Oxford Chemistry Primers: Foundations of Surface Science

Solutions for Chapter Two: Symmetry and Structure

2.1. The space group of an ideal *fcc*-{211} surface is *p1m*. List all possible space groups that it could display after either reconstruction or adsorption. Which additional space groups would be possible for the {110} surface of the same material?

Upon reconstruction, or adsorption of an overlayer, the symmetry of a surface may be lowered to any of its sub-groups, as summarised by Fig. 2.4 in Section 2.3, so to answer the first part of this question we must simply identify the sub-groups of the *p1m* space group.

Consulting Fig. 2.4, we see that space groups *c1m* and *p1m* are mutual sub-groups of each other. This means that a surface conforming to the *c1m* sub-group could change its symmetry to *p1m* by reconstruction or adsorption, and equally a surface conforming to the *p1m* sub-group could change its symmetry to *c1m*. The latter is, therefore, one possible outcome for the {211} surface.

In addition, the *p1g* space group is a direct sub-group of *p1m*, and the *p1* sub-group is in turn a sub-group of *p1g*. In all, therefore, the result of adsorption or reconstruction on the {211} surface of an *fcc* crystal must conform to one out of the *p1m*, *c1m*, *p1g* or *p1* space groups. Note that we are able to reach these conclusions without having to sketch the {211} surface at all, let alone having to think about possible adsorption sites or atomic displacements.

Moving on, the question does not provide us with the space group for the ideal {110} surface of an *fcc* crystal, but this is stated to be *p2mm* in Fig. 2.5 (Section 2.4). Even if this hint were not present, however, we could come to this conclusion by examination of the structure shown in this figure, as follows. It is clear, in the first place, that the surface does not possess 6-fold, 4-fold or 3-fold rotational symmetry, but it does possess 2-fold rotational symmetry. This immediately restricts the possible space groups of the ideal surface to *c2mm*, *p2mm*, *p2mg*, *p2gg* or *p2*. The latter three may then be ruled out on the basis that the surface possesses two distinct mirror symmetries (parallel and perpendicular to the close-packed rows of its structure). Finally, the two-dimensional lattice of the surface is rectangular in nature, which rules out the *c2mm* space group (with its implied rhombic lattice) leaving us to conclude that the ideal {110} surface does indeed conform to *p2mm* symmetry.

The sub-groups of the *p2mm* space group include its mutual sub-group, *c2mm*, so this is certainly one possible result of adsorption or reconstruction. The only other direct sub-group is *p2mg*, but this in turn counts *p1m* and *c1m* as direct sub-groups, and hence all of the previously listed space groups obtainable on the {211} surface would also be obtainable on the {110} surface.

Furthermore, however, the *p2mg* space group also has another direct sub-group, namely the *p2gg* space group, from which one may descend either to the *p1g* space group (already counted amongst those accessible via the *p1m* or *c1m* sub-groups) or to the *p2* sub-group (which also permits access to the already-counted *p1* sub-group). In all, therefore, the possible results of adsorption or reconstruction upon the ideal {110} surface of an *fcc* crystal include, alongside all of those space groups listed previously for the ideal {211} surface, the space groups denoted *p2mm*, *c2mm*, *p2mg*, *p2gg* and *p2*.

2.2. For all of the surfaces depicted in Fig. 2.5, work out the coordination number of atoms in each of the top four layers. Given that the primitive unit cell areas for $\{111\}$, $\{100\}$, $\{110\}$, $\{311\}$, $\{210\}$, and $\{531\}$ surfaces are in the ratio 3: $2\sqrt{3}$: $2\sqrt{6}$: $\sqrt{33}$: $2\sqrt{15}$: $\sqrt{105}$, estimate the order of stability amongst these surfaces.

First let us note that these are surfaces of materials that take the face-centred cubic crystal structure, so the coordination number of atoms in the bulk is 12. We can most easily work out the coordination numbers of atoms near the surface by working out how many nearest neighbours each atom has in the layers above and below.

