects of surface impurities on the transition temperature. Neon and krypton impurities were considered. Argon-impurity interactions were represented by Lennard-Jones 6-12 potentials based on impurity-impurity and argon-argon potentials. It was found that the effect of the impurity depended greatly on whether the impurity went into a shifted or a normal position and on the nature of the impurity. For instance, a 5% concentration of neon impurity atoms in the shifted rows lowers the transition temperature to 72°K; but krypton impurities in the unshifted rows raise the transition temperature. Surface impurities can greatly influence the temperature at which the C(2×1) structure is formed from the (1×1).

The effect of a vacancy in the surface layer was considered. If a vacancy is introduced into a shifted row, even if the vacancy is adjacent to an impurity atom, the entire row of atoms collapses back into the unshifted configuration as the atoms are no longer located at potential minima. At high enough temperatures, the normal formation of surface vacancies could cause the C(2×1) structure to transform back to a (1×1) structure.

Many possible surface structures can be obtained by shifting some rows of surface atoms. We have carried out calculations for a C(5×1) structure in which two of every five rows are shifted, Fig. 3. The temperature at which this structure becomes stable relative to the (1×1) is essentially the same as that required for formation of the C(2×1) from the (1×1) structure. Another C(5×1) structure can be formed by shifting one row of every five; a C(3×1) could be formed by shifting one row in three. All of these structures would be expected to form at roughly the same temperature as their entropies and energies of formation should be proportional to the number of atoms shifted. Many different surface structures can be formed by shifting surface rows. All such structures must be classifiable as C(n×1) as parallel rows of atoms are shifted. When many similar structures can be formed, it is possible that the one which is formed is determined by the distribution of impurities on the surface.

IV. CORRELATION OF THEORY WITH LEED DATA

We have found that it is possible to form a variety of C(n×1) surface structures on the (100) face of a face-centered-cubic 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 (n×1) LEED patterns on (100) surfaces.

If we examine the appearance of (110) face of a FCC crystal, Fig. 4a, we see that it is possible to form distinct (n×1) 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. Thus 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 (n×1) structures on (110) surfaces having only one of two conceivable orientations. Lyon[10] has, in fact, observed (2×1) and (3×1) 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.

We now turn to the (111) face, Fig. 5. Any attempt to shift a row of surface atoms an appreciable distance in any direction will bring the atoms into close proximity with both substrate atoms and other surface atoms. This occurs because the (111) surface layer is close packed. Furthermore, if we shift a row of surface atoms, they will be moved to positions of low symmetry which would lead us to expect the absence of a potential minimum for the shifted row. Thus we would expect that we cannot form (n×1) structures on (111) surfaces by shifting some rows of atoms. LEED patterns corresponding to (n×1) structures have not been observed on (111) faces of FCC crystals.

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 (1×1). The expected sensitivity of structure to impurities may determine which of several possible surface structures is observed. On the nickel (110) surface,[7] only a (1×1) pattern is observed except in the presence of oxygen. (2×1) structures are observed on the (110) and (100) surfaces of copper[11] after exposure to oxygen.

We expect the formation of shifted row surface structures to be a normal first order phase transformations. There is no reason to expect that it should not be reversible. LEED experiments have shown that once an (n×1) pattern is formed, it disappears on cooling and reappears on heating, just as though an ordinary reversible phase change occurs.[9]

We have found that formation of surface vacancies will cause our shifted row structures to revert to (1×1). Experimentally, (n×1) structures disappear as the temperature is raised.[9]

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. Lyon and Somorjai[9] have found that either a (5×1) or a (2×1) LEED pattern can be observed from a (100) platinum surface in the same temperature region. They found that prolonged heating of the (2×1) pattern surface caused the (2×1) pattern to disappear and a (5×1) to appear. After the (5×1) structure was formed, the (2×1) 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[12] 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.

The theory presented in Sec. III has been shown above to account for many of the properties of the structures observed by LEED. There is one piece of experimental data for (n×1) structures for which it does not account. The extra spots of the (5×1) structure on the gold[5] and platinum[9] (100) surfaces (that is, spots on the (5×1) LEED pattern which are not present in the (1×1) pattern) are not single spots. They are slightly split into pairs. Our model does not account for this splitting. It is possible that a careful calculation of LEED patterns based on our (5×1) structure model and considering multiple scattering effects would give rise to these pairs.

