Diophantine Approach to the Classification of Two-Dimensional Lattices: Surfaces of Face-Centred Cubic Materials

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The long-range periodic order of a crystalline surface is generally represented by means of a two-dimensional Bravais lattice, of which only five symmetrically distinct types are possible. Here, we explore the circumstances under which each type may or may not be found at the surfaces of face-centred cubic materials, and provide means by which the type of lattice may be determined with reference only to the Miller indices of the surface; the approach achieves formal rigour by focussing upon the number theory of integer variables rather than directly upon real geometry. We prove that the {100} and {111} surfaces are, respectively, the only exemplars of square and triangular lattices. For surfaces exhibiting a single mirror plane, we not only show that rectangular and rhombic lattices are the only two possibilities but also capture their alternation in terms of the parity of the indices. In the case of chiral surfaces, oblique lattices predominate, but rectangular and rhombic cases are also possible and arise according to well-defined rules, here partially recounted.

INTRODUCTION

When a three-dimensional crystal is ideally truncated to form an unrelaxed surface, the positions of the remaining atoms are completely determined by the orientation of the truncation plane. This orientation may, in turn, be precisely defined by specifying three integer Miller indices [1] and hence these three integers must in some sense *encode* all relevant information pertaining to the structure and symmetry of the corresponding surface. Any facts that can subsequently be elicited by a detailed empirical investigation of the surface atomic positions must, in principle, be implicit in the Miller indices themselves and ought, therefore, to be deducible from them *without* recourse to mere empiricism. To take a concrete example relating to the face-centred cubic (*fcc*) structure, one might wish to investigate the (643) surface, say, and certainly could do so by constructing a detailed geometrical model incorporating the positions of all the atoms down to some arbitrary depth. The fact that this particular surface lacks all improper symmetry elements, and is therefore chiral, would then emerge naturally from empirical examination of the geometrical model. Alternatively, however, one could make use of the proven fact [3, 4] that all surfaces of *fcc* materials having three non-zero Miller indices of differing magnitudes are chiral, without troubling to construct a geometrical model at all. Once this handy rule-of-thumb is discovered, the practical business of categorising surfaces according to their symmetry is massively simplified.

In an earlier paper [5], several similar rules-of-thumb were provided that enable one to deduce the presence of certain surface symmetries (mirror, glide, etc) and the presence of certain surface structures (steps, kinks, etc) directly from the Miller indices, not only for the surfaces of *fcc* crystals, but also for those of *bcc* (body-centred cubic) and *hcp* (hexagonal close-packed) crystals. One intriguing problem was deferred until later, however, namely that of determining the nature of the surface's two-dimensional Bravais lattice from its Miller indices alone. This two-dimensional lattice describes the fundamental crystalline periodicity of the surface, dictates the patterns obtained in surface diffraction experiments, constrains the supercell that must be employed in computational modelling of the surface, yet remains something that surface scientists are content to view as an entirely contingent feature of the surface geometry. We typically construct a detailed geometrical model of the surface we wish to study, and note only after-the-fact that it has either a square, a triangular, a rectangular, a rhombic or an oblique Bravais lattice [2] (Fig. 1). On the contrary, however, it ought to be possible *in principle* to extract this information directly from the Miller indices without first constructing a geometrical model, in just the same way as it is possible to identify the attribute of chirality or the presence of steps.

Before doing so, it will be advisable to clarify one point of potential confusion. Since the space group of the surface must necessarily be a sub-group of the bulk space group, it is evidently (relatively) straightforward to obtain the former by judiciously striking out symmetry elements from the latter that are broken by the truncation of the crystal. The resulting space group will belong to one of just seventeen possible cases, each of which is associated with a particular lattice of minimal symmetry. For example, the {100} surfaces of the *fcc* structure will be found to conform to the *p4m* space group, which implies a lattice of at least square symmetry, and indeed we find that the two-dimensional lattice of such a surface is square as expected. The {100} surfaces of the *diamond* structure, on the other hand, conform only to the *pmm* space group, which implies only a lattice of

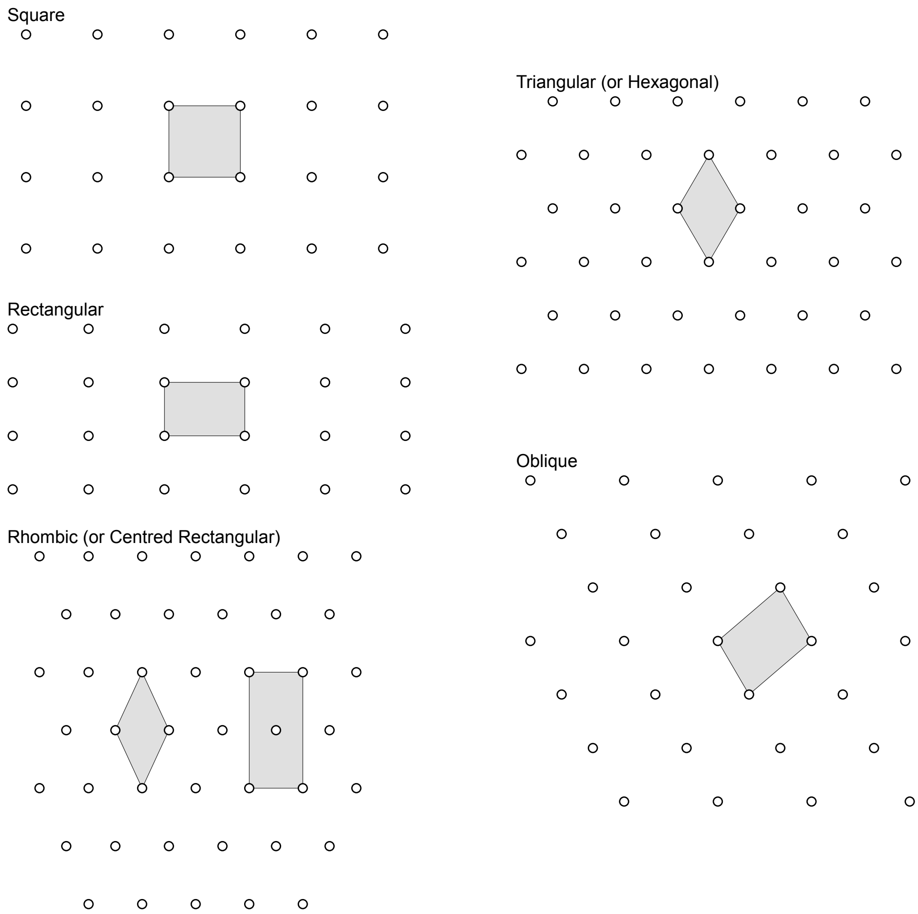

FIG. 1. Two-dimensional Bravais lattices of square, triangular, rectangular, rhombic and oblique symmetry. In each case, the primitive unit cell of maximum symmetry is shaded; in the rhombic case, a conventional (non-primitive) rectangular unit cell is also depicted.

at least rectangular symmetry; nevertheless, the actual periodicity of the surface again corresponds to a square lattice. It has been suggested (e.g. [6]) that one should indeed consider such a case as corresponding to a rectangular two-dimensional lattice whose lattice constants just happen to be "accidentally the same," which seems less than satisfactory to the present author; the primitive lattice vectors are constrained to be of equal length in this case because the ideal surface is *necessarily* commensurate with the underlying bulk crystal, and surely a rectangle whose sides are *necessarily* constrained to be equal in length can be described as nothing other than a square. For absolute clarity, the convention employed within this paper is that two-dimensional lattices are to be categorised according to their actual symmetry properties, including any that arise because of the unavoidable constraint that the ideal surface is commensurate with the underlying bulk.

The present work will be limited to the *fcc* case, which is quite difficult enough to unravel without adding the *bcc* and *hcp* cases. In seeking to decode the information carried by the Miller indices, we shall find ourselves dealing with Diophantine equations (i.e. equations involving only integer variables) and often making arguments based upon the parity of variables (i.e. whether they are even or odd) rather than their actual values. The application of number theory to problems in surface crystallography is extremely powerful and has a long history dating back at least to the pioneering work of Voigt [7] and Minkowski [8] in the early twentieth century. Several examples are very well summarised in an excellent introductory textbook on the subject by Hermann [9]. As this remains quite unfamiliar territory for most surface scientists, however, we begin with some rather fundamental observations about the bulk geometry of three-dimensional crystals, which nevertheless illustrate just how subtle the application of number theory to vector geometry can be.

