Missing spots in low-energy electron-diffraction patterns

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A method for the deduction of structural information from the regular distribution of zero-intensity reflections, or missing spots, in LEED (low-energy electron-diffraction) patterns is described. The method applies to the cases in which LEED spots are missing at all incident electron energies and angles. Applications are discussed for the cases of C{001}2×1 (for which a structural model is derived), Si{001}2×2 (which is found to be inconsistent with the missing-spot pattern observed), and Ge{111}$c(2\times8)$ [which is shown to be consistent with experiment, while a $p(2\times8)$ structure is not].

I. INTRODUCTION

It is well known in x-ray crystallography that certain types of symmetry affect the diffraction pattern of crystals with those types of symmetry; in particular, certain types of reflection may be absent. These so-called systematic absences of certain types of reflection can give valuable clues to the atomic arrangement in the crystal studied; they may limit the possibilities to two or three arrangements, or even to a single type of arrangement.[1] Similarly, in surface crystallography, certain types of symmetry affect the low-energy electron-diffraction (LEED) pattern of surfaces with those symmetry elements. Systematic absences of certain types of reflection occur in LEED patterns as well, but comparatively little attention has been devoted to them heretofore. In LEED crystallography, the systematic absences are commonly referred to as "missing spots" because on the fluorescent screen of display-type LEED equipment the spots that correspond to the absent reflections are missing. In simple cases, such as the formation of a $c(2\times2)$ (or $\sqrt{2}\times\sqrt{2}-45°$) superstructure over a square-net surface, the missing spots of the type $\frac{1}{2}h\ \frac{1}{2}k$ with $h+k$ odd have long been recognized as indicative of a centered net,[2] but are simply a consequence of the use of nonprimitive net vectors. In other, more complicated, cases, missing spots have been shown to be caused by the existence of glide lines[3] and have indeed proved useful in the search for structural information.[4,5] These types of missing spots, however, depend upon the relative orientation of the incident wave vector with respect to the surface structure—spots that are missing at normal incidence may be observable at nonnormal incidence. A third type of missing spots is caused simply by the fact that the intensity of the corresponding reflection is very weak and therefore not observed [see, e.g., the LEED patterns of Ge{111}2×1−8 and Ge{111}1×1-Al (Ref. 6)].

In the present study we are concerned with what we may call "absolute" missing spots in LEED patterns, namely, the spots that are missing at all incident-electron energies and all incident angles. The quotation marks on the word "absolute" are meant to indicate that the spots are missing because the corresponding reflections have vanishing structure factors only in the limit of kinematic scattering. Two important examples of such "absolute" missing spots are found in the LEED patterns of diamond, C{111}2×1, and Ge{111}$c(2\times8)$, both discussed below. The LEED patterns from these two surfaces are reproduced schematically in Figs. 2 and 8, respectively, where the "absolute" missing spots are indicated with crosses. The cases that we are going to consider are those in which the missing spots are *regularly distributed* in the LEED pattern so that we can recognize well-defined *missing-spot nets*. In Sec. II we develop a procedure that allows one to deduce structural information from the properties of such missing-spot nets. In Sec. III, we apply the procedure, in turn, to the reconstructed diamond {111} surface, the Si{001}2×2 structure, and the reconstructed Ge{111} surface.

II. METHOD

Since the phase shifts of atoms are functions of energy, the existence of "absolute" missing spots implies that the unit mesh of the surface structure must contain two or more *identical* atoms or groups of atoms—the waves scattered from different atoms cannot cancel one another for some reflections for *all* energies. Thus, we assume that the unit mesh of the surface contains N identical atoms, or groups of atoms, located at positions $\vec{R}_i (i=1 \text{ to } N)$ with respect to the origin of the unit mesh. In order for a reflection, i.e., a LEED spot, to be missing in the kinematic approximation, the structure factor must vanish, i.e.,

$$\sum_{i=1}^{N} \exp[-i(\vec{k}^{\,\text{inc}} - \vec{k}^{\,\text{scat}})\cdot\vec{R}_i] = 0 , \tag{1}$$

where $\vec{k}^{\,\text{inc}}$ and $\vec{k}^{\,\text{scat}}$ are the incident and scattered wave vectors, respectively.

Note that for the reflection considered Eq. (1) must be valid at all energies because the LEED spot is missing at all energies. In order to see the consequence of this fact

we rewrite Eq. (1) taking into account the relations

$$\vec{k}^{\,\mathrm{inc}}=\vec{k}^{\,\mathrm{inc}}_{\mathrm{perp}}+\vec{k}^{\,\mathrm{inc}}_{\mathrm{par}},\quad \vec{k}^{\,\mathrm{scat}}=\vec{k}^{\,\mathrm{scat}}_{\mathrm{perp}}+\vec{k}^{\,\mathrm{scat}}_{\mathrm{par}}\ , \tag{2}$$

where the subscripts perp and par refer to the perpendicular and parallel (to the surface plane) components, respectively, and

$$\vec{k}^{\,\mathrm{scat}}_{\mathrm{par}}=\vec{k}^{\,\mathrm{inc}}_{\mathrm{par}}+\vec{g}\ , \tag{3}$$

with $\vec{g}$ a reciprocal-net vector. We obtain

$$\sum_{i=1}^{N}\exp[-i(\vec{k}^{\,\mathrm{inc}}-\vec{k}^{\,\mathrm{scat}})\cdot\vec{R}_i]$$
$$=\sum_{i=1}^{N}\exp[-i(\vec{k}^{\,\mathrm{inc}}_{\mathrm{perp}}-\vec{k}^{\,\mathrm{scat}}_{\mathrm{perp}})\cdot\vec{R}_i]\exp(i\vec{g}\cdot\vec{R}_i)=0\ . \tag{4}$$

In the last sum the first factor is the one that varies with energy. Hence, for Eq. (4) to be valid at all energies we must require that the first factor be constant. There are two possibilities.

(i) $\vec{k}^{\,\mathrm{inc}}_{\mathrm{perp}}\equiv\vec{k}^{\,\mathrm{scat}}_{\mathrm{perp}}$. This is possible only for the specular reflection, or 00 spot. However, the 00 spot is never missing because its $\vec{g}$ is equal to 0 and hence Eq. (4) cannot be fulfilled.