Starting with the $\{111\}$ surface, we can see by inspection that each atom within a given layer has 6 nearest neighbours within its own layer, 3 nearest neighbours within the layer below, and would (in bulk) have a further 3 nearest neighbours in the layer above. For atoms in the uppermost layer, these latter 3 neighbours are missing, giving a coordination number of 9. For the atoms in every layer lower than this (including the second, third and fourth layers) all nearest neighbours are present, so the coordination number is 12.

Turning to the $\{100\}$ surface, we can see (again by inspection) that each atom within a given layer has just 4 nearest neighbours within its own layer, 4 nearest neighbours within the layer below, and would (in bulk) have a further 4 nearest neighbours in the layer above. For atoms in the top layer, these latter 4 neighbours are missing, giving a coordination number of 8. For the atoms in every layer lower than this (including the second, third and fourth layers) all nearest neighbours are present, so the coordination number is 12.

Things get a little trickier to visualise for the $\{110\}$ surface, where each atom within a given layer clearly has only 2 nearest neighbours within its own layer. Careful inspection of the structure allows us to note 4 nearest neighbours for this atom in the layer below, and 1 nearest neighbour in the layer below that. Similarly, in bulk there would be 4 nearest neighbours in the layer above, and 1 nearest neighbour in the layer beyond. A quick summation confirms that this makes 12 in all. Based on this, we can see that an atom in the uppermost layer lacks 5 nearest neighbours (from the two layers that would have been present above it in the bulk) and hence has a coordination number of 7. An atom in the second layer, on the other hand, lacks only 1 nearest neighbour (from the next layer above but one) and hence has a coordination number of 11. An atom in the third layer lacks no nearest neighbours, and so has a coordination number of 12, and this is also true for the fourth and deeper layers.

For the $\{311\}$ surface, we again see that that each atom within a given layer possesses 2 nearest neighbours within its own layer. We can now, however, count for this atom only 3 nearest neighbours in the layer immediately below, but there are 2 further nearest neighbours in the layer below that. Similarly, each atom (in the bulk) would have 3 nearest neighbours in the layer above, and 2 nearest neighbours in the next layer above but one. Again, these numbers correctly sum to a coordination number of 12 for the bulk material. In the uppermost layer, however, each atom lacks 5 nearest neighbours (from the two layers that would have been present above it in the bulk) and hence has a coordination number of 7. An atom in the second layer, on the other hand, lacks only 2 nearest-neighbour atoms (from the next layer above but one) and hence has a coordination number of 10. An atom in the third layer lacks no nearest neighbours, and so has a coordination number of 12, and this is also true for the fourth and deeper layers.

Matters are trickier still for the $\{210\}$ surface, but the same systematic approach works nevertheless. Each atom within a given layer now has no nearest neighbours at all within its own layer, but has 3 in the layer immediately below, 2 in the layer below that, and 1 in the next layer down but two. Similarly, in the bulk it would have 3 nearest neighbours in the layer immediately above, 2 in the layer above that, and 1 in the next layer above but two. Consequently, in the uppermost layer, we see that each atom lacks 6 nearest neighbours (from the three layers that would have been present above it in the bulk) and hence has a coordination number of 6. In the second layer, each atom has 3 nearest neighbours more than this, due to the layer immediately above, and hence has a coordination number of 9. In the third layer, meanwhile, each atom has a further 2 nearest neighbours, due to the next layer above but one, giving a coordination number of 11. Atoms in the fourth layer and below have the full bulk coordination number of 12.

Finally, for the {531} surface, each atom within a given layer again has no nearest neighbour at all within its own layer, but it does have 2 nearest neighbours in the layer immediately below, 2 nearest neighbours in the layer below that, 1 nearest neighbour in the next layer down but two, and a further 1 nearest neighbour in the next layer down but three. As one might expect, this pattern is mirrored for the four layers above. This means that each atom in the uppermost layer lacks 6 nearest neighbours (from the four layers that would have been present above it in the bulk) and hence has a coordination number of 6. Each atom in the second layer has 2 additional nearest neighbours, due to the layer immediately above, giving a coordination number of 8, while each atom in the third layer has another 2 nearest neighbours, from the next layer above but one, giving a coordination number of 10. In the fourth layer, each atom lacks only 1 nearest neighbour and thus has a coordination number of 11. From the fifth layer down, all atoms have the bulk coordination number of 12.