Our model also cannot account for the (n×m) structures observed on a number of metals and nonmetals. It is possible that these structures arise by some surface atoms relaxing outwards perpendicularly to the surface as predicted by Feuchtwang[15] and Haneman.[6]

V. SOME POSSIBLE EXPERIMENTAL TESTS

We have calculated the potential diagrams for adsorption of an argon atom on the (1×1), C(2×1), and C(5×1) structures of the argon (100) surface. These potential plots are shown in Figs. 6, 7, and 8. As can be seen from these figures, the adsorption energy of argon on argon is reduced from ~1380 cal/mole on the (1×1) structure to ~1200 cal/mole on the C(2×1) and 1100-1200 cal/mole on the C(5×1). All adsorption sites are equivalent on the (1×1) structure while there are two energetically different sites on the C(2×1) structure and five on the C(5×1) structure. This suggests that very careful studies of heats of adsorption at very low coverages could distinguish between these structures.

Figures 6, 7, and 8 show that the symmetry of the adsorption sites varies from one structure to another. Thus, the three structures may have very different catalytic properties.

Figures 6, 7, and 8 also show that the energy barriers to ad-atom surface diffusion vary from structure to structure. The (1×1) structure is isotropic and the diffusion barrier is ~380 cal/mole. The C(2×1) structure barriers vary from ~100 to ~270 cal/mole. The C(5×1) barriers vary from ~70 to ~260 cal/mole. The shifted rows of atoms in the C(2×1) and C(5×1) structures create pipes which allow very low energy ad-atom diffusion in the direction of the shift. Thus, it may be possible to observe very fast ad-atom diffusion on the shifted row structures. Such fast diffusion may be more readily observed on (110) surfaces than on (100) surfaces as it is possible to form shifted row structures on (110) surfaces in which all the pipes have the same crystal orientation.

We have also calculated Einstein vibrational frequencies for the surface atoms in the (1×1) and C(2×1) structures of the argon (100) surface, Table II. The vibrational frequencies parallel to the surface plane are lowered significantly in the shifted row structure--by about 30%. Such a change in surface frequency may be detectable by LEED Debye-Waller factor measurements.[16,17]

VI. CONCLUSIONS

It is possible for phase transitions to occur on crystal surfaces without any change in the structure of the bulk crystal. In these transitions, rows of surface atoms are shifted parallel to the crystal surface, forming surface structures which do not have the same symmetry as the bulk crystal. Such phase transitions can occur on (100) and (110) surfaces of FCC crystals, but not on (111) surfaces. The phase transitions are sensitive to surface impurities. At sufficiently high temperatures, the generation of surface vacancies can cause the transformed structure to disappear. These characteristics of the predicted phase transformations correlate very well with LEED data.

The transformed surface structures should behave differently than the normal structures in catalysis experiments, in adsorption experiments, and in ad-atom surface diffusion experiments. The vibrational frequencies in the transformed structures are drastically altered from the frequencies in the normal structures; this change in frequency may be detectable by LEED studies.

ACKNOWLEDGMENT

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Table I. Observed LEED surface structures for the face-centered-cubic metals. (The temperature region of observation of each structure is given when available. Only data for clean surfaces are included.)

Metal	Surface	Structure	Temperature	Reference
Pd	(100)	(1x1)		
		(2x1)	200°-300°C	3
		(2x2)	250°-550°C	3
Pt	(100)	(1x1)		
		(5x1)	350°-500°C	9
		(2x1)	300°-500°C	9
	(110)	(1x1)		
		(2x1)		10
		(3x1)		10
		(4x1)		10
	(111)	(1x1)		
		(2x2)	800°-1000°C	9
		(3x3)	800°-1000°C	9
Ag	(100)	(1x1)		
		(2x2)	600°-750°C	3
Au	(100)	(1x1)		
		(5x1)	150°-400°C	3
		(6x6)	350°-700°C	3

Table II. The Einstein vibrational frequencies of atoms in the (1×1) and C(1×1) and C(2×1) structures of the argon (100) surface. Frequencies are given for vibrations parallel and perpendicular to the surface plane.