BULK LATTICE VECTORS

The treatment of bulk lattice vectors in this section does not, in itself, contribute any new revelations. Indeed, the same conclusions have been drawn previously by others, and the interested reader is once again referred to the work of Hermann for further details [9]. Nevertheless, the notation used in the later sections of the present paper are most easily introduced in the bulk context and so it seems appropriate to recapitulate the three-dimensional case at this stage.

In *fcc* crystals, the set of all lattice vectors contains elements of two types. Firstly, there are those that may be represented as linear combinations of the vectors spanning the conventional cubic unit cell, thus

$$\mathbf{u} = a\langle xyz\rangle \qquad (1)$$

with a being the lattice constant and the vector components x, y and z taking integer values with any combination of signs (note that, for *fcc* lattices, angle brackets imply that the order and sign of the vector components may be permuted at will). Secondly, there are those that can be obtained from the first type by adding a vector of the form $\frac{a}{2}\langle 110\rangle$, yielding

$$\mathbf{u} = a\langle xyz\rangle + \frac{a}{2}\langle 110\rangle = \frac{a}{2}\langle (2x+1)\ (2y+1)\ 2z\rangle \qquad (2)$$

where clearly the integers $2x+1$, $2y+1$ and $2z$ have well-defined parities of odd, odd and even respectively. Indeed, the two types of lattice vector may be written together in a single expression

$$\mathbf{u} = \frac{2a}{f(u_x+u_y+u_z)}\langle u_x u_y u_z\rangle \qquad (3)$$

with u_x, u_y and u_z all integers, and where

$$f(x) = 3 + (-1)^x \qquad (4)$$

is a useful "parity discriminator function" returning values $f(x) = 2$ for odd-integer x and $f(x) = 4$ for even-integer x.

The veracity of Eqn. 3 may be confirmed by setting $u_x = 2x+1$, $u_y = 2y+1$ and $u_z = 2z$ to yield the complete set of vectors defined by Eqn. 2, whilst setting $u_x = 2x$, $u_y = 2y$ and $u_z = 2z$ to yield the complete set of vectors defined by Eqn. 1. No vectors failing to conform either to Eqn. 1 or to Eqn. 2 can be formed by inserting any other parity combinations of u_x, u_y and u_z into Eqn. 3.

The lengths of the general *fcc* lattice vectors thus take the form

$$L = \frac{2Ua}{f(u_x+u_y+u_z)}. \qquad (5)$$

where we have introduced

$$U^2 = u_x^2 + u_y^2 + u_z^2 \qquad (6)$$

as a convenient shorthand.

Alternatively, in units of the shortest lattice vector length, $L_0 = a/\sqrt{2}$, we have

$$L = \frac{2\sqrt{2}UL_0}{f(u_x+u_y+u_z)} \qquad (7)$$

which we can simplify further by considering two cases separately. Firstly, when $u_x+u_y+u_z$ is odd, we obtain

$$L = \sqrt{2}UL_0 \qquad (8)$$

with U^2 odd, and secondly, when $u_x+u_y+u_z$ is even, we get

$$L = \sqrt{2}UL_0/2 \qquad (9)$$

with U^2 even. It is evident, therefore, that lattice vector lengths in *fcc* must take the form $L_0\sqrt{n}$, with integer n. The question we now wish to address is that of which values of n are possible.

We start by noting the theorem (first postulated by Legendre, and subsequently proved by Gauss [10]) that any integer can be represented as the sum of three squares *except* for those that may be expressed as $4^b(8m+7)$ with m and b integers and $b \geq 0$. We can certainly, therefore, find values of u_x, u_y and u_z for which $U^2 = 2n$, so long as $2n \neq 4^b(8m+7)$. It follows that we can generate lattice vectors with lengths $L = L_0\sqrt{n}$ from Eqn. 9 subject only to the constraint that $n \neq 2^{2b-1}(8m+7)$ with $b > 0$.

Furthermore, lengths with n equal to $2^{2b-1}(8m+7)$ cannot be obtained from Eqn. 8 either, since this would require $U^2 = 4^{b-1}(8m+7)$ with $b > 0$, which is itself a subset of the integers disallowed as the sum of three squares by the theorem of Legendre and Gauss.

Thus, the set of allowed lengths for *fcc* lattice vectors consists of the values $L = L_0\sqrt{n}$, with n being any integer not of the form $2^{2b-1}(8m+7)$ with $b > 0$. Alternatively, in terms of the lattice constant, we have $L = a\sqrt{n/2}$. Either way, lengths with $n = 1, 2, ..., 13$ are allowed, for example, but $n = 14$ is not. Then, lengths with $n = 15, 16, ..., 29$ are found, but $n = 30$ is not, and so on.

SCARCITY OF SQUARE AND TRIANGULAR TWO-DIMENSIONAL SURFACE LATTICES

Surface scientists are, of course, familiar with the fact that the $\{100\}$ surfaces of *fcc* materials feature a square two-dimensional lattice, while the $\{111\}$ surfaces feature a triangular one. The present author is not, however, aware of any rigorous proof that these are the *only* two classes of surfaces to conform to these lattice types. Although the matter "feels" as if it ought to be trivial, we here present a formal proof based upon number theory and integer (Diophantine) equations.

The Square Surface Lattice

Imagine that a bulk *fcc* lattice has been cut to create a surface in which the first (i.e. outermost) layer of lattice points forms a square two-dimensional lattice. We label the corners of one square primitive unit cell in this layer as $\mathbf{O}_1$, $\mathbf{A}_1$, $\mathbf{B}_1$ and $\mathbf{C}_1$ (Fig. 2). Now, since all lattice points in the bulk must have had identical environments, the second layer of lattice points must also form a square two-dimensional lattice, and again four points $\mathbf{O}_2$, $\mathbf{A}_2$, $\mathbf{B}_2$ and $\mathbf{C}_2$ may be labelled, such that each point in the second-layer is displaced laterally from its correspondingly labelled point in the first layer by a distance d_x measured along the $\hat{x}$ direction and by a distance d_y measured along the $\hat{y}$ direction. Furthermore, let the side-length of the two-dimensional square lattice in each layer be $L_0\sqrt{n}$, as required by the fact that this surface has been created from a bulk *fcc* lattice (with a restriction on allowed values of the integer n, as discussed above). The area of the square $\mathbf{O}_1\mathbf{A}_1\mathbf{B}_1\mathbf{C}_1$ is thus nL_0^2, and the volume of the parallelopiped $\mathbf{O}_1\mathbf{A}_1\mathbf{B}_1\mathbf{C}_1\mathbf{O}_2\mathbf{A}_2\mathbf{B}_2\mathbf{C}_2$ is $nL_0^2 d_z$, where d_z is the interplanar spacing.

Now, clearly this parallelopiped must be a primitive unit cell of the bulk *fcc* lattice, and as such should have a volume $a^3/4$, which is equivalent to $L_0^3/\sqrt{2}$. Thus, we have $nL_0^2 d_z = L_0^3/\sqrt{2}$, and hence

$$d_z = \frac{L_0}{n\sqrt{2}} \tag{10}$$

for the interplanar spacing.