Collating these results (Table I) we can see immediately that the total number of missing nearest neighbours per primitive surface unit cell (B_0) increases for each surface in the series (recall that there will be one atom per layer within such a cell, and that the number of missing nearest neighbours for each atom is simply the difference between its coordination number and the bulk coordination number of 12).

Surface	C_1	C_2	C_3	C_4	B_0	A_0	B_0/A_0	
{111}	9	12	12	12	3	3	1	$= 1.000$
{100}	8	12	12	12	4	$2\sqrt{3}$	$2\sqrt{3}/3$	$= 1.155$
{110}	7	11	12	12	6	$2\sqrt{6}$	$\sqrt{6}/2$	$= 1.225$
{311}	7	10	12	12	7	$\sqrt{33}$	$7\sqrt{33}/33$	$= 1.219$
{210}	6	9	11	12	10	$2\sqrt{15}$	$\sqrt{15}/3$	$= 1.291$
{531}	6	8	10	11	13	$\sqrt{105}$	$13\sqrt{105}/105$	$= 1.269$

Table 1: Coordination numbers (C_n) for atoms in layer n of various *fcc* surfaces. Also listed are primitive surface unit cell areas, A_0, normalised to an area of 3 for the {111} surface, and the total number of missing nearest neighbours, B_0, summed over the primitive surface unit cell.

In order to estimate surface stability, we can reasonably assume that the specific surface energy will be approximately proportional to B_0/A_0, where A_0 is the area of the primitive surface unit cell. Choosing our (arbitrary) units such that $A_0 = 3$ for the $\{111\}$ cell simplifies matters, since the area ratios given in the question can then be used directly to obtain A_0 for the other cells with minimal effort. It also happens to give $B_0/A_0 = 1$ for the $\{111\}$ surface, so that our estimated specific surface energies are expressly in units relative to that of the $\{111\}$ surface.

Notably, the two flat surfaces, $\{111\}$ and $\{100\}$, have the lowest estimated specific surface energies (1.000 and 1.155), while the two stepped surfaces, $\{110\}$ and $\{311\}$, have higher estimated specific surface energies (1.225 and 1.219) but are very similar to one another. The highest specific surface energies of all are estimated for the kinked $\{210\}$ and $\{531\}$ surfaces (1.291 and 1.269) although here the difference between the two is a little greater. All of these estimates, it should be stressed, fail to take into account (i) the role of interactions beyond nearest-neighbour level; (ii) the possibility that even nearest-neighbour interactions may vary with the local environment; and (iii) the stabilising effect of surface relaxations, which may be of greater importance for less symmetric and more structurally sparse surfaces than for relatively more symmetric and close-packed ones. Nevertheless, the predicted increase in specific surface energy from flat surfaces (no step edges) to stepped surfaces (straight step edges) to kinked surfaces (step edges with kinks) is typically borne out not only by more sophisticated models but also by experiment.

A further point to note, in passing, relates to the stability of surfaces against disorder. On a kinked surface, the coordination number in the uppermost layer is precisely half that of the underlying bulk (whether the bulk material be face-centred cubic, as here, or any other crystal structure). This means that removal of an atom from the ideal surface, thus creating a vacancy, involves breaking precisely the same number of nearest-neighbour interactions as would be re-made in placing that atom elsewhere on the ideal surface, thus creating an adatom. Accordingly, the creation of an adatom–vacancy pair would be essentially thermoneutral, if one were to ignore relaxation and longer-range interactions, and entropy would therefore favour the random creation of many such pairs. At any reasonable temperature, therefore, we expect kinked surfaces to be highly disordered. For stepped and flat surfaces, where the coordination number in the uppermost layer always exceeds that of any kinked surface, there is a distinct enthalpy cost to the creation of adatom–vacancy pairs, so disorder of this type occurs only at elevated temperatures (higher for flat surfaces than for stepped ones).