Structure	Atom	Vibration	Frequency
(1×1)		Parallel	1.2×10^{12} cycles/sec
(1×1)		Perpendicular	$.9\times10^{12}$ cycles/sec
C(2×1)	unshifted	Parallel	.9 cycles/sec
C(2×1)	unshifted	Perpendicular	.9 cycles/sec
C(2×1)	shifted	Parallel	.8 cycles/sec
C(2×1)	shifted	Perpendicular	.9 cycles/sec

FIGURE CAPTIONS

Fig. 1 The (1×1) structure of the (100) surface of a FCC crystal. 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.

Fig. 2 The C(2×1) structure of the (100) surface of a FCC crystal. The solid circles represent shifted atoms. (a) Top view: the intersections of the lines are the normal surface sites. The unit cell is shown by heavy lines. Unshifted surface atoms are open circles and second layer atoms are pluses. (b) Cross section: atoms in unshifted positions are open circles.

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 surface 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 (1×1) structure. (b) A C(2×1) structure with shaded atoms shifted along the long axis. (c) A C(2×1) structure with shaded atoms shifted along the short axis.

Fig. 5 The normal (111) surface of a FCC crystal. The intersections of the lines are the normal surface sites. The surface atoms are open circles and the pluses second layer atoms. The unit cell is indicated by heavy lines.

Fig. 6 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.

Fig. 7 The heat of adsorption of an argon atom on the C(2×1) structure of the argon (100) surface. The heaviest lines are the boundaries of the unit cell. The open circles are the unshifted surface atoms and the shaded circle is a shifted surface atom. The pluses are second layer atoms. Energy contours are given in calories per mole.

Fig. 8 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 unshifted surface atoms and the shaded circles are shifted surface atoms. The pluses are second layer atoms. Energy contours are given in calories per mole.

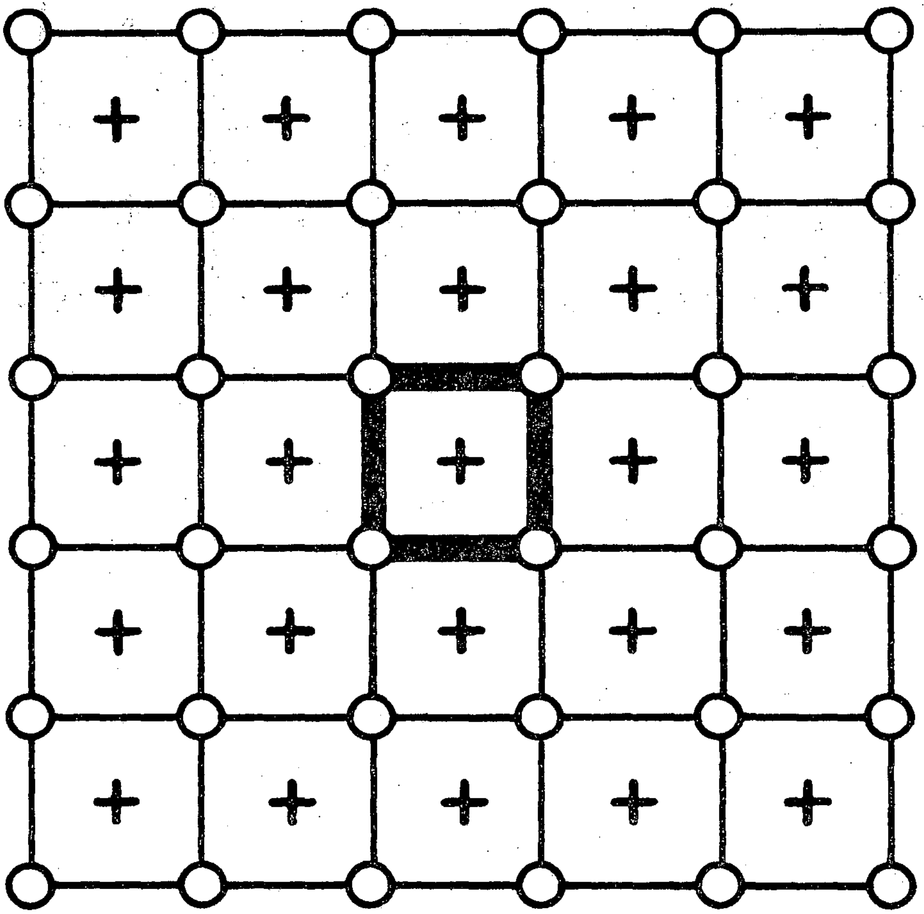
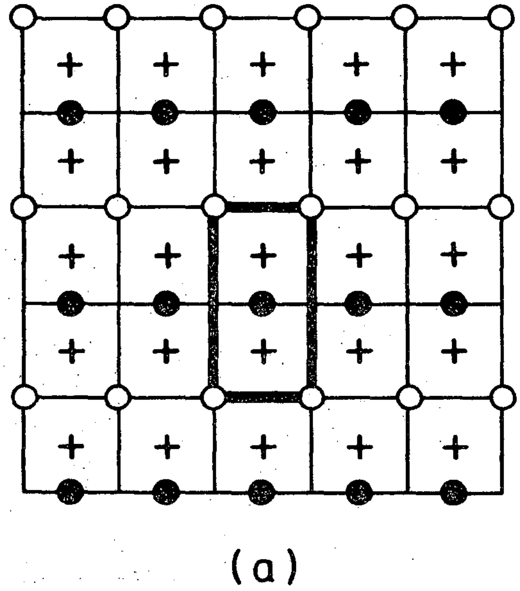