Invoking the requirement that $\mathbf{O}_1\mathbf{O}_2$ must be a bulk *fcc* lattice vector, we insist that

$$d_x^2 + d_y^2 + d_z^2 = pL_0^2 \tag{11}$$

with p being a positive integer (as per the preceding discussion of bulk lattice vector lengths). Similarly, the requirement that $\mathbf{A}_1\mathbf{O}_2$ must be a bulk *fcc* lattice vector dictates that

$$(L_0\sqrt{n} - d_x)^2 + d_y^2 + d_z^2 = qL_0^2 \tag{12}$$

and the same restriction for $\mathbf{C}_1\mathbf{O}_2$ imposes the constraint

$$d_x^2 + (L_0\sqrt{n} - d_y)^2 + d_z^2 = rL_0^2 \tag{13}$$

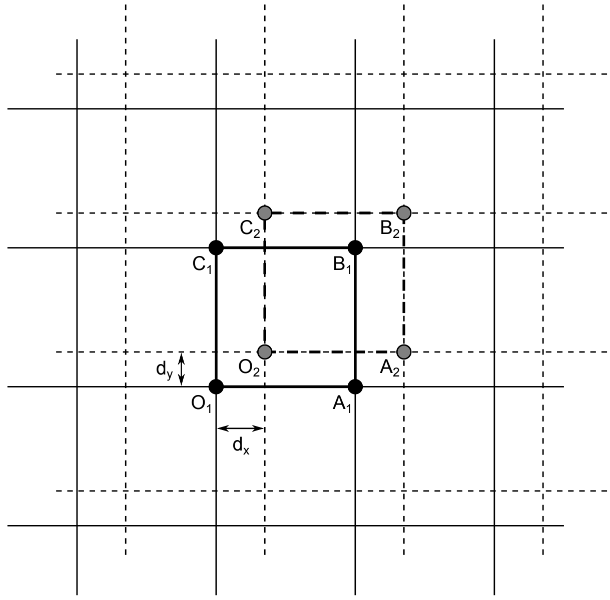

FIG. 2. Schematic illustration of a surface with a square two-dimensional lattice. Full lines indicate the two-dimensional lattice formed by the uppermost layer of bulk lattice points, while dashed lines show the displaced two-dimensional lattice of the second layer. A single primitive unit cell is highlighted in each layer.

with q and r both positive integers.

Solving Eqns. 11–13 simultaneously, and inserting our expression for d_z from Eqn. 10, permits us to write

$$d_x = \frac{L_0}{2\sqrt{n}}(n + p - q) \tag{14}$$

$$d_y = \frac{L_0}{2\sqrt{n}}(n + p - r) \tag{15}$$

and thus to fully locate the lateral position of $\mathbf{O}_2$ relative to $\mathbf{O}_1$ if the integer variables p, q and r were to be known. We may, without loss of generality, insist that $p \leq q \leq r$ by invoking the symmetry of the lattice.

Crucially, however, it must *also* be the case that $\mathbf{B}_1\mathbf{O}_2$ is a bulk *fcc* lattice vector, which means that we should have

$$(L_0\sqrt{n} - d_x)^2 + (L_0\sqrt{n} - d_y)^2 + d_z^2 = sL_0^2 \tag{16}$$

where s is yet another positive integer, which we may deduce satisfies $s \geq r$. But, substituting our expressions for d_x, d_y and d_z into this, we obtain

$$s = \frac{1}{4n}\left[(n + q - p)^2 + (n + r - p)^2 + 2/n\right] \tag{17}$$

which can only be true if the factor in square brackets is an integer divisible by $4n$. Since the squared terms are necessarily integers, it follows that we must insist upon an integer value for $2/n$, which in turn dictates that $n \geq 3$ is impossible. Moreover, one can show that the sum of two squares must always be expressible as $4t + u$ with t an integer and u an integer smaller than three, allowing one to rule out the $n = 2$ case on the grounds that the factor in square brackets cannot then be divisible by $4n$.

Consequently, we conclude that the only case that does not lead to a contradiction is that in which $n = 1$, having the sole solution $p = q = r = s = 1$, and corresponding to the $\{100\}$ family of surfaces. No other surface of an *fcc* lattice can have a square two-dimensional lattice.

The Triangular Surface Lattice

We can tackle the case of a triangular two-dimensional lattice in much the same way as we approached the square two-dimensional lattice in the preceding section. Imagine now that the first layer of lattice points forms a triangular two-dimensional lattice, and label the corners of one primitive unit cell in this layer as $\mathbf{O}_1$, $\mathbf{A}_1$, $\mathbf{B}_1$ and $\mathbf{C}_1$ (Fig. 3). Now, since all lattice points in the bulk must have had identical environments, the second layer of lattice points must also form a triangular two-dimensional lattice, and again four points $\mathbf{O}_2$, $\mathbf{A}_2$, $\mathbf{B}_2$ and $\mathbf{C}_2$ may be labelled, such that each point in the second-layer is displaced laterally from its correspondingly labelled point in the first layer by a distance d_x measured along the $\hat{x}$ direction and by a distance d_y measured along the $\hat{y}$ direction. As before, we insist that the side-length of the two-dimensional triangular lattice in each layer must be $L_0\sqrt{n}$ (with now-familiar restrictions on the value of n). The area of the two-dimensional primitive unit cell $\mathbf{O}_1\mathbf{A}_1\mathbf{B}_1\mathbf{C}_1$ is thus $nL_0^2\sqrt{3}/2$, and the volume of the parallelopiped $\mathbf{O}_1\mathbf{A}_1\mathbf{B}_1\mathbf{C}_1\mathbf{O}_2\mathbf{A}_2\mathbf{B}_2\mathbf{C}_2$ is $nL_0^2\sqrt{3}d_z/2$, where d_z is the interplanar spacing.

Now, as before, we note that this parallelopiped must be a primitive unit cell of the bulk *fcc* lattice, having therefore a volume of $L_0^3/\sqrt{2}$. Thus, we have $nL_0^2\sqrt{3}d_z/2 = L_0^3/\sqrt{2}$, and hence

$$d_z = \sqrt{\frac{2}{3}}\frac{L_0}{n} \tag{18}$$

for the interplanar spacing.

Invoking the requirement that $\mathbf{O}_1\mathbf{O}_2$ must be a bulk *fcc* lattice vector, we insist that

$$d_x^2 + d_y^2 + d_z^2 = pL_0^2 \tag{19}$$

with p being a positive integer. Similarly, the requirement that $\mathbf{A}_1\mathbf{O}_2$ must be a bulk *fcc* lattice vector dictates that

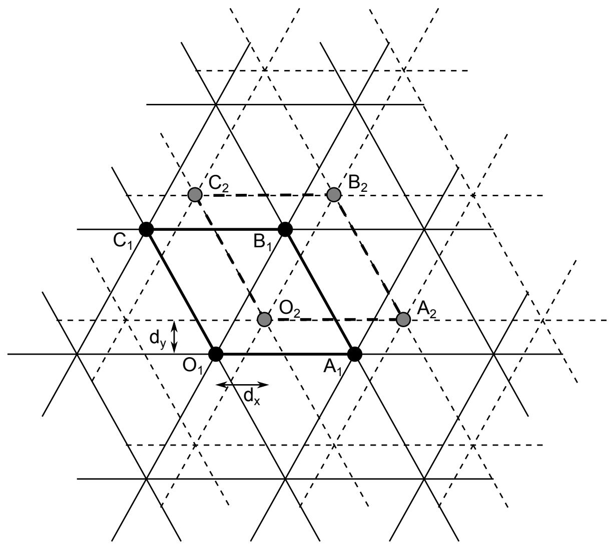

FIG. 3. Schematic illustration of a surface with a triangular two-dimensional lattice. Full lines indicate the two-dimensional lattice formed by the uppermost layer of bulk lattice points, while dashed lines show the displaced two-dimensional lattice of the second layer. A single primitive unit cell is highlighted in each layer.

$$(L_0\sqrt{n}/2 - d_x)^2 + (L_0\sqrt{3n}/2 + d_y)^2 + d_z^2 = qL_0^2 \tag{20}$$

and the same restriction for $\mathbf{C}_1\mathbf{O}_2$ imposes the constraint

$$(L_0\sqrt{n}/2 - d_x)^2 + (L_0\sqrt{3n}/2 - d_y)^2 + d_z^2 = rL_0^2 \tag{21}$$

with q and r both positive integers.

Solving Eqns. 19–21 simultaneously, and inserting our expression for d_z from Eqn. 18, permits us to write

$$d_x = \frac{L_0}{2\sqrt{n}}(2n + 2p - q - r) \tag{22}$$

$$d_y = \frac{L_0}{2\sqrt{n}}(r - q) \tag{23}$$

and thus, once again, to fully locate the lateral position of $\mathbf{O}_2$ relative to $\mathbf{O}_1$ if the integer variables p, q and r were to be known. Here, the symmetry of the lattice allows us to again insist upon $p \leq q \leq r$, without loss of generality.