(ii) Each vector $\vec{R}_i$ is perpendicular to $(\vec{k}^{\,\mathrm{inc}}_{\mathrm{perp}}-\vec{k}^{\,\mathrm{scat}}_{\mathrm{perp}})$, i.e., each $\vec{R}_i$ is parallel to the surface plane. In this case, Eqs. (1) and (4) can be rewritten as

$$\sum_{i=1}^{N}\exp(i\vec{g}\cdot\vec{R}_i)=0\ . \tag{5}$$

This equation states that the missing spot characterized by the reciprocal-net vector $\vec{g}$ is missing *independently* of the direction of the incident radiation—it is a characteristic of the unit mesh considered. (Note that this condition is different from the case of missing spots caused by glide lines, where the incidence direction plays an important role.) Thus, we have reached the conclusion that if a surface structure gives a LEED pattern with reflections missing at all electron energies and all incidence directions, then its unit mesh must contain two or more identical atoms, or groups of atoms, which lie on a plane parallel to the surface.

There are N vectors $\vec{R}_i$ to be determined. We can, of course, choose the origin of the unit mesh at the position of one of the N atoms, leaving $N-1$ unknown $\vec{R}_i$ vectors to be determined. Since for each vector we must determine direction and magnitude, we have $2(N-1)$ unknown quantities to determine. If we knew the value of N, we could try and use $2(N-1)$ missing spots to get $2(N-1)$ equations obtained from Eq. (5). For example, for the jth missing spot, setting

$$\vec{g}_j=h_j\vec{a}^{\,*}_s+k_j\vec{b}^{\,*}_s\ , \tag{6}$$

with $\vec{a}^{\,*}_s$ and $\vec{b}^{\,*}_s$ the primitive vectors of the surface reciprocal net, we get the jth equation,

$$\sum_{i=1}^{N-1}\exp(ih_j\vec{a}^{\,*}_s\cdot\vec{R}_i)\cdot\exp(ik_j\vec{b}^{\,*}_s\cdot\vec{R}_i)=-1\ . \tag{7}$$

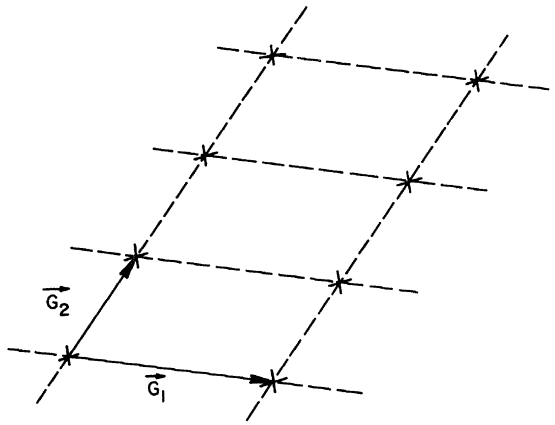

FIG. 1. Missing spots (crosses) form a net characterized by two vectors $\vec{G}_1$ and $\vec{G}_2$.

Note that the sum extends only to $N-1$ because the Nth atom is at the origin ($R_N\equiv 0$) and hence the sum must equal -1. In principle, we could solve the $2(N-1)$ equations obtained from (7) for $2(N-1)$ missing spots and thus determine all the $\vec{R}_i$'s but in practice the task is difficult as soon as N becomes larger then, say, 2, and most importantly, N is usually unknown. However, if the missing spots are distributed with well-defined periodicities over the LEED pattern, then there exists a rather simple procedure for determining the $\vec{R}_i$'s. In the following, we first introduce two useful theorems and then describe the procedure with an example based on the reconstructed diamond {111} surface.

(i) Theorem 1. If each missing spot in a LEED pattern belongs to a net of missing spots which is defined by two net vectors $\vec{G}_1$ and $\vec{G}_2$ (as shown in Fig. 1), then each vector $\vec{R}_i$ defining the position of equal atoms (or group of atoms) in the unit mesh of the direct lattice must satisfy the conditions

$$\vec{G}_1\cdot\vec{R}_i=2m_i\pi\ \text{ and }\ \vec{G}_2\cdot\vec{R}_i=2n_i\pi\ , \tag{8}$$

where m_i and n_i are integers.

(ii) Proof of theorem 1. The condition for a spot defined by a reciprocal-net vector $\vec{g}$ to be missing is given by Eq. (5) or, taking the Nth atom at the origin, by the equation

$$\sum_{i=1}^{N-1}\exp(i\vec{g}\cdot\vec{R}_i)=-1\ . \tag{9}$$

If the missing spot $\vec{g}$ belongs to a net of missing spots defined by the vectors $\vec{G}_1$ and $\vec{G}_2$, then it follows that the spot $\vec{g}+\vec{G}_1$ is also missing, i.e.,

$$\sum_{i=1}^{N-1}\exp[i(\vec{g}+\vec{G}_1)\cdot\vec{R}_i]=\sum_{i=1}^{N-1}\exp(i\vec{g}\cdot\vec{R}_i)\exp(i\vec{G}_1\cdot\vec{R}_i)=-1\ . \tag{10}$$