Fig. 1



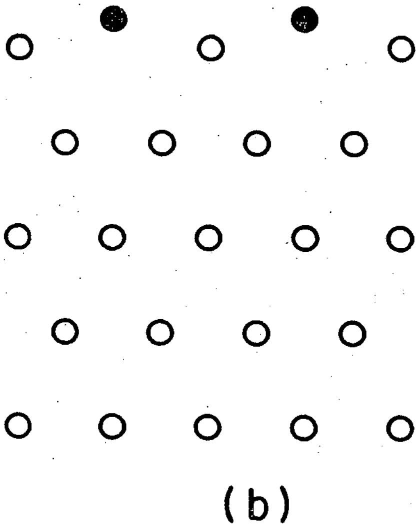


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Fig. 2

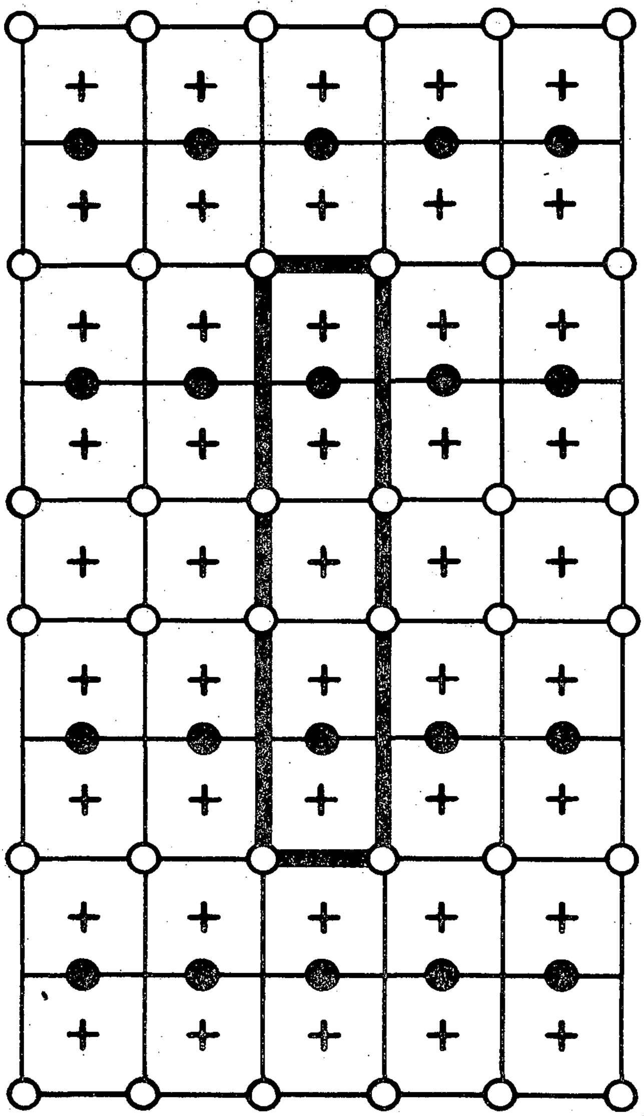

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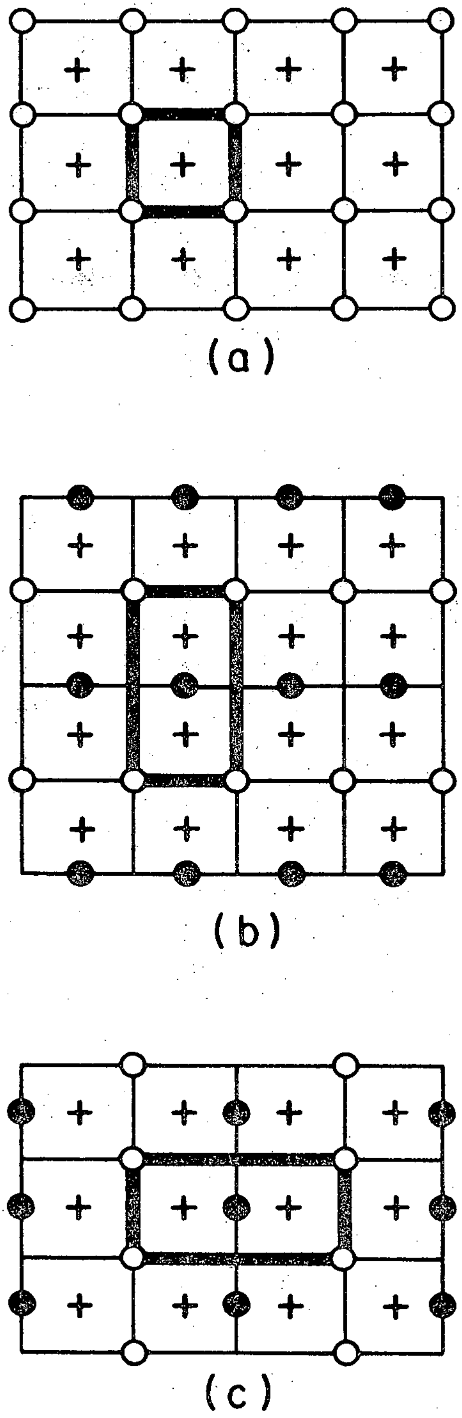
Fig. 3



(a)

(b)

(c)