2.3. For each of the reconstructions depicted in Fig. 2.7, indicate the translational periodicity by means of both Wood's notation and matrix notation.

For the reconstruction of *fcc*-{100} shown in panel (a) of the figure, we have some flexibility in our labelling of the ideal primitive lattice vectors whilst satisfying the conditions of Eqn. 2.6 from Section 2.5. With the choice shown in Fig. 1.a, the unit cell of the reconstruction has one side that is identical to the $\mathbf{a}_1$ vector, and another that is five times longer than (and in the same direction as) the $\mathbf{a}_2$ vector. Wood's notation for this would then simply be (1×5) or p(1×5). A different valid choice of primitive lattice vectors, however, would give us (5×1) or p(5×1) instead. Retaining our original choice would give us a matrix notation of (1, 0; 0, 5), while the alternate choice would imply (5, 0; 0, 1).

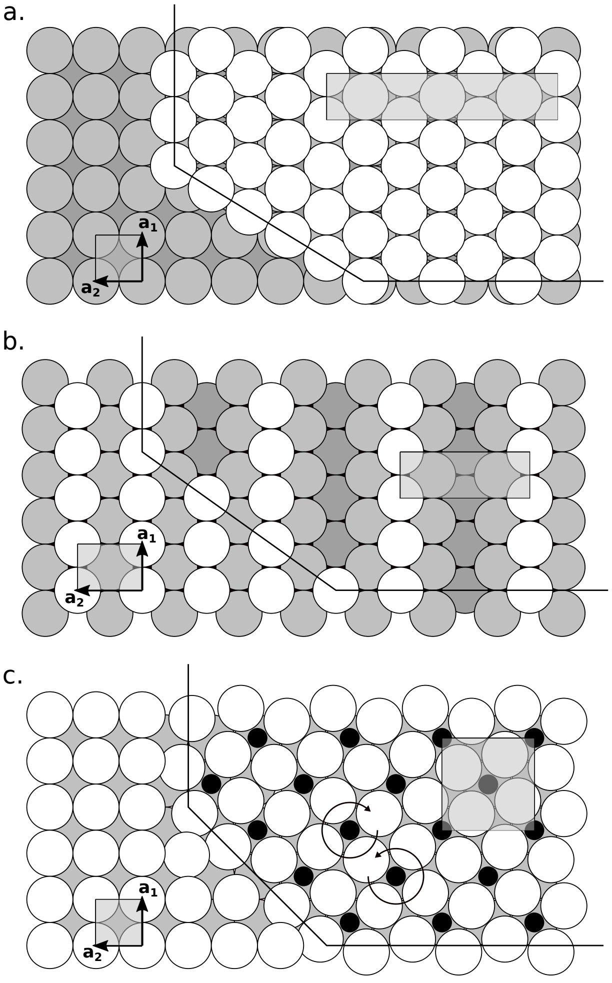

Figure 1: *Labelling of ideal primitive lattice vectors for the reconstructions shown in Fig. 2.7.*

Panel (b) shows a possible reconstruction of the *fcc*-{110} surface, and we have less flexibility in our choice of ideal primitive lattice vectors if we are to satisfy the conditions from Eqn. 2.6. Using the choice shown in Fig. 1.b, we see that the unit cell of the reconstruction has one side that is identical to the $\mathbf{a}_1$ vector, and another that is twice the length of (and in the same direction as) the $\mathbf{a}_2$ vector. Wood's notation for this would then simply be (1×2) or p(1×2), and no alternative choice for $\mathbf{a}_1$ and $\mathbf{a}_2$ satisyfing Eqn. 2.6 would yield anything different. In matrix notation, we would have (1, 0; 0, 2).

For panel (c) we return to the *fcc*-{100} surface, and again make the same choice as for panel (a) above (see Fig. 1.c). In this case, the unit cell of the reconstruction has one side that is twice the length of (and in the same direction as) the $\mathbf{a}_1$ vector, and another that is twice the length of (and in the same direction as) the $\mathbf{a}_2$ vector. Wood's notation for this situation is then simply (2×2) or p(2×2), and the corresponding matrix notation is (2, 0; 0, 2). Note that although the adatoms are arranged in a c(2×2) pattern, this would not be a correct designation for the overall superstructure, due to the incompatible displacements of the substrate atoms.