Fulfillment of (9), however, requires that

$$\exp(i\vec{G}_1\cdot\vec{R}_i)=1 \tag{11}$$

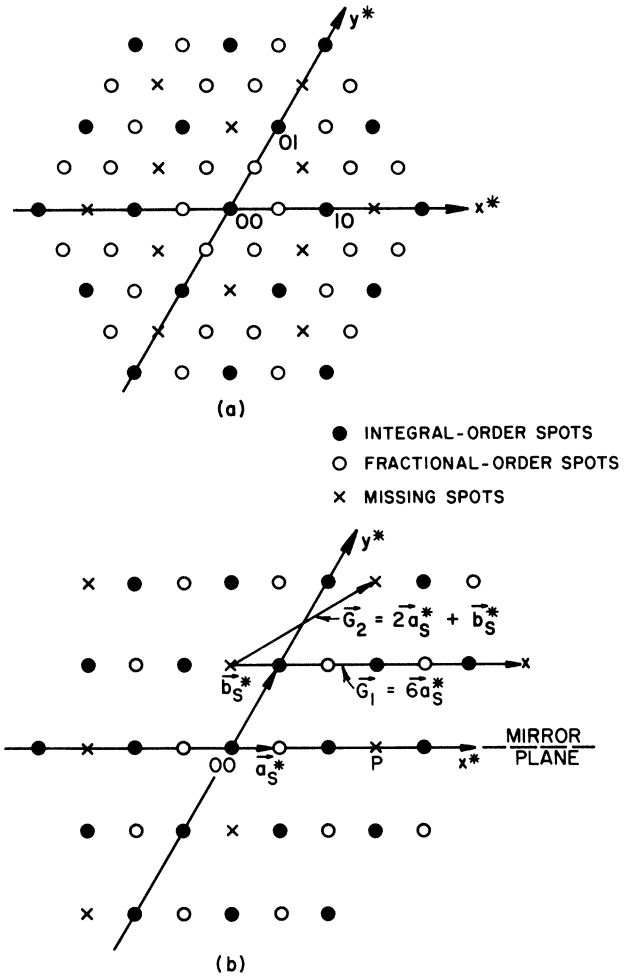

FIG. 2. (a) Observed LEED pattern of three-domain C{111}2×1 structure (schematic). (b) Single-domain LEED pattern of C{111}2×1 structure. $\vec{a}_s^*$ and $\vec{b}_s^*$ are the primitive vectors of the surface reciprocal net; $\vec{G}_1$ and $\vec{G}_2$ define a net of missing spots.

for all $\vec{R}_i$'s, i.e., that

$$\vec{G}_1\cdot\vec{R}_i = 2m_i\pi \ ,$$

where m_i is an integer. An analogous argument leads also to the requirement

$$\vec{G}_2\cdot\vec{R}_i = 2n_i\pi \ ,$$

where n_i is an integer.

(iii) Theorem 2. If there exists a set of vectors $\vec{R}_i$ defining the positions of N equal atoms (or equal groups of atoms) in the unit mesh of the direct lattice, such that Eq. (5) is satisfied with $\vec{g}$ being a reciprocal net vector that identifies a particular missing spot in a net of missing spots defined by vectors $\vec{G}_1$ and $\vec{G}_2$, then the same set of $\vec{R}_i$'s will satisfy Eq. (5) for any missing spots in the same missing-spot net.

(iv) Proof of theorem 2. Given a set of $\vec{R}_i$'s such that $\vec{G}_1\cdot\vec{R}_i = 2m_i\pi$ and $\vec{G}_2\cdot\vec{R}_i = 2n_i\pi$ [Eq. (8)], and furthermore $\sum_{i=1}^{N}\exp(i\vec{g}\cdot\vec{R}_i)=0$ [Eq. (5)], or $\sum_{i=1}^{N-1}\exp(i\vec{g}\cdot\vec{R}_i) = -1$ [Eq. (9)], then the theorem claims that

$$\sum_{i=1}^{N-1}\exp[i(\vec{g}+m\vec{G}_1+n\vec{G}_2)\cdot\vec{R}_i] = -1 \ , \tag{12}$$

m and n being integers. We see that

$$\begin{aligned}\sum_{i=1}^{N-1}&\exp[i(\vec{g}+m\vec{G}_1+n\vec{G}_2)\cdot\vec{R}_i] \\ &= \sum_{i=1}^{N-1}\exp(i\vec{g}\cdot\vec{R}_i)\exp(im\vec{G}_1\cdot\vec{R}_i)\exp(in\vec{G}_1\cdot\vec{R}_i) \\ &= \sum_{i=1}^{N-1}\exp(i\vec{g}\cdot\vec{R}_i)\exp(im\,2m_i\pi)\exp(in\,2n_i\pi) \\ &= \sum_{i=1}^{N-1}\exp(i\vec{g}\cdot\vec{R}_i) = -1 \ , \quad \text{Q.E.D.}\end{aligned}$$

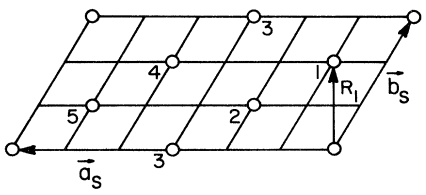

FIG. 3. Possible distribution of atoms on the C{111}2×1 surface. Vectors $\vec{a}_s$ and $\vec{b}_s$ are the unit-mesh vectors of the surface direct lattice. Circles indicate possible atomic positions. $\vec{R}_i$ vectors can be drawn from the origin to the five positions indicated by circles (only $\vec{R}_1$ has been drawn).

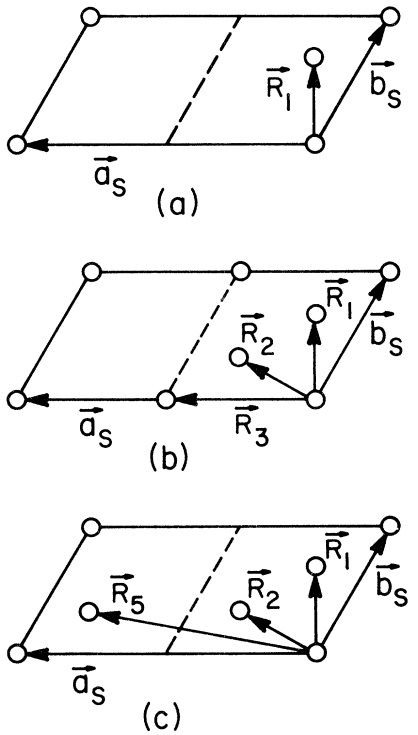

FIG. 4. Configurations (a)—(c) are all consistent with the missing-spot net observed in LEED patterns from C{111}2×1.