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Fig. 4

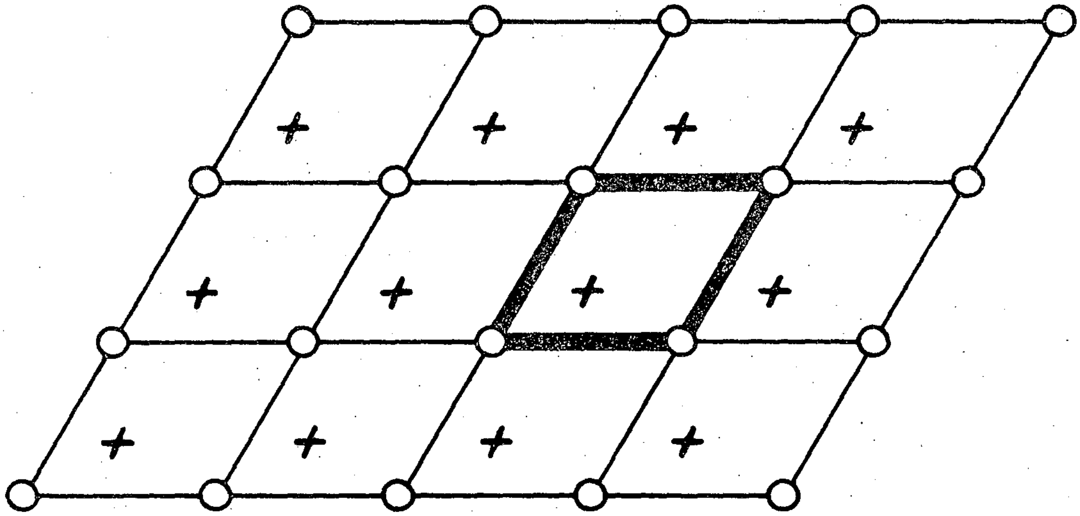

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Fig. 5

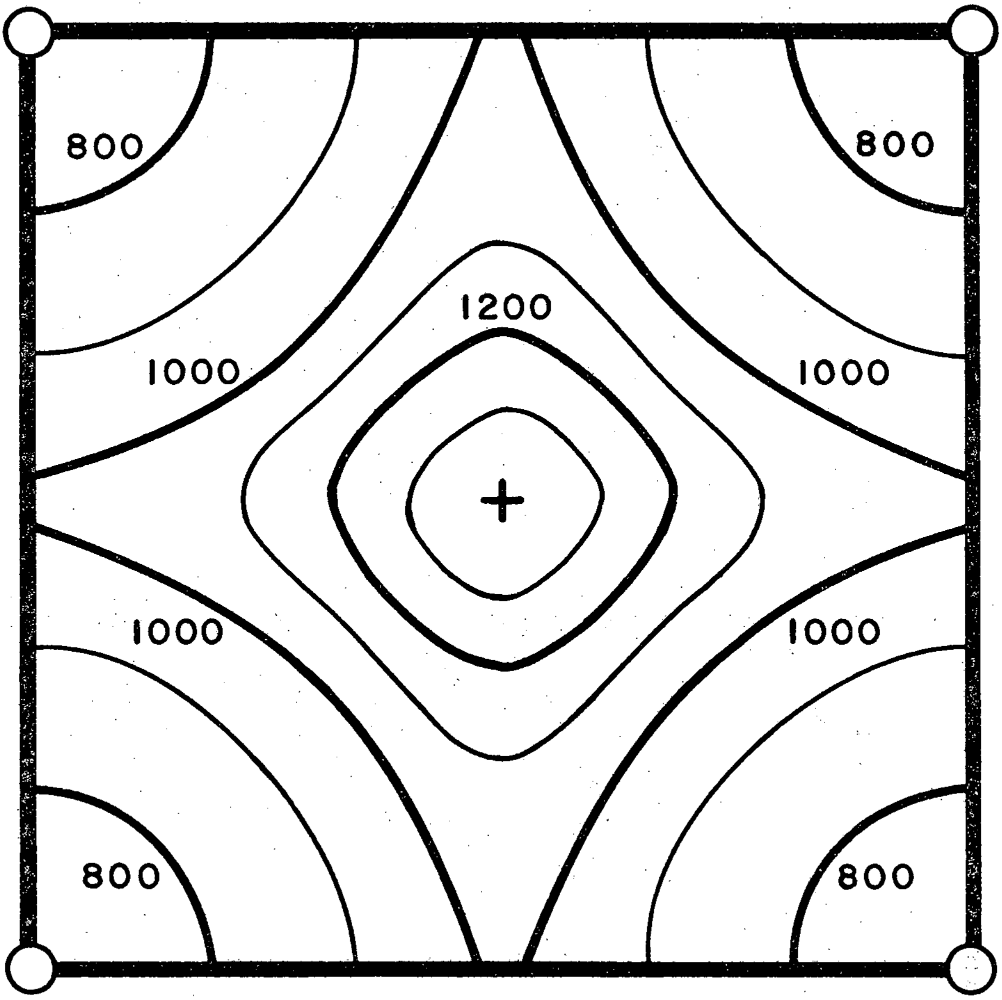