We proceed, as before, by noting that it must *also* be the case that $\mathbf{B}_1\mathbf{O}_2$ is a bulk *fcc* lattice vector, which means that we should have

$$(L_0\sqrt{n} - d_x)^2 + d_y^2 + d_z^2 = sL_0^2 \tag{24}$$

where s is a positive integer that we may restrict, by invoking the symmetry of the lattice, to the range $q \leq s \leq r$. Upon substituting our expressions for d_x, d_y and d_z into this, we obtain (after some algebra)

$$s = \frac{1}{6n}\left[3(p-r)^2 + 3(p-q)^2 - (r-q)^2 + 4/n\right] \quad (25)$$

which can only be true if the factor in square brackets is an integer divisible by $6n$. Since the squared terms are necessarily integers, it follows that we must insist upon an integer value for $4/n$, which now dictates that $n = 1$, $n = 2$ and $n = 4$ are the only valid possibilities. Of these, the case with $n = 1$ has the sole solution $p = q = s = 1$ with $r = 2$, and corresponds to the $\{111\}$ family of surfaces. In contrast, the only *fcc* lattice vectors of length $L_0\sqrt{2}$ are those of $\langle 100 \rangle$ type, which meet only at right angles, whereas the only *fcc* lattice vectors of length $L_0\sqrt{4}$ are those of $\langle 220 \rangle$ type, which are simple multiples of shorter lattice vectors and hence cannot span a primitive unit cell. We therefore conclude that only the $\{111\}$ family of surfaces displays a triangular two-dimensional surface lattice.

RECTANGULAR, RHOMBIC AND OBLIQUE TWO-DIMENSIONAL SURFACE LATTICE

General Strategy

Consider the (hkl) surface, which in a cubic system has a surface normal parallel to the $[hkl]$ lattice vector [11]. The round and square brackets used here indicate that permutation in the sign and order of the vector components will not be allowed in this Section (i.e. that we refer always to a specific surface orientation and surface normal relative to the crystallographic axes, not to the family of symmetry-related planes and normals that would be indicated by curly and angle brackets respectively). We will furthermore insist that the Miller indices h, k and l must be coprime (i.e. share no common divisors) though not necessarily pairwise coprime (i.e. any pair of indices may share a common divisor) conforming to the most widespread usage within the surface science community.

Let us begin, then, by identifying a particular pair of *fcc* lattice vectors, $\mathbf{u}$ and $\mathbf{v}$, which span an orthogonal two-dimensional unit cell (not necessarily a *primitive* unit cell) lying in the surface plane. That is,

$$\mathbf{u} = \frac{2a}{f(u_x + u_y + u_z)}[u_x u_y u_z] \quad (26)$$

and

$$\mathbf{v} = \frac{2a}{f(v_x + v_y + v_z)}[v_x v_y v_z] \quad (27)$$

with

$$u_x v_x + u_y v_y + u_z v_z = 0 \quad (28)$$

$$u_x h + u_y k + u_z l = 0 \quad (29)$$

$$v_x h + v_y k + v_z l = 0 \quad (30)$$

and the vector components u_x, u_y and u_z being coprime (though not necessarily pairwise coprime) as are the vector components v_x, v_y and v_z. Since the vectors $\mathbf{u}$ and $\mathbf{v}$ are thus precluded from being simple multiples of shorter lattice vectors, the area spanned by them is a *candidate* for consideration as a primitive unit cell, but to determine whether this is *actually* the case will require a calculation of the included area.

Now, the area A, spanned by the vectors $\mathbf{u}$ and $\mathbf{v}$, must satisfy the equation

$$A^2 = \frac{16a^4}{\alpha^2}U^2V^2 \quad (31)$$

with

$$\alpha = f(u_x + u_y + u_z)f(v_x + v_y + v_z) \quad (32)$$

and

$$V^2 = v_x^2 + v_y^2 + v_z^2 \quad (33)$$

as may be seen simply by multiplying the squared vector lengths (U^2 has already been defined, analogously to V^2, in Eqn. 6). It would be useful, however, to express this in terms of the Miller indices, rather than as a function of the vector components of the cell sides. To achieve this, we write

$$\omega(h,k,l) = (u_y v_z - u_z v_y, u_z v_x - u_x v_z, u_x v_y - u_y v_x) \quad (34)$$

where the Miller indices are written explicitly as the vector product of the cell side vectors, guaranteeting that Eqns. 29 and 30 are satisified, and where ω is defined as the greatest common divisor shared by the three vector components on the right hand side. That is,

$$\omega = gcd(u_y v_z - u_z v_y, u_z v_x - u_x v_z, u_x v_y - u_y v_x) \quad (35)$$

where the *gcd* function returns the (positive) greatest common divisor of its arguments.

We may then note (after some algebra, and making use of Eqn. 28) that

$$\omega^2 M^2 = U^2 V^2 \tag{36}$$

with

$$M^2 = h^2 + k^2 + l^2 \tag{37}$$

from which it follows that

$$A^2 = \frac{16a^4}{\alpha^2}\omega^2 M^2 \tag{38}$$

On the other hand, it can be shown [5] that the area of a primitive unit cell, A_0, for an *fcc* surface satisfies the relation

$$A_0^2 = \frac{16a^4}{\beta^2} M^2 \tag{39}$$

with

$$\beta = \frac{32}{f(hkl)} \tag{40}$$

and, consequently, we conclude that

$$\frac{A}{A_0} = \left(\frac{\beta}{\alpha}\right)\omega \tag{41}$$

which will turn out to be of great value in ascertaining the type of two-dimensional lattice displayed by the surface.

For a given choice of h, k and l, we must determine the particular combination of three u and three v components that minimises A/A_0 whilst satisfying Eqns. 28–30. In the event that the minimum value of A/A_0 is unity, then the two-dimensional lattice must be rectangular (i.e. the smallest possible unit cell with orthogonal sides is proven to be a primitive unit cell). If the minimum value of A/A_0 is two, however, then the two-dimensional lattice must be rhombic (i.e. the smallest possible unit cell with orthogonal sides is twice the area of a primitive unit cell). And if the minimum value of A/A_0 exceeds two, then the two-dimensional lattice must be oblique. Strictly speaking, this test would count a square lattice as a special case of the rectangular lattice, and the triangular lattice as a special case of the rhombic lattice, but the arguments presented in the preceding sections allow us to eliminate the square and triangular possibilities for all but the {100} and {111} surfaces respectively.

Permitted Parity Combinations

Given nine variables (the three u and three v components, together with h, k and l) each of which may take either an even or an odd value, one might imagine that a total of $2^9 = 512$ different parity combinations could conceivably arise. The stipulation that the vector components u_x, u_y and u_z be coprime, however, implies that it is not possible for all three to be even numbers. Similarly, the fact that the vector components v_x, v_y and v_z are coprime implies that they too cannot all be even, and the same is separately true for h, k and l. A total of 188 parity combinations may thus be eliminated from our enquiries, leaving "only" 324. Moreover, consideration of Eqns. 28–30 introduces further restrictions upon the parity of these variables, for example the necessity that *precisely one* of the variables v_x, v_y or v_z must be even in the event that u_x, u_y and u_z are all odd. Collating all such restrictions, we can eliminate a further 297 parity combinations, leaving only 27 that are consistent with our fundamental requirements; these are enumerated in Table 1, together with the values of α and β that are implied in each case. The division of rows into four blocks within the table highlights that only four distinct combinations of α and β can arise, and each of these leads in turn to one of just three distinct expressions for A/A_0 tabulated in the penultimate column. Furthermore, for all the parity combinations listed in the upper two blocks of Table 1 we find that ω must be odd, while for all combinations in the lower two blocks we deduce that ω must be even, as indicated in the final column.

Restrictions on the ω Parameter

Now, the foregoing discussion indicates that there are only three possible expressions linking the ratio A/A_0 to the value of ω. Specifically, this ratio is either equal to ω, twice ω or half ω. Furthemore, we are particularly interested only in the cases where the ratio itself takes the values of one (indicating a rectangular two-dimensional lattice) or two (indicating a rhombic two-dimensional lattice). Clearly these situations can only arise when ω is equal to either one, two or four, so let us now examine carefully the question of whether these values can actually occur in practice.