We now describe the procedure for determining the vectors $\vec{R}_i$ by considering as an example the reconstructed {111} surface of diamond, denoted as C{111}2×1. Figure 2(a) depicts the schematic LEED pattern of a three-domain C{111}2×1 structure as it is observed experimentally, and Fig. 2(b) shows schematically the LEED pattern that a single-domain C{111}2×1 structure would produce. In general, we can write the unit-mesh vectors $\vec{G}_1$ and $\vec{G}_2$ of the missing-spot net in terms of the primitive vectors $\vec{a}_s^*$ and $\vec{b}_s^*$ of the surface reciprocal net as follows:

$$\vec{G}_1=H_1\vec{a}_s^*+K_1\vec{b}_s^*,\quad \vec{G}_2=H_2\vec{a}_s^*+K_2\vec{b}_s^* . \tag{13}$$

We see from Fig. 2(b) that for C{111}2×1, $H_1=6$, $K_1=0$, $H_2=2$, and $K_2=1$. If we define the vectors $\vec{R}_i$ in terms of the unit-mesh vectors $\vec{a}_s$ and $\vec{b}_s$ of the reconstructed 2×1 structure in direct space,

$$\vec{R}_i=R_{ia}\vec{a}_s+R_{ib}\vec{b}_s , \tag{14}$$

with $0\le R_{ia}\le 1$ and $0\le R_{ib}\le 1$, then the requirements of theorem 1,

$$\vec{G}_1\cdot\vec{R}_i=2m_i\pi \text{ and } \vec{G}_2\cdot\vec{R}_i=2n_i\pi ,$$

can be rewritten as

$$H_1R_{ia}+K_1R_{ib}=m_i ,\quad H_2R_{ia}+K_2R_{ib}=n_i . \tag{15}$$

Hence, we get for the components of $\vec{R}_i$,

$$R_{ia}=\begin{vmatrix} m_i & K_1 \\ n_i & K_2 \end{vmatrix}\frac{1}{D},\quad R_{ib}\begin{vmatrix} H_1 & m_i \\ H_2 & n_i \end{vmatrix}\frac{1}{D},\quad D=\begin{vmatrix} H_1 & K_1 \\ H_2 & K_2 \end{vmatrix} . \tag{16}$$

TABLE I. C{111}2×1, N is the possible number of atoms or group of atoms in the unit cell; Comb. is the combination of $\vec{R}_i$'s from (18) that satisfies Eq. (9); Model represents the conclusions about the resulting structural models.

N	Comb.	Model
2	$\vec{R}_1$	Fig. 4(a)
	$\vec{R}_3$	1×1, excluded
	$\vec{R}_5$	Fig. 4(a)
3	None	
4	$\vec{R}_1,\vec{R}_2,\vec{R}_3$	Fig. 4(b)
	$\vec{R}_1,\vec{R}_2,\vec{R}_5$	Fig. 4(c)
	$\vec{R}_2,\vec{R}_3,\vec{R}_5$	1×1, excluded
	$\vec{R}_1,\vec{R}_3,\vec{R}_4$	1×1, excluded
	$\vec{R}_1,\vec{R}_4,\vec{R}_5$	Fig. 4(c)
	$\vec{R}_3,\vec{R}_4,\vec{R}_5$	Fig. 4(b)
5	None	
6	$\vec{R}_1,\vec{R}_2,\vec{R}_3,\vec{R}_4,\vec{R}_5$	1×1, excluded

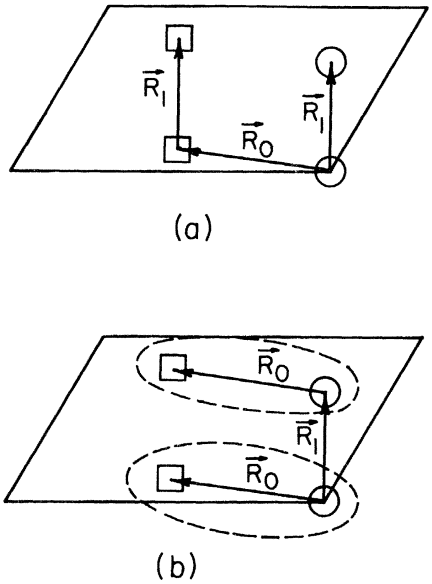

FIG. 5. In hypothetical case (a) $N=4$, but these are two different subgroups of two atoms each that produce the same missing-spot pattern ($\vec{R}_0$ is unknown). This case can be reduced to $N=2$ with larger but equal atom groups [shown by dashed lines in (b)].

In the case of C{111}2×1, we obtain

$$R_{ia}=m_i/6 \text{ and } R_{ib}=n_i-2R_{ia} , \tag{17}$$

and the possible $\vec{R}_i$ vectors are those drawn from the origin to the circles in Fig. 3 (in the figure only $\vec{R}_1$ has been drawn). Thus, the maximum value that N can have is 6, and therefore there are five possible values of $\vec{R}_i$ (R_6 being at the origin),

$$\vec{R}_1=\vec{a}_s/6+2\vec{b}_s/3 ,\quad \vec{R}_2=\vec{a}_s/3+\vec{b}_s2/3,\quad \vec{R}_3=\vec{a}_s/2 ,$$
$$\vec{R}_4=2\vec{a}_s/3+2\vec{b}_s/3,\quad \vec{R}_5=5\vec{a}_s/6+\vec{b}_s/3 . \tag{18}$$

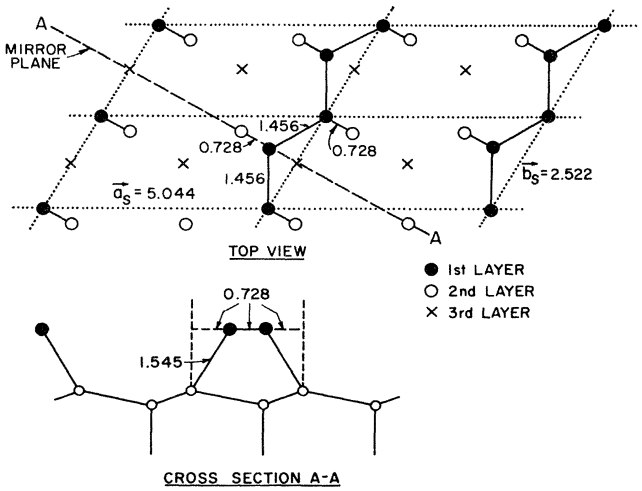

FIG. 6. Possible structure of the C{111}2×1 surface.

Only certain combinations of these vectors will generate the missing-spot net observed (Fig. 2), namely, those combinations that satisfy Eq. (9) with $N \leq 6$ and any $\vec{g}$ pointing to a missing spot in the LEED pattern.