2.4. Potassium is adsorbed on a Ni{110} surface, forming an overlayer with c(2×2) periodicity. Assuming that no multilayer forms, suggest the most likely value of the coverage in ML units, and hence estimate the surface area per alkali metal adatom (taking the nickel lattice parameter to be 3.52 Å in its *fcc* crystal structure; the metallic and ionic radii of potassium may be taken as 2.20 Å and 1.52 Å respectively).

Here it will be useful to have at least an approximate idea of the surface unit cell dimensions. Let us start by converting the given lattice parameter of bulk nickel into a value for the metallic diameter of a nickel atom. In the *fcc* crystal structure, a diagonal drawn across one face of the conventional unit cell is equivalent to two metallic diameters, assuming the atoms to be close-packed spheres. With a cube side-length of 3.52 Å, this means that the metallic diameter of nickel must be 2.49 Å (multiplying by $\sqrt{2}$ to get the diagonal length, and dividing by 2 to get the diameter). Sketching the surface structure (Fig. 2, lower left in each panel) we see that the (1×1) cell of the {110} surface will have one side of length 2.49 Å, and another of 3.52 Å (i.e. a factor of $\sqrt{2}$ larger). The area of this cell will therefore be 8.76 Å^2.

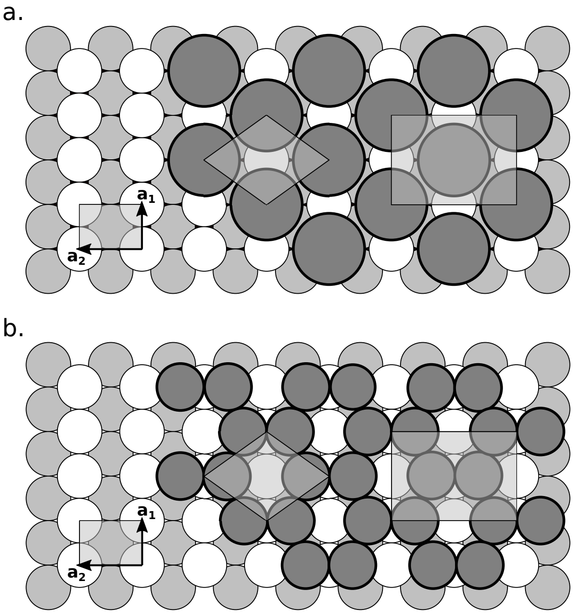

Figure 2: *Models for a c(2×2) potassium overlayer on Ni{110}, assuming (a) one adatom per primitive unit cell, and (b) two adatoms per primitive unit cell. The clean surface is shown for reference in the lower left in each case, with its primitive unit cell marked.*

Now, for a c(2×2) reconstruction one can construct a cell with doubled dimensions along both the $\mathbf{a}_1$ and $\mathbf{a}_2$ directions, and hence an area of 35.04 Å^2, but this will not be primitive. The prefix "c" implies that its central point is equivalent to its corners. A primitive cell would be lozenge-shaped, having an area just twice that of the (1×1) cell, which is to say 17.52 Å^2. Cells of both types are shown in Fig. 2.a. Also shown in that figure is one possible model for the overlayer, with precisely one potassium adatom per primitive unit cell. This would correspond to the lowest conceivable coverage consistent with the observed c(2×2) reconstruction. Note that the model shown assumes that the adatoms lie in atop sites, but one could easily slide the overlayer sideways to involve other sites instead. We cannot distinguish between sites on the basis of the information given in the question.

For the model shown, the spacing between the centres of two nearest-neighbour adatoms would be equal in length to the diagonal of the (1×1) cell, which can be determined (as the hypotenuse of a right-angled triangle) to be 4.31 Å. If the adatoms are thought of as non-overlapping spheres, this would give a maximum possible diameter for potassium that is not at all dissimilar to twice the metallic radius of the element given in the question ($2\times2.20 = 4.40$ Å) and would be consistent with the formation of a very slightly expanded metallic overlayer. Note that the maximum possible packing fraction (i.e. fraction of the cell area actually covered by the circular cross-section of its contained adatom) is just $\pi(4.31/2)^2/17.52 = 0.83$.