To begin, consider Eqn. 36, which involves two factors on the right-hand side (RHS) and one on the left-hand side (LHS) that are each formed as the sum of the squares of three coprime integers. Now, it is an interesting fact that such a sum can never be divisible by four [12], so we can write

$$[U^2] \bmod 4 \equiv \gamma \tag{42}$$

TABLE 1. Parity combinations and their implications.

u_x	u_y	u_z	v_x	v_y	v_z	h	k	l	α	β	A/A_0	ω
Even	Even	Odd	Even	Odd	Even	Odd	Even	Even	4	8	2ω	Odd
Even	Even	Odd	Odd	Even	Even	Even	Odd	Even	4	8	2ω	Odd
Even	Odd	Even	Even	Even	Odd	Odd	Even	Even	4	8	2ω	Odd
Even	Odd	Even	Odd	Even	Even	Even	Even	Odd	4	8	2ω	Odd
Odd	Even	Even	Even	Even	Odd	Even	Odd	Even	4	8	2ω	Odd
Odd	Even	Even	Even	Odd	Even	Even	Even	Odd	4	8	2ω	Odd
Even	Even	Odd	Odd	Odd	Even	Odd	Odd	Even	8	8	ω	Odd
Even	Odd	Even	Odd	Even	Odd	Odd	Even	Odd	8	8	ω	Odd
Odd	Even	Even	Even	Odd	Odd	Even	Odd	Odd	8	8	ω	Odd
Even	Odd	Odd	Odd	Even	Even	Even	Odd	Odd	8	8	ω	Odd
Odd	Even	Odd	Even	Odd	Even	Odd	Even	Odd	8	8	ω	Odd
Odd	Odd	Even	Even	Even	Odd	Odd	Odd	Even	8	8	ω	Odd
Even	Odd	Odd	Odd	Odd	Odd	Even	Odd	Odd	8	8	ω	Odd
Odd	Even	Odd	Odd	Odd	Odd	Odd	Even	Odd	8	8	ω	Odd
Odd	Odd	Even	Odd	Odd	Odd	Odd	Odd	Even	8	8	ω	Odd
Odd	Odd	Odd	Even	Odd	Odd	Even	Odd	Odd	8	8	ω	Odd
Odd	Odd	Odd	Odd	Even	Odd	Odd	Even	Odd	8	8	ω	Odd
Odd	Odd	Odd	Odd	Odd	Even	Odd	Odd	Even	8	8	ω	Odd
Even	Odd	Odd	Even	Odd	Odd	Even	Odd	Odd	16	8	$\omega/2$	Even
Odd	Even	Odd	Odd	Even	Odd	Odd	Even	Odd	16	8	$\omega/2$	Even
Odd	Odd	Even	Odd	Odd	Even	Odd	Odd	Even	16	8	$\omega/2$	Even
Even	Odd	Odd	Even	Odd	Odd	Odd	Even	Even	16	8	$\omega/2$	Even
Odd	Even	Odd	Odd	Even	Odd	Even	Odd	Even	16	8	$\omega/2$	Even
Odd	Odd	Even	Odd	Odd	Even	Even	Even	Odd	16	8	$\omega/2$	Even
Even	Odd	Odd	Even	Odd	Odd	Odd	Odd	Odd	16	16	ω	Even
Odd	Even	Odd	Odd	Even	Odd	Odd	Odd	Odd	16	16	ω	Even
Odd	Odd	Even	Odd	Odd	Even	Odd	Odd	Odd	16	16	ω	Even

$$[V^2] \bmod 4 \equiv \delta \tag{43}$$

$$[M^2] \bmod 4 \equiv \epsilon \tag{44}$$

where γ, δ and ϵ can take only the values 1, 2 or 3.

It follows immediately that the RHS of Eqn. 36 cannot be divisible by 16 (it is the product of two factors that are each not multiples of four) and hence that no solutions with $\omega = 4$ are possible (since they would require that the LHS *would* be divisible by 16).

The case with $\omega = 2$, on the other hand, is not so easily dismissed, since this only requires that the LHS be divisible by four. Let us proceed by taking Eqn. 36 modulo four, to make this more explicit

$$[\omega^2 M^2] \bmod 4 = [U^2 V^2] \bmod 4 \tag{45}$$

from which we may deduce

$$[\omega^2 \epsilon] \bmod 4 = [\gamma\delta] \bmod 4 \tag{46}$$

and hence that if we have $\omega = 2$ then the product $\gamma\delta$ must be divisible by four. Since this product can only take values of $1, 2, 3, 4, 6$ or 9, it follows that we must have $\gamma = \delta = 2$ in this case. The RHS of Eqn. 36 is then the product of two even numbers not divisible by four, which is entirely consistent with the LHS being divisible by four due to its factor of ω^2. It is important to note, however, that the RHS of Eqn. 36 cannot ever be divisible by eight (since we already know that it is not divisible by four) and hence that there can be no $\omega = 2$ solutions if the factor M^2 on the LHS is even (i.e. if there are precisely two odd Miller indices).

Finally, turning to the $\omega = 1$ case, we deduce from Eqn. 46 that

$$[\epsilon - \gamma\delta] \bmod 4 = 0 \tag{47}$$

which can be solved with $\epsilon = 1$ and $\gamma\delta = 9$, or with $\epsilon = 2$ and $\gamma\delta = 2$ or 6, but which *cannot* be solved with $\epsilon = 3$ for any value of $\gamma\delta$. It therefore follows that $\omega = 1$ solutions are not possible if the factor $h^2 + k^2 + l^2$ on the LHS of Eqn. 36 yields remainder three upon division by four (i.e. if all three Miller indices are odd).

Collating these results, we may be confident (i) that no $\omega = 1$ solutions are possible if all three Miller indices are odd, (ii) that no $\omega = 2$ solutions are possible if there are precisely two odd Miller indices, and (iii) that no $\omega = 4$ solutions are possible under any circumstances. The first of these statements adds no further information to that already implied by Table 1, but the second and third do provide additional restrictions.

Identification of Lattice Types

In the case where all three Miller indices are odd, it is evident that only the parity combinations listed in the final block of Table 1 can occur, and since this implies $A/A_0 = \omega$, with an even value of ω, it follows that such a surface can never possess a rectangular two-dimensional lattice (which would require $A/A_0 = 1$). A rhombic two-dimensional lattice, on the other hand, *may* be indicated, but only if it is possible to find a combination of u and v components that satisfy Eqn. 36 with $\omega = 2$. There is no general prohibition against finding a solution with $\omega = 2$ for the case where all three Miller indices are odd, but neither is there a guarantee that one may be found for any particular set of indices. If no such combination can be found, the surface must necessarily display an oblique two-dimensional lattice.

In the case where precisely two Miller indices are odd, half of the parity combinations from the third block of Table 1 can occur, as can all of those from the second block. A general prohibition exists against finding solutions to Eqn. 36 with $\omega = 2$ in this case, however, so the third-block combinations with two odd Miller indices can never indicate a rectangular two-dimensional lattice (nor a rhombic one, since $\omega = 4$ solutions are similarly prohibited). According to the second-block combinations, on the other hand, a rectangular two-dimensional lattice will be indicated if it is possible to satisfy Eqn. 36 with $\omega = 1$. If this is not possible, then the surface must necessarily display an oblique two-dimensional lattice.

Finally, in the case where just one Miller index is odd, all of the parity combinations from the first block of Table 1, and half of those from the third block, can occur. A rectangular two-dimensional lattice can never be revealed by one of the first-block parity combinations, since for these A/A_0 is guaranteed to be even, but (according to the final three combinations of the third block) a rectangular two-dimensional lattice *will* be indicated if it is possible to satisfy Eqn. 36 with $\omega = 2$. Alternatively, a rhombic lattice is indicated (according to parity combinations in the first block of Table 1) if it is possible to satisfy Eqn. 36 with $\omega = 1$. The final three parity combinations in the third block can never indicate a rhombic lattice, since it is never possible to find solutions satisfying Eqn. 36 with $\omega = 4$. Aside from these situations, the surface must again display an oblique two-dimensional lattice.

In effect, therefore, it is possible to determine the nature of the two-dimensional lattice for a given surface from its Miller indices alone, simply by searching for all solutions to Eqn. 36 with $\omega = 1$ or 2, and cross-referencing against the number of odd Miller indices. If a valid solution with $\omega = 2$ can be found for a case with one odd Miller index, or if a valid solution with $\omega = 1$ can be found for a case with two odd Miller indices, then the surface must have a rectangular two-dimensional lattice. If, on the other hand, one can find either a valid solution with $\omega = 1$ for a case with one odd Miller index, or a valid solution with $\omega = 2$ for a case with three odd Miller indices, then the surface must have a rhombic two-dimensional lattice. Otherwise, the two-dimensional lattice must be concluded to be oblique.