To find out which combinations are acceptable we select, e.g., the missing spot P in Fig. 2(b), so that $\vec{g}=3\vec{a}_s^*$, and then calculate the following relations:

$$\exp(i\vec{g}\cdot\vec{R}_1)=-1,\quad \exp(i\vec{g}\cdot\vec{R}_2)=1,\quad \exp(i\vec{g}\cdot\vec{R}_3)=-1,$$
$$\exp(i\vec{g}\cdot\vec{R}_4)=1,\quad \exp(i\vec{g}\cdot\vec{R}_5)=-1\ . \tag{19}$$

We now assume that $N=2$. Only one of the $\vec{R}_i$'s will then be possible (remember that one of the N atoms or group of atoms is at the origin): $\vec{R}_2$ and $\vec{R}_4$ are excluded because they do not satisfy Eq. (9). But either $\vec{R}_1$ or $\vec{R}_3$ or $\vec{R}_5$ satisfies Eq. (9): $\vec{R}_1$ would produce the structural model shown in Fig. 4(a), $\vec{R}_3$ would produce a 1×1 structure ($\vec{a}$ and $\vec{b}$ were defined as the unit-mesh vectors of the 2×1 structure) and is therefore excluded as inconsistent with the observed 2×1 pattern, and $\vec{R}_5$ would produce the same model as $\vec{R}_1$. Trying all possible values of N in a similar fashion, we get the results summarized in Table I. The only three possible models are drawn schematically in Fig. 4. These results represent all we can get from considerations of the missing-spot pattern. Other considerations may allow further reduction of the number of possible models as discussed in the next section.

It is possible that the N equal atoms or groups of atoms can be subdivided into two or more subsets, each of which produces the same missing spots. For example, a structure with $N=4$ can be treated as the sum of two $N=2$ structures, a structure with $N=5$ as the sum of one $N=2$ and one $N=3$ structure, etc. This procedure could be applied to the case $N=4$ in Table I, i.e., the surface unit mesh could contain two subsets of atom groups, and in each subset the equal groups would be related to one another by way of vector $\vec{R}_1$, as depicted schematically in Fig. 5(a). Unknown in this case would be the translational vector $\vec{R}_0$ which translates one subset to the other. Obviously, however, such a structure could be treated as one with $N=2$, the groups related by $\vec{R}_1$ now being larger, as shown in Fig. 5(b). The internal constitution of the groups would still be unknown. Thus, in the example of C{111}2×1 treated above, we still would obtain the models drawn in Fig. 4 as consistent with the missing-spot net observed experimentally.

III. APPLICATIONS

A. C{111}2×1

In Sec. II, three structural models shown schematically in Figs. 4(a)–4(c) were found to produce the missing-spot net defined in Fig. 2. However, two of these models [Figs. 4(b) and (c)] involve four atoms per reconstructed unit cell and are therefore rejected as unlikely. The model depicted in Fig. 4(a) for the first atomic layer seems reasonable and we will discuss it further.

To determine the registry of the top layer with respect to the bulk, we recall that the experiment revealed the ex-

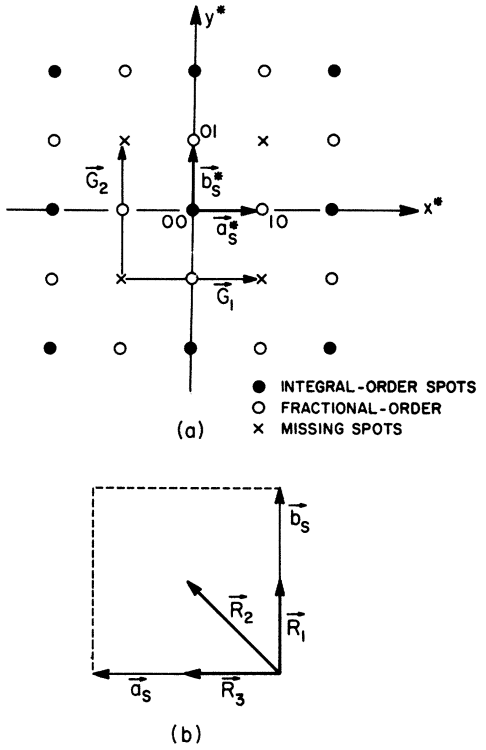

FIG. 7. Study of a Si{001}2×2 structure: (a) LEED pattern, and (b) possible vectors joining equal atoms.

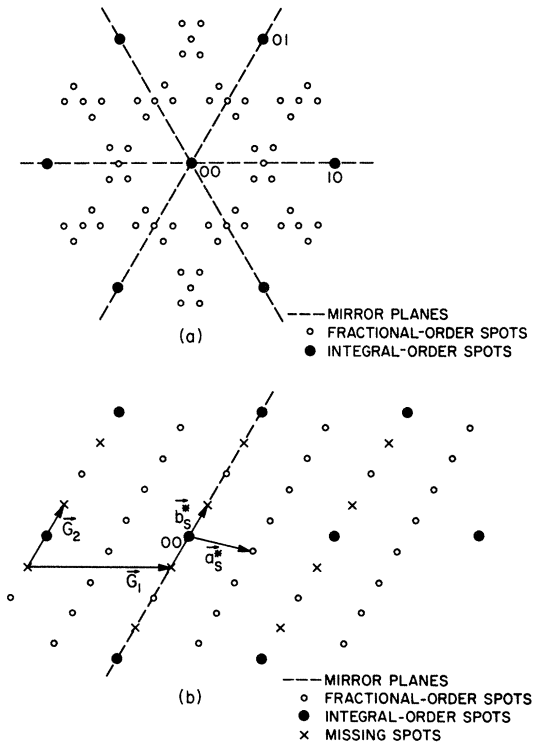

FIG. 8. Ge{111}$c(2\times8)$: (a) observed three-domain LEED pattern (schematic), and (b) single-domain LEED pattern. $\vec{a}_s^*$ and $\vec{b}_s^*$ are primitive vectors of the reciprocal net; $\vec{G}_1$ and $\vec{G}_2$ are unit-mesh vectors of the missing-spot net.

istence of a mirror plane along the doubling direction $\vec{a}_s^*$ (Fig. 2) and hence perpendicular to $\vec{b}_s$ in direct space. This requirement leads to the model depicted in Fig. 6. The C—C bonds within the first layer are 1.456 Å long. We recall that the C—C bond length in bulk diamond is 1.542 Å and in graphite it is 1.420 Å, the latter having "one-third double-bond character."[7] Thus, in the model of Fig. 6, the top-layer bonds have about 18% double-bond character. This model involves only reconstruction of the top-layer, with the deeper layers maintaining the bulk structure. In principle, distortions of the second and third atomic layers cannot be excluded, but, if present, they must be consistent with the existence of the mirror plane and with the requirements of Fig. 4(a).