It is rather harder to visualise what an overlayer model containing two adatoms per primitive cell might look like, but an example is shown in Fig. 2.b. Clearly the overlayer atoms must be only slightly larger than the underlying nickel atoms if they are to be described as non-overlapping spheres. A little geometry (left as an exercise to the reader) will confirm that this particular model requires potassium atoms to be no more than about 8% greater in diameter than the nickel atoms, and that the packing fraction will be about 0.65. In this case, the circular cross-section of each adatom would have to be no larger than $17.52 \times 0.65/2 = 5.69$ Å^2, and the corresponding radius no larger than $\sqrt{(5.69/\pi)} = 1.35$ Å. This is substantially less than even the ionic radius given in the question (let alone the metallic radius) suggesting that the model coverage is far too high. Note, however, that our conclusion is not really based upon the specific details of our proposed model. We could shift the adatom around within the unit cell, to create any number of alternative models, but it is hard to imagine that any would have higher packing fractions than about 0.65, and so our logic would still hold. We therefore rule out all models containing two (or more) adatoms per primitive unit cell.

As a side note, we might mention the discussion of alkali-metal adsorption from Section 3.4, whereby ionic binding dominates at low coverage, giving way to more metallic bonding at high coverage. The results here are consistent with the notion that maximum packing within a single surface layer seems to be dictated by the metallic radius of potassium, rather than by its (smaller) ionic radius.

Finally, to return to the question, we are at last able to answer that the maximum coverage is 0.5 ML (i.e. one adatom per primitive $c(2\times2)$ cell, and hence half an adatom per (1×1) cell). The surface area per adatom is thus equal to the area of the primitive $c(2\times2)$ cell, or 17.52 Å^2.

2.5. The (135) surface of a face-centred cubic material possesses a two-dimensional real-space lattice that may be generated from the primitive real-space lattice vectors

$$\mathbf{a}_1 = \hat{\mathbf{x}} - 2\hat{\mathbf{y}} + \hat{\mathbf{z}}$$
$$\mathbf{a}_2 = 2\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}$$

where $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$ and $\hat{\mathbf{z}}$ are unit vectors aligned with the sides of the conventional bulk unit cell. Identify the lattice type, obtain the primitive reciprocal lattice vectors, and sketch the shape of the surface 1BZ.

It is good practice to convince ourselves, at the outset, that the given primitive real-space lattice vectors do, in fact, lie within the surface plane. We can do this by first calculating a supposed surface-normal unit vector consistent with these vectors (which we shall need later anyway) and checking that it lines up with our expectations based on the given Miller indices.

To do this, we shall first evaluate the vector product (also known as the cross product) between our two given primitive real-space lattice vectors, since this is guaranteed to yield a vector perpendicular to both. In fact, the vector product between two general vectors, **A** and **B**, may conveniently be calculated by expanding the following determinant

$$\begin{vmatrix} \hat{\mathbf{x}} & \hat{\mathbf{y}} & \hat{\mathbf{z}} \\ A_x & A_y & A_z \\ B_x & B_y & B_z \end{vmatrix}$$

where A_x, A_y and A_z are components of **A** along the $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$ and $\hat{\mathbf{z}}$ directions, and where B_x, B_y and B_z are similarly defined components of **B**. This produces a perpendicular vector of length equal to $AB\sin\theta$, with A and B being the lengths of **A** and **B** respectively, and with θ being the angle between them.