In searching for solutions matching a given set of Miller indices, h, k and l, it may, of course, be possible that solutions of Eqn. 36 with $\omega \neq 1$ or 2 are found, which in no way precludes the possibility that a solution with $\omega = 1$ or 2 may be found subsequently. In general, one would have to search through all combinations of u and v components compatible with the known size of the primitive unit cell, before concluding which values of ω are possible for that set of Miller indices. To determine the limits of compatibility, we may make use of our previous expression for the area of a primitive unit cell (Eqn. 39) to deduce that the smallest orthogonal unit cell of a surface having a rectangular or rhombic two-dimensional lattice must have a longest side length, L, that satisfies

$$L^2 < \frac{128a^2}{\beta^2} M^2 \tag{48}$$

and hence to further deduce that no solutions need be sought for which either U^2 or V^2 exceeds $8M^2$.

Now, letting Ω be the smallest value of ω found during the search within these limits, the nature of the two-dimensional lattice is given simply by the entries in Table 2. Note, however, that values of $\omega = 1$ and of $\omega = 2$ are mutually exclusive, so that the search may be terminated unambiguously as soon as *either* result is obtained, with Ω taking the corresponding value of ω. A flow-chart crystallises the resulting procedure (Fig. 4). The computational cost of this approach is not dissimilar to the method of Minkowski reduction, which generates a high-symmetry unit cell from an arbitrary two-dimensional lattice by iterative means [9].

Implementation of this simple and efficient algorithm allows one readily to enumerate surfaces having either rectangular, rhombic or oblique two-dimensional lattices. Doing so, one finds that those having oblique lattices dominate, with rectangular lattices being the next most common and rhombic lattices the least. As one progressively includes surfaces of higher and higher index, the

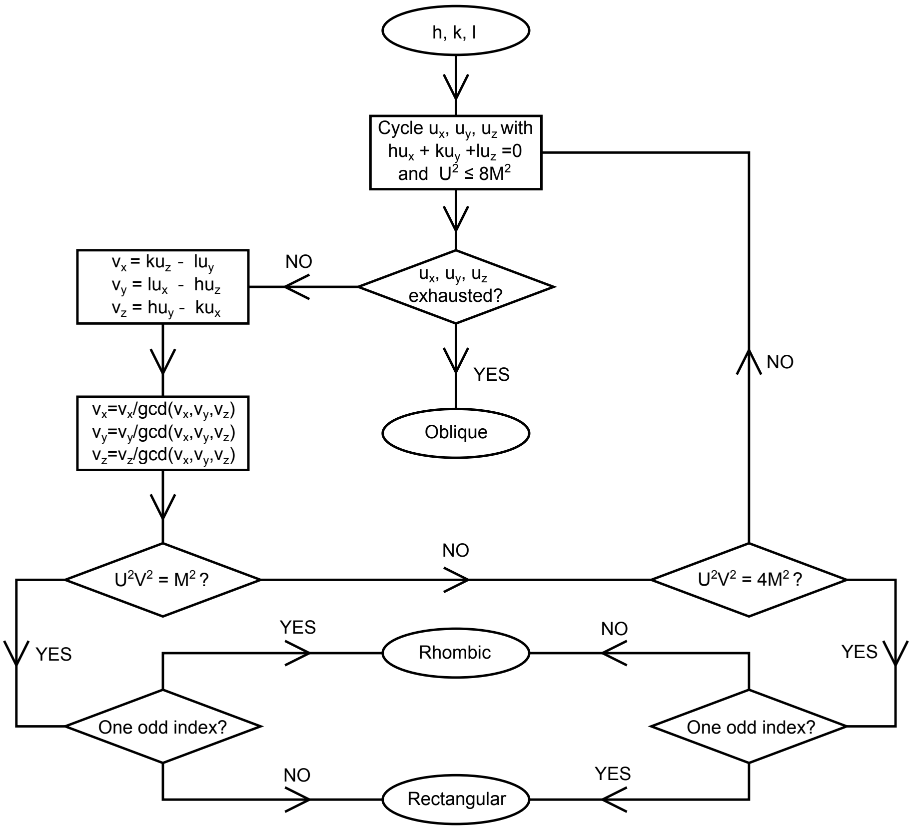

FIG. 4. Flow-chart to determine whether a given {hkl} surface has a rectangular, rhombic or oblique two-dimensional lattice.

TABLE 2. Lattice types implied by Miller index parity and the Ω parameter (i.e. the smallest possible value of ω compatible with Eqn. 36).

	1 Odd Index	2 Odd Indices	3 Odd Indices
$\Omega = 1$	Rhombic	Rectangular	Impossible
$\Omega = 2$	Rectangular	Impossible	Rhombic
$\Omega \neq 1, 2$	Oblique	Oblique	Oblique

TABLE 3. Proportions of chiral *fcc* surfaces having rhombic, rectangular and oblique two-dimensional lattices, as a function of the maximum permitted magnitude of Miller index.

Maximum Index	Rhombic	Rectangular	Oblique
8	8%	17%	75%
16	6%	11%	83%
32	4%	7%	89%
64	3%	4%	93%

dominance of oblique lattices becomes ever more pronounced, but the imbalance between rectangular and rhombic lattices becomes less so (see Table 3). The full set of chiral surfaces with Miller indices not exceeding a magnitude of eight are categorised according to their two-dimensional lattices in Table 4.

TABLE 4. Chiral *fcc* surfaces with rhombic, rectangular or oblique two-dimensional lattices (up to a maximum Miller index of eight).

Rhombic	Rectangular	Oblique
{531}	{421}	{321}, {731}, {832}
{542}	{521}	{431}, {732}, {841}
{751}	{541}	{432}, {742}, {843}
{854}	{652}	{532}, {743}, {851}
	{653}	{543}, {753}, {853}
	{741}	{621}, {754}, {861}
	{752}	{631}, {761}, {863}
	{852}	{632}, {762}, {865}
	{871}	{641}, {763}, {872}
		{643}, {764}, {873}
		{651}, {765}, {874}
		{654}, {821}, {875}
		{721}, {831}, {876}

CLOSED EXPRESSIONS

Although the algorithm presented above is simple, efficient and based only upon integer operations (i.e. it is ideal for computational implementation) it would, of course, be highly desirable to be able to deduce the lattice status of a surface directly by inspection of its Miller indices. That is, we would like to possess a closed expression for one of the indices (let us say the l index, for the sake of argument) in terms of the other two (in this case, h and k) for rhombic, rectangular or oblique cases. One could simply then ascertain whether the closed expression is satisfied for any given surface, without the need for any iterative procedure at all, however simple and efficient.

Family 1

Let us first focus, in pursuit of this goal, on surfaces whose smallest orthogonal unit cell features at least one side defined by a lattice vector parallel to a $[p\ \overline{q}\ 0]$ direction, where p and q are coprime. For such surfaces, we can set $u_x = p$, $u_y = -q$ and $u_z = 0$ without loss of generality (as it makes no practical difference whether we associate this particular direction with the **u** vector or the **v** vector in the analysis). Doing so, we can immediately infer that we must have $v_x = rq$ and $v_y = rp$ in order to satisfy Eqn. 28, whereas we are free to set $v_z = -s$ without any restriction on the values of either r or s except that they must be coprime integers. Inserting these assignments into Eqn. 34, we find

$$\omega(h,k,l) = (qs, ps, r(p^2+q^2)) \tag{49}$$

with ω the greatest common divisor shared by qs, ps and $r(p^2+q^2)$. Systematically scanning through all possible combinations of p, q, r and s (with p and q coprime, and similarly r and s coprime) will then produce a variety of Miller index sets, (h,k,l), each with its own specific value of ω, whose parities can be looked up in Table 2 to determine the type of two-dimensional surface lattice for that surface.