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Fig. 6

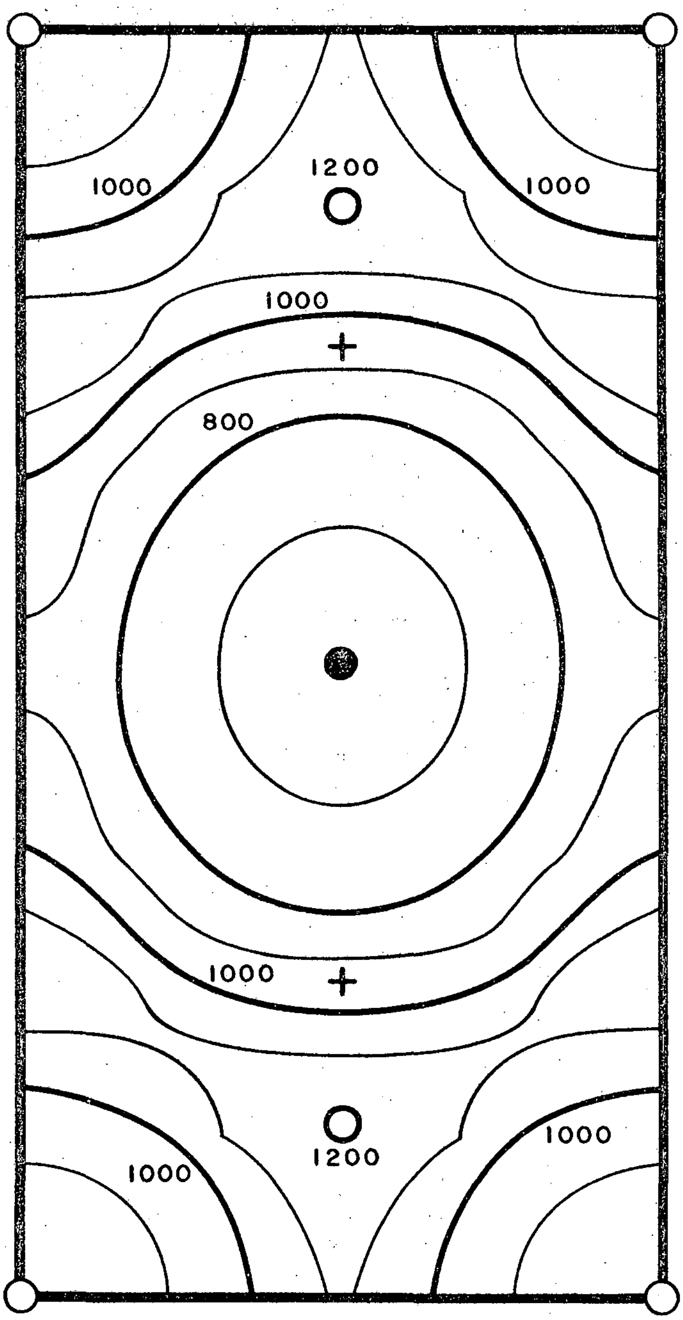

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Fig. 7

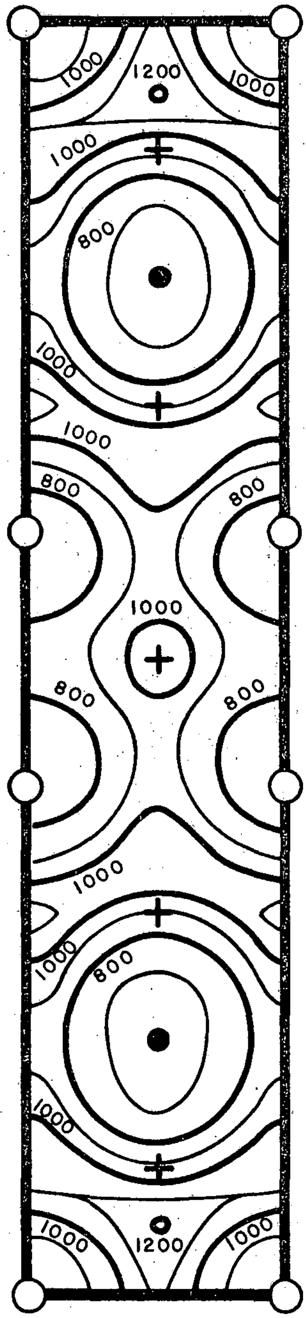

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Fig. 8