Using the primitive real-space lattice vectors given in the question, we get

$$\mathbf{a}_1 \times \mathbf{a}_2 = \begin{vmatrix} \hat{\mathbf{x}} & \hat{\mathbf{y}} & \hat{\mathbf{z}} \\ 1 & -2 & 1 \\ 2 & 1 & -1 \end{vmatrix} = \hat{\mathbf{x}} + 3\hat{\mathbf{y}} + 5\hat{\mathbf{z}}$$

and the length of this is simply $\sqrt{(1^2 + 3^2 + 5^2)} = \sqrt{35}$, giving us

$$\hat{\mathbf{n}} = \frac{1}{\sqrt{35}}\left[\hat{\mathbf{x}} + 3\hat{\mathbf{y}} + 5\hat{\mathbf{z}}\right]$$

as the supposed surface-normal unit vector.

As a (technically unnecessary) double-check on our arithmetic, we can now calculate the scalar product (also known as the dot product) of this vector with each of our primitive real-space lattice vectors. Recall that the scalar product of two general vectors, **A** and **B**, is just given by

$$\mathbf{A}.\mathbf{B} = A_x B_x + A_y B_y + A_z B_z$$

where the components of **A** and **B** are defined as before. It is left as an exercise for the reader to confirm that the scalar product of $\hat{\mathbf{n}}$ with either $\mathbf{a}_1$ or $\mathbf{a}_2$ will yield a result of precisely zero. Since an alternative form of the scalar product is simply $AB\cos\theta$, this then confirms that both $\mathbf{a}_1$ and $\mathbf{a}_2$ must lie at right-angles to the surface-normal unit vector.

The question, then, is whether the supposed surface-normal unit vector we have just calculated does, indeed, point in the same direction as would be implied by the Miller indices. In a general case, we really ought to refer to the definition of Miller indices given in Section 2.3 of the text, where the surface plane (hkl) is determined by its intercepts with the primitive real-space lattice vectors falling at fractional distances $1/h$, $1/k$, and $1/l$. Proving that our calculated surface-normal unit vector does indeed lie perpendicular to the surface plane will then generally involve us in some potentially quite tricky geometry. Fortunately, however, the system we are discussing here is cubic, and this allows us to make use of the following very convenient observation...

In cubic systems (and *only* in cubic systems) the surface-normal unit vector simply points in the direction $h\hat{\mathbf{x}} + k\hat{\mathbf{y}} + l\hat{\mathbf{z}}$ (so long as our cubic bulk unit cell was aligned with the $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$ and $\hat{\mathbf{z}}$ unit vectors). This statement is emphatically **not true** for non-cubic lattices, and was omitted from the main text of this book because it is *dangerous* to have it lurking in one's head as a possible way to define the surface normal. Now that you have seen this statement, you must solemnly promise to remember not to rely upon it unless your system is cubic. Since our present system *is* cubic, however, we can use it to confirm that our vector $\hat{\mathbf{n}}$ does, indeed, point in the correct direction for the (135) surface.

After this rather lengthy preamble, we may now move on to tackle the problem we have actually been set.

First, we might usefully check whether the given primitive real-space lattice vectors are of equal length or not. In this instance, we can see quite readily that this is true, since $\sqrt{(1^2+2^2+1^2)} = \sqrt{(2^2+1^2+1^2)} = \sqrt{6}$ in whatever units we happen to be using. This rules out the rectangular and oblique lattice types, for which a pair of primitive real-space lattice vectors cannot be of equal length.

Next, we need to work out the angle between our two vectors, which is most easily done by first evaluating their scalar product, obtaining $\mathbf{a}_1.\mathbf{a}_2 = (1\times 2) - (2\times 1) - (1\times 1) = -1$ in our case. Remembering that the scalar product of two vectors can also be thought of as the product of their two lengths and the cosine of the angle between them, and knowing that the lengths in this case are both $\sqrt{6}$, we have

$$\cos\theta = -1/6$$

and thus $\theta = 99.6^\circ$. This eliminates the square and triangular lattices, for which the corresponding angle would be 90° or 120° respectively, leaving the rhombic lattice as the only remaining possibility.