Now, unpacking the content of Eqn. 49, we see that

$$p = k/\gcd(h,k) \tag{50}$$

$$q = h/\gcd(h,k) \tag{51}$$

where $\gcd(h,k)$ is the greatest common divisor of h and k (equal to s/ω). Accordingly, the expression

$$\omega l = r(p^2+q^2) \tag{52}$$

may be written as

$$l = \frac{r(h^2+k^2)}{\omega[\gcd(h,k)]^2} \tag{53}$$

with r being, as noted above, any integer coprime with s. Since we may write $s = \omega \gcd(h,k)$, however, it follows that r must be separately coprime with both ω and $\gcd(h,k)$.

TABLE 5. Expressions for l, in terms of h and k, that imply rhombic or rectangular lattices belonging to Family 1. Here, m is any integer, defined in such a way as to ensure that the integers r snd ω appearing in Eqn. 54 are coprime.

	1 Odd Index	2 Odd Indices	3 Odd Indices
Rhombic	$\frac{m(h^2+k^2)}{[gcd(h,k)]^2}$	–	$\frac{(2m+1)(h^2+k^2)}{2[gcd(h,k)]^2}$
Rectangular	$\frac{(2m+1)(h^2+k^2)}{2[gcd(h,k)]^2}$	$\frac{m(h^2+k^2)}{[gcd(h,k)]^2}$	–

Surfaces within this family, therefore, must have Miller indices conforming to the type

$$\left\{h, k, \frac{r(h^2+k^2)}{\omega[\gcd(h,k)]^2}\right\} \tag{54}$$

and the value of ω, combined with the parity of the indices, will allow one to determine the symmetry of the surface lattice. If it is possible to write any permutation of the Miller indices in this form whilst setting $\omega = 1$, then a rhombic two-dimensional lattice will be implied, if there is a single odd Miller index, or a rectangular two-dimensional lattice, if there are two. Alternatively, if one can find a permutation of the Miller indices in this form whilst setting $\omega = 2$, then a rectangular two-dimensional lattice will be implied if there is one odd Miller index, or a rhombic two-dimensional lattice if there are three. If the Miller indices can be permuted into this form only by setting $\omega > 2$, then we can conclude that this surface does not have either a rectangular or a rhombic two-dimensional lattice within this particular family; this does *not* preclude the possibility that the surface may yet possess such a lattice, but the **u** and **v** vectors spanning it must not conform to the type considered above. These results are summarised in Table 5.

By way of example, consider setting $h = 1$ and $k = 3$, with $m = 0$ in Table 5, yielding $l = 5$ and thus identifying the $\{531\}$ surfaces as having rhombic two-dimensional lattices within the presently discussed family (noting that there are three odd indices). Indeed, inspection reveals that the smallest orthogonal unit cell of a $\{531\}$ surface is spanned by primitive surface lattice vectors of $\langle 3\overline{1}0\rangle$ and $\langle 13\overline{2}\rangle$ type, conforming to our expectations.

Family 2

If we now consider surfaces whose smallest orthogonal unit cell features at least one side defined by a lattice vector parallel to a $[p\ p\ \overline{q}]$ direction, where p and q are coprime and $q \neq 0$, then we can set $u_x = u_y = p$ and $u_z = -q$ with no loss of generality. Setting $v_x = -r$, $v_y = s$ and $v_z = t$, with r, s and t coprime, though not necessarily pairwise coprime, we must insist that

$$p(s-r) = qt \tag{55}$$

in order to satisfy Eqn. 28. Then, from Eqn. 34, we find

$$q\omega(h,k,l) = (p^2(s-r)+q^2 s, p^2(r-s)+q^2 r, pq(s+r)) \tag{56}$$

having eliminated t, from which we may readily determine that

$$\omega(h+k) = q(s+r) \tag{57}$$

and hence that

$$p(h+k) = ql \tag{58}$$

whereupon the requirement that p and q are coprime then implies that we must have

$$p = l/\gcd(l, h+k) \tag{59}$$

$$q = (h+k)/\gcd(l, h+k) \tag{60}$$

with $\gcd(l, h+k)$ being the greatest common divisor of l and $h+k$.

Inserting these expressions for p and q into Eqns. 55 and 56, we can solve simultaneously for r, s and t, obtaining

$$r = \frac{\omega \gcd(l,h+k)[l^2 + k(h+k)]}{2l^2 + (h+k)^2} \tag{61}$$

$$s = \frac{\omega \gcd(l,h+k)[l^2 + h(h+k)]}{2l^2 + (h+k)^2} \tag{62}$$

$$t = \frac{\omega \gcd(l,h+k) l(h-k)}{2l^2 + (h+k)^2} \tag{63}$$

All that remains, to ensure that we have located a surface with either a rectangular or a rhombic two-dimensional lattice, is to confirm that r, s and t are coprime, but not necessarily pairwise coprime, integers. Equivalently, we must determine whether h, k and l satisfy

$$\frac{2l^2 + (h+k)^2}{\omega \gcd(l,h+k)} = \gcd(l^2 + k(h+k), l^2 + h(h+k), l(h-k)) \tag{64}$$

or some cyclic permutation of the same.

After some manipulation, one can show that this requirement may be stated equivalently as

$$l = \sqrt{\frac{m^2 n(h+k)^2}{\omega\theta - 2m^2 n}} \tag{65}$$

TABLE 6. Expressions for l^2, in terms of h and k, that imply rhombic or rectangular lattices belonging to Family 2. Here, m and n are any pair of coprime integers, and θ is defined by Eqn. 66.

	1 Odd Index	2 Odd Indices	3 Odd Indices
Rhombic	$\frac{m^2n(h+k)^2}{\theta-2m^2n}$	–	$\frac{m^2n(h+k)^2}{2(\theta-m^2n)}$
Rectangular	$\frac{m^2n(h+k)^2}{2(\theta-m^2n)}$	$\frac{m^2n(h+k)^2}{\theta-2m^2n}$	–

with

$$\theta = \gcd(m^2(h+k) + n^2 k, m^2(h+k) + n^2 h, (h-k)nm) \tag{66}$$

where m and n are a pair of coprime integers.

Surfaces within this family, therefore, must have Miller indices conforming to the type

$$\left\{h, k, \sqrt{\frac{m^2 n(h+k)^2}{\omega\theta - 2m^2 n}}\right\} \tag{67}$$

and again the value of ω, combined with the parity of the indices, will allow one to determine the symmetry of the surface lattice. If it is possible to write any permutation of the Miller indices in this form whilst setting $\omega = 1$, then a rhombic two-dimensional lattice will be implied, if there is a single odd Miller index, or a rectangular two-dimensional lattice, if there are two. Alternatively, if one can find a permutation of the Miller indices in this form whilst setting $\omega = 2$, then a rectangular two-dimensional lattice will be implied if there is one odd Miller index, or a rhombic two-dimensional lattice if there are three. As for the previous family, if the Miller indices can be permuted into this form only by setting $\omega > 2$, then we can conclude that this surface does not have either a rectangular or a rhombic two-dimensional lattice within this particular family; this does *not* preclude the possibility that the surface may yet possess such a lattice, but the $\mathbf{u}$ and $\mathbf{v}$ vectors spanning it must not conform to the type considered above. These results are summarised in Table 6.

Once again, let us examine a typical example, setting $h = 2$ and $k = \overline{4}$, with $m = 1$ and $n = 2$ in Table 6, yielding $\theta = 6$ and hence $l = 1$. This, proves that surfaces of $\{421\}$ type, having but a single odd index, possess rectangular two-dimensional lattices within the presently discussed family. Indeed, the smallest orthogonal unit cell of a $\{421\}$ surface is spanned by primitive surface lattice vectors of $\langle\overline{1}12\rangle$ and $\langle 1\overline{3}2\rangle$ type, again conforming to our expectations.

MIRROR-SYMMETRIC SPECIAL CASES

Although the general criteria outlined above are rather complex, they do collapse to quite simple rules for special cases in which the surface possesses mirror symmetry.

Surfaces on the $\langle 110\rangle$ Zones

Let us consider surfaces whose smallest orthogonal unit cell has the $\frac{a}{2}[1\bar{1}0]$ lattice vector as one of its sides. We can ascertain the nature of the two-dimensional lattice for surfaces of this type from Eqn. 49 simply by setting $p = q = 1$, yielding

$$\omega(h, k, l) = (s, s, 2r) \tag{68}$$

with

$$\omega = gcd(s, 2) \tag{69}$$

by virtue of s and r being coprime.