There is some qualitative similarity between the model presented in Fig. 6 and the π-bonded chain model proposed by Pandey for the cleaved Si{111}2×1 structure.[8] However, the latter model involves *two* chains and in general does not cause systematically missing spots. Structural differences between the C and the Si surfaces are not surprising, not only because different, albeit similar, atoms are involved, but also because the C{111}2×1 structure was prepared by thermal annealing, whereas the Si{111}2×1 surface can only be obtained by cleavage in an ultrahigh vacuum.

B. Si{001}2×2

It has been suggested by several authors[9,10] that the reconstruction of Si{001} surfaces might include several superstructures, and among others, a Si{001}2×2 superstructure, provided that the $(\frac{1}{2}\,\frac{1}{2})$-like beams have always very weak or vanishing intensities. We ask here, as an exercise for the missing-spot analysis presented above, whether a Si{001}2×2 structure can exist that has zero intensity, i.e., missing spots, at all $(\frac{1}{2}\,\frac{1}{2})$-like positions in the LEED pattern.

We assume, therefore, that the LEED pattern looks like the one depicted in Fig. 7(a), and we identify the net of missing spots with the two vectors $\vec{G}_1$ and $\vec{G}_2$ drawn in that figure. Thus, $\vec{G}_1=\vec{2a}_s^*$, and $\vec{G}_2=\vec{2b}_s^*$. Using (8) and (14) we find that $R_{ia}=m_i/2$ and $R_{ib}=n_i/2$, resulting in three possible vectors $\vec{R}_1$, $\vec{R}_2$, and $\vec{R}_3$ as shown in Fig. 7(b). Thus N can be either 2, 3, or 4. For $N=2$, either $\vec{R}_1$ alone, $\vec{R}_2$ alone, or $\vec{R}_3$ alone must be considered. It is easy to see that $\vec{R}_1$ alone and $\vec{R}_2$ alone would generate a 2×1 structure, whereas $\vec{R}_3$ alone would generate a $c(2\times2)$ structure, all of which contradict the original assumption of a 2×2 structure. Hence, we reject the case $N=2$. For $N=3$ we find that either $\vec{R}_1$ and $\vec{R}_2$, $\vec{R}_1$ and $\vec{R}_3$, or $\vec{R}_2$ and $\vec{R}_3$ produce the same structure, but when we test Eq. (9) for the missing spot at $\vec{g}=\vec{a}^*+\vec{b}^*$, we find that the sum of exponentials equals -2, and hence Eq. (9) is not satisfied. For $N=4$ we see immediately that the resulting structure would be 1×1. Hence, we must conclude that a Si{001}2×2 superstructure with all $(\frac{1}{2}\,\frac{1}{2})$-like spots rigorously missing is *not* possible.

C. Ge{111}c(2×8)

The observed three-domain LEED pattern and the corresponding single-domain LEED pattern are depicted schematically in Fig. 8. Figure 9 shows, in direct space, the primitive vectors $\vec{a}$ and $\vec{b}$ of the bulk unit mesh and the boundaries, with dashed lines, of a 2×8 surface unit mesh. If this unit mesh is centered then a smaller unit mesh can be drawn (solid lines in Fig. 9) as defined by the vectors $\vec{a}_s$ and $\vec{b}_s$. Since $\vec{a}_s=2\vec{a}$ and $\vec{b}_s=\vec{a}+4\vec{b}$, we label this structure with the matrix $\begin{pmatrix}2 & 0\\ 1 & 0\end{pmatrix}$.

In Fig. 8(b), we define a net of missing spots with the two unit-mesh vectors $\vec{G}_1=2\vec{a}_s^*+\vec{b}_s^*$ and $\vec{G}_2=\vec{2b}_s^*$, and from Eq. (8) we find three possible $\vec{R}_i$'s.

$$\vec{R}_1=\vec{a}_s/4+\vec{b}_s/2,\quad \vec{R}_2=3\vec{a}_s/4+\vec{b}_s/2,\quad \vec{R}_3=\vec{a}_s/2\,,$$

which have been drawn in the unit mesh in Fig. 9. First assume that all three occur, i.e., that $N=4$. In this case

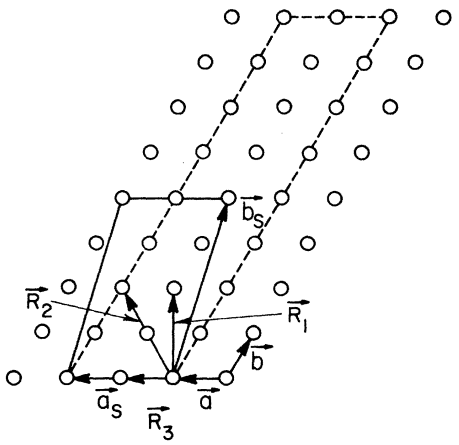

FIG. 9. Unit mesh of $c(2\times8)$ structure (dashed line) and unit mesh of $\begin{pmatrix}2 & 0\\ 1 & 4\end{pmatrix}$ structure on Ge{111} (solid line). $\vec{a}_s$ and $\vec{b}_s$ are unit mesh vectors; $\vec{R}_1$, $\vec{R}_2$, and $\vec{R}_3$ are possible vectors joining equal atom groups to explain the missing-spot pattern.

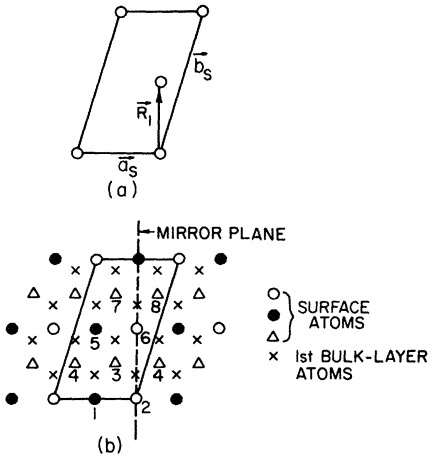

FIG. 10. (a) Schematic distribution of equal atom groups in the unit mesh of the Ge{111}c(2×8) structure. (b) Possible structure involving eight atoms per unit mesh and two equal groups of atoms (1,2,3,4 and 5,6,7,8) consistent with (a).