Now, in the case that s is odd, we necessarily have $\omega = 1$, which implies that

$$(h, k, l) = (s, s, 2r) \tag{70}$$

and that the two-dimensional lattice is rectangular (see Table 2). This case encompasses all surfaces on the $[1\bar{1}0]$ zone having precisely two odd indices.

On the other hand, if s is even, we get $\omega = 2$, implying

$$(h, k, l) = (s/2, s/2, r) \tag{71}$$

for which the two-dimensional lattice is rectangular when r is even and $s/2$ odd (repeating the same surfaces found with odd s) but also when r is odd and $s/2$ even (encompassing all surfaces on the $[1\bar{1}0]$ zone having precisely one odd index). We now, however, also find surfaces with rhombic two-dimensional lattices, in the case where both r and $s/2$ are odd, encompassing all surfaces on the $[1\bar{1}0]$ zone having three odd indices.

We have thus proved that all surfaces lying on the $[1\bar{1}0]$ zone have the $\frac{a}{2}[1\bar{1}0]$ lattice vector as one side of their smallest orthogonal unit cell, and consequently that all surfaces lying on a $\langle 110\rangle$ zone have an $\frac{a}{2}\langle 1\bar{1}0\rangle$ lattice vector as one side of *their* smallest orthogonal unit cell. Furthermore, all such surfaces may be categorised as having either rectangular or rhombic two-dimensional lattices based purely upon the parity of their Miller indices – three odd indices imply that the two-dimensional lattice is rhombic, and any other situation that it is rectangular.

Surfaces on the $\langle 100\rangle$ Zones

In a similar fashion to the preceding section, let us now consider surfaces whose smallest orthogonal unit cell has the $\frac{a}{2}[100]$ lattice vector as one of its sides. We can ascertain the nature of the two-dimensional lattice for surfaces of this type from Eqns. 49 simply by setting $p = 1$ and $q = 0$, yielding

$$\omega(h, k, l) = (0, s, r) \tag{72}$$

with

$$\omega = 1 \tag{73}$$

by virtue of s and r being coprime.

Immediately, we see that Table 2 specifies a rectangular surface if two indices are odd (which will require that both s *and* r must be odd) and a rhombic surface if only one index is odd (which will require that only s *or* r must be odd, but not both). Once again, the set of surfaces defined in this way happens to encompass all possible surfaces lying on the [100] zone.

Thus, we conclude that all surfaces lying on the [100] zone have the $\frac{a}{2}[100]$ lattice vector as one side of their smallest orthogonal unit cell, and consequently that all surfaces lying on a $\langle 100\rangle$ zone have an $\frac{a}{2}\langle 100\rangle$ lattice vector as one side of *their* smallest orthogonal unit cell. Furthermore, all such surfaces may be categorised as having either rectangular or rhombic two-dimensional lattices based purely upon the parity of their Miller indices – one odd index implies that the two-dimensional lattice is rhombic, and any other situation that it is rectangular.

CONCLUSIONS

We have examined the two-dimensional lattice types presented by the surfaces of face-centred cubic materials, taking a number-theoretic approach rooted in the solution of diophantine equations. The {100} and {111} surfaces are shown to be the only examples resulting, respectively, in square and triangular two-dimensional lattices. For the mirror-symmetric surfaces, only rhombic or rectangular two-dimensional lattices are possible – for those surfaces lying on a $\langle 110\rangle$ zone the rhombic cases occur when all three Miller indices are odd, all others being rectangular, while for those lying on a $\langle 100\rangle$ zone the rhombic cases occur when one (and only one) Miller index is odd.

Amongst surfaces that do not lie upon either $\langle 110\rangle$ or $\langle 100\rangle$ zones (i.e. those possessed of three inequivalent and non-zero Miller indices) two-dimensional lattices of rhombic, rectangular and oblique form may be found, but simple rules to distinguish between these on the basis of Miller indices alone are difficult to derive. We can, however, assert that surfaces with three odd indices can never display a rectangular two-dimensional lattice, while those having two odd indices can never possess a rhombic one.

Closed forms have been derived, relating one Miller index to the other two, for surfaces with either rectangular or rhombic two-dimensional lattices that fall within two well-defined families, but a completely general expression remains to be determined. Surfaces with rectangular or rhombic two-dimensional lattices that do *not* fall within one or other of these families certainly exist, but cannot yet be rendered in closed form. An efficient integer algorithm has been presented, however, that captures all cases.

The general approach taken in the present work, based on assessment of the area ratio between orthogonal and primitive unit cells, ought to be readily applicable to other crystal structures. The body-centred cubic case should be quite straightforward to analyse, for instance, but less symmetric materials are likely to prove more troublesome. Clearly the returns from conducting such analysis must be weighed against the frequency with which any given structure occurs in nature. On this basis, the hexagonal close-packed structure would be an attractive non-cubic example to attempt.

It is to be hoped that the analysis presented here will raise awareness of the latent symmetries present in the two-dimensional lattice of the surface, even when the surface space group is of lower symmetry. In the study of chiral surfaces, for example, it is rare to find attention drawn to rectangular or rhombic two-dimensional lattices, and this state of affairs downplays the key role of layers beneath the topmost in breaking the latent mirror symmetry. The proper recognition of the highest symmetry two-dimensional lattice for a surface is, therefore, an outcome greatly to be desired.

[1] Ashcroft, N.W.; Mermin, N.D. *Solid State Physics* (Saunders, 1976).

[2] That there are only five possible Bravais lattices in two dimensions is an inherent property of space. Whether the surfaces of any specific three-dimensional crystal will collectively display examples of all five types is, on the other hand, contingent upon the symmetry of the parent three-dimensional Bravais lattice. In the case of the face-centred cubic crystal structure, considered here, it is well known that examples of all five two-dimensional lattice types may be found amongst its various surfaces.

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[11] Here it is worth noting explicitly that we adhere to the convention wherein Miller indices are divisors of the orthogonal axes of the conventional cubic unit cell for all cubic materials (whether simple, body-centred or face-centred). The alternative approach, in which Miller indices are multipliers of the primitive reciprocal lattice vectors, is practically essential in non-cubic materials, but it is not in common use for the cubic case.

[12] The squares of even numbers are always divisible by four; those of odd numbers always yield a remainder of unity upon division by four. Since three coprime integers must include one, two or three odd integers, it follows that the sum of their squares must yield remainder one, two or three upon division by four.

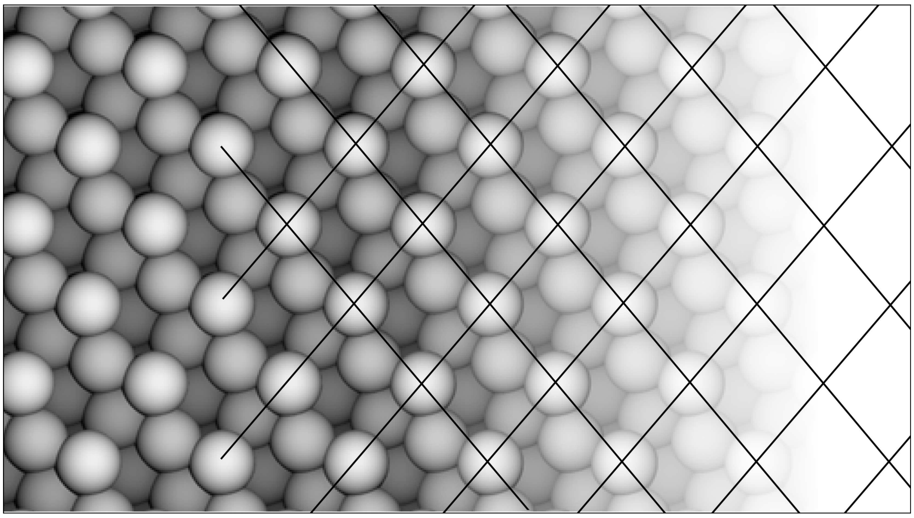

FIG. 5. **Table of Contents Graphic** - No matter how complex the surface, its periodic repetition reflects one of only five two-dimensional lattices; here a $\{531\}$ surface of a face-centred cubic metal displays its rhombic symmetry.