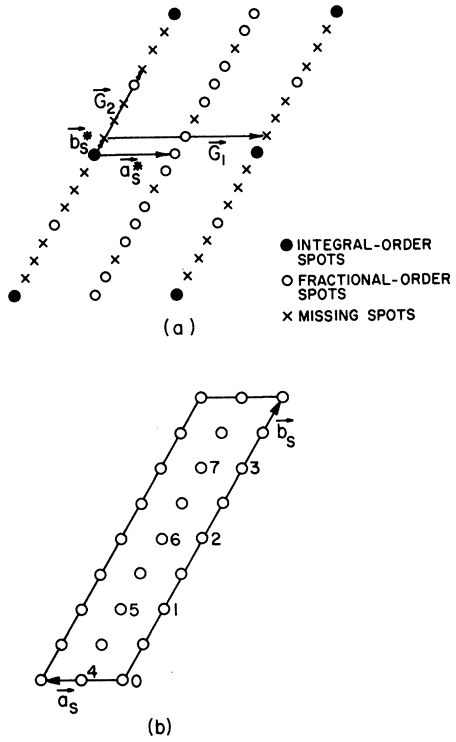

FIG. 11. (a) Single-domain LEED pattern of hypothetical Ge{111}2×8 structure. (b) 2×8 unit mesh: Numbers indicate the terminations of the vectors $\vec{R}_1, \ldots, \vec{R}_7$ discussed in the text.

the surface structure could be described by a smaller unit mesh than the one defined by $\vec{a}_s$ and $\vec{b}_s$ mentioned above, namely, by the unit mesh defined by $\vec{R}_1$ and $\vec{R}_3$ (Fig. 9). Since we see from Fig. 9 that $\vec{R}_3=\vec{a}$ and $\vec{R}_1=\vec{a}+2\vec{b}$, then the structure would be defined by the matrix $\begin{pmatrix}1 & 0\\ 1 & 2\end{pmatrix}$, different from the $\begin{pmatrix}2 & 0\\ 1 & 4\end{pmatrix}$ we started from, and hence $N=4$ is excluded. If $N=3$, we have three possibilities, and for each possibility, we check whether (9) is satisfied for a missing spot, say, $\vec{g}=\vec{b}_s^*$ [Fig. 8(b)]: (i) $\vec{R}_1$ and $\vec{R}_2$ (see Fig. 9) do not satisfy (9), (ii) $\vec{R}_1$ and $\vec{R}_3$ do not satisfy (9), and (iii) $\vec{R}_2$ and $\vec{R}_3$ do not satisfy (9). Hence, the case $N=3$ must be excluded.

We are left with the case $N=2$, which allows three possibilities: either $\vec{R}_1$, $\vec{R}_2$, or $\vec{R}_3$. The latter can be excluded immediately because we see from Fig. 9 that with $\vec{R}_3$ we can redefine the unit mesh to the structure $\begin{pmatrix}1 & 0\\ 1 & 4\end{pmatrix}$, which is different from the starting structure and hence unacceptable. The choices of $\vec{R}_1$ alone or $\vec{R}_2$ alone lead to the same structure, so we will consider the solution $\vec{R}_1$ only, repeated for clarity in Fig. 10(a). Thus, the observed periodic arrangement of missing spots leads us to the distribution of equal atoms or groups of atoms depicted in Fig. 10(a). We do not know the atomic arrangement inside each group and we do not know the registry of the surface net with respect to the bulk. If we assume that there are eight atoms in each surface unit mesh, as shown in Fig. 10(b), then the result of the missing-spot analysis tells us that the group of atoms 1,2,3,4 is equal to the group 5,6,7,8. This model is indeed the same as that proposed by Chadi and Chiang.[11] The experiment (see, e.g., Jona[12]), shows that there is a mirror plane along $\vec{R}_1$ (parallel to $\vec{b}_s^*$). Hence, atoms 7 and 8 [Fig. 10(b)] must be mirror images of one another (excluding, e.g., simple buckling models). Furthermore, the surface-net registry must respect the presence of this mirror plane, as done, e.g., by the model of Fig. 10(b).

D. Ge{111}2×8

The observed LEED pattern of a clean, reconstructed Ge{111} surface has been ascribed in the literature to surface unit meshes with 8×8, 4×8, and 2×8 periodicities.[12–14] As pointed out by Chadi and Chang[10] [who suggested the $c(2\times8)$ unit mesh discussed above], all the unit meshes proposed earlier reproduce all the observed LEED spots, but, in addition, each one produces an appreciable number of LEED spots which are not observed experimentally. We ask here whether a 2×8 unit mesh is consistent with the observed missing-spot net. A single-domain Ge{111}2×8 LEED pattern would look like the one depicted schematically in Fig. 11(a).

The missing-spot net is defined by the vectors $\vec{G}_1=2\vec{a}_s^*$ and $\vec{G}_2=4\vec{b}_s^*$, and the unit mesh of this net contains four missing spots, one each at $\vec{g}_1=\vec{b}_s^*$, $\vec{g}_2=2\vec{b}_s^*$, $\vec{g}_3=3\vec{b}_s^*$, and $\vec{g}_4=\vec{a}_s^*+2\vec{b}_s^*$. From Eq. (8) we get,

$$R_{ia}=m_i/2 \quad \text{and} \quad R_{ib}=n_i/4\ ,$$

that is,

$$R_{ia}=0,\tfrac{1}{2},1 \quad \text{and} \quad R_{ib}=0,\tfrac{1}{4},\tfrac{1}{2},\tfrac{3}{4},1\ .$$

TABLE II. Values of $\exp(i\vec{g}_i\cdot\vec{R}_j)$ for the four vectors $\vec{g}_i$, $i=1$ to 4 and the seven vectors $\vec{R}_j$, $j=1$ to 7, listed horizontally and vertically, respectively.

	$\vec{g}_1=\vec{b}_s^*$	$\vec{g}_2=2\vec{b}_s^*$	$\vec{g}_3=3\vec{b}_s^*$	$\vec{g}_4=\vec{a}_s^*+2\vec{b}_s^*$
$\vec{R}_1=\vec{b}_s/4$	i	-1	$-i$	-1
$\vec{R}_2=\vec{b}_s/2$	-1	1	-1	1
$\vec{R}_3=3\vec{b}_s/4$	$-i$	-1	i	-1
$\vec{R}_4=\vec{a}_s/2$	1	1	1	-1
$\vec{R}_5=\vec{a}_s/2+\vec{b}_s/4$	i	-1	$-i$	1
$\vec{R}_6=\vec{a}_s/2+\vec{b}_s/2$	-1	1	-1	-1
$\vec{R}_7=\vec{a}_s/2+3\vec{b}_s/4$	$-i$	-1	i	1

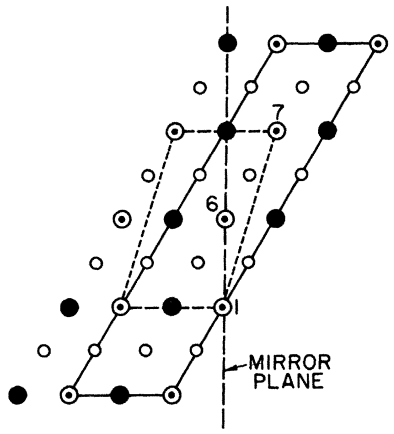

FIG. 12. Sole allowed distribution of atoms in the 2×8 unit mesh (solid lines) reduces the structure to the $c(2\times8)$ or $\begin{pmatrix}2&0\\1&4\end{pmatrix}$ unit mesh depicted in Fig. 9 (dashed lines).

Hence, the possible $\vec{R}_i$'s are,

$$\vec{R}_1=\vec{b}_s/4,\quad \vec{R}_2=\vec{b}_s/2\ ,$$
$$\vec{R}_3=3\vec{b}_s/4,\quad \vec{R}_4=\vec{a}_s/2\ ,$$
$$\vec{R}_4=\vec{a}_s/2\ ,$$
$$\vec{R}_5=\vec{a}_s/2+\vec{b}_s/4,\quad \vec{R}_6=\vec{a}_s/2+\vec{b}_s/2\ ,$$
$$\vec{R}_7=\vec{a}_s/2+3\vec{b}_s/4\ .$$

These vectors $\vec{R}_1,\ldots,\vec{R}_7$ can be visualized in the schematic 2×8 unit mesh depicted in Fig. 11(b) as the vectors joining the origin O to the points labeled $1,\ldots,7$, respectively. Next, we must test whether Eq. (5), or (9), is satisfied for all four missing spots identified by $\vec{g}_1$, $\vec{g}_2$, $\vec{g}_3$, and $\vec{g}_4$. For this purpose we construct Table II. We note that in the columns for $\vec{g}_2$ and $\vec{g}_4$ the values of exp $(i\vec{g}_i\cdot\vec{R}_j)$ are either 1 or -1, so in order to satisfy Eq. (9) we can only take combinations of odd numbers of $\vec{R}_j$, i.e., N must be even, that is, $N=2$, 4, 6, or 8.

For $N=2$ only one $\vec{R}_j$ is eligible at the time. We see from Table II that none of the rows adds up to -1, so Eq. (9) is not satisfied. Thus $N=2$ is excluded. For $N=4$ we consider all possible groups of three $\vec{R}_j$'s at the time. Of the 15 possible combinations all but one must be excluded [e.g., the combination R_1, R_2, and R_3 indeed satisfies Eq. (9) but we see from Fig. 11(b) that in this case the structure would be 2×2, not 2×8 as assumed initially]. The only combination allowed is $\vec{R}_1$, $\vec{R}_6$, and $\vec{R}_7$, which we discuss below. For $N=6$, we consider groups of five $\vec{R}_j$'s at the time and find that none of the 21 possible combinations satisfies Eq. (9). For $N=8$, we see immediately, from Fig 11(b) that the resulting structure would be 2×2 and thus excluded.

The combination $\vec{R}_1$, $\vec{R}_6$, and $\vec{R}_7$ therefore, is the only one allowed by the missing-spot analysis. We see from Fig. 12 that this 2×8 structure is in reality a $c(2\times8)$ structure and can be defined by the matrix $\begin{pmatrix}2&0\\1&4\end{pmatrix}$. We conclude therefore that a Ge$\{111\}2\times8$, structure is incompatible with the observed missing-spot net, and we find again that the $c(2\times8)$ or $\begin{pmatrix}2&0\\1&4\end{pmatrix}$, structure is acceptable. A longer analysis would be required to exclude the Ge$\{111\}8\times8$ structure.

ACKNOWLEDGMENTS

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[1]See, e.g., C. W. Bunn, *Chemical Crystallography* (Clarendon, Oxford, 1952), Chap. VII.
[2]See, e.g., F. Jona, J. A. Strozier, Jr., and W. S. Yang, Rep. Prog. Phys. 45, 527 (1982).
[3]B. W. Holland and D. P. Woodruff, Surf. Sci. 36, 488 (1973).
[4]M. K. Debe and D. A. King, Phys. Rev. Lett. 39, 708 (1977).
[5]J. H. Onuferko, D. P. Woodruff, and B. W. Holland, Surf. Sci. 87, 357 (1979).
[6]W. S. Yang and F. Jona, Solid State Commun. 42, 49 (1982).
[7]L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1973), p. 235.
[8]K. C. Pandey, Phys. Rev. Lett. 47, 1913 (1981).
[9]F. Jona, H. D. Shih, D. W. Jepsen, and P. M. Marcus, J. Phys. C 12, L455 (1979).
[10]D. J. Chadi, J. Vac. Sci. Technol. 16, 1290 (1979); Appl. Opt. 19, 3971 (1980).
[11]D. J. Chadi and C. Chiang, Phys. Rev. B 23, 1843 (1981).
[12]F. Jona, IBM J. Res. Dev. 9, 375 (1965).
[13]P. W. Palmberg and W. T. Peria, Surf. Sci. 6, 57 (1967).
[14]M. Taubenblatt, E. So, P. Sih, A. Kahn, and P. Mark, J. Vac. Sci. Technol. 15, 1143 (1978).