To obtain the primitive reciprocal lattice vectors, we need to evaluate the expressions from Eqn. 2.11 in Section 2.6, namely

$$\mathbf{b}_1 = 2\pi\frac{\mathbf{a}_2\times\hat{\mathbf{n}}}{|\mathbf{a}_1\times\mathbf{a}_2|};\quad \mathbf{b}_2 = 2\pi\frac{\hat{\mathbf{n}}\times\mathbf{a}_1}{|\mathbf{a}_1\times\mathbf{a}_2|}$$

where we are indeed fortunate to have already calculated both the surface-normal unit vector, $\hat{\mathbf{n}}$, and the length of the vector $\mathbf{a}_1\times\mathbf{a}_2$.

We then have

$$\mathbf{a}_2 \times \hat{\mathbf{n}} = \frac{1}{\sqrt{35}} \begin{vmatrix} \hat{\mathbf{x}} & \hat{\mathbf{y}} & \hat{\mathbf{z}} \\ 2 & 1 & -1 \\ 1 & 3 & 5 \end{vmatrix} = \frac{1}{\sqrt{35}} \left[8\hat{\mathbf{x}} - 11\hat{\mathbf{y}} + 5\hat{\mathbf{z}}\right]$$

and

$$\hat{\mathbf{n}} \times \mathbf{a}_1 = \frac{1}{\sqrt{35}} \begin{vmatrix} \hat{\mathbf{x}} & \hat{\mathbf{y}} & \hat{\mathbf{z}} \\ 1 & 3 & 5 \\ 1 & -2 & 1 \end{vmatrix} = \frac{1}{\sqrt{35}} \left[13\hat{\mathbf{x}} + 4\hat{\mathbf{y}} - 5\hat{\mathbf{z}}\right]$$

for our numerators. Using these, we find

$$\begin{aligned} \mathbf{b}_1 &= \frac{2\pi}{35} \left[8\hat{\mathbf{x}} - 11\hat{\mathbf{y}} + 5\hat{\mathbf{z}}\right] \\ \mathbf{b}_2 &= \frac{2\pi}{35} \left[13\hat{\mathbf{x}} + 4\hat{\mathbf{y}} - 5\hat{\mathbf{z}}\right] \end{aligned}$$

as our primitive reciprocal lattice vectors. Despite looking quite different in form, these are of equal length to one another $(2\pi\sqrt{(8^2 + 11^2 + 5^2)}/35 = 2\pi\sqrt{(13^2 + 4^2 + 5^2)}/35 = 2\pi\sqrt{210}/35)$ reflecting the fact that the primitive real-space lattice vectors were themselves of equal length.

If we are sufficiently confident in our working, it may be acceptable to move on to the final part of the question, but it is better practice to double-check our results. We can do this because the expressions in Eqn. 2.11 are explicitly designed to ensure that the following identity holds true

$$\mathbf{a}_p.\mathbf{b}_q = 2\pi\delta_{pq}$$

where δ_{pq} is the Kronecker delta (i.e. unity if the indices are equal, zero if unequal). This, in turn, guarantees that the scalar product between any one of our real-space lattice vectors and any one of our reciprocal lattice vectors must be an integer multiple of 2π (see Eqn. 2.10 in Section 2.6).

For our first check, setting $p = q = 1$, we get

$$\begin{aligned} \mathbf{a}_1.\mathbf{b}_1 &= \frac{2\pi}{35} \left[\hat{\mathbf{x}} - 2\hat{\mathbf{y}} + \hat{\mathbf{z}}\right].\left[8\hat{\mathbf{x}} - 11\hat{\mathbf{y}} + 5\hat{\mathbf{z}}\right] \\ &= \frac{2\pi}{35} \left[(1 \times 8) + (2 \times 11) + (1 \times 5)\right] \\ &= 2\pi \end{aligned}$$

while with $p = 1$ and $q = 2$ we have

$$\begin{aligned} \mathbf{a}_1.\mathbf{b}_2 &= \frac{2\pi}{35} \left[\hat{\mathbf{x}} - 2\hat{\mathbf{y}} + \hat{\mathbf{z}}\right].\left[13\hat{\mathbf{x}} + 4\hat{\mathbf{y}} - 5\hat{\mathbf{z}}\right] \\ &= \frac{2\pi}{35} \left[(1 \times 13) - (2 \times 4) - (1 \times 5)\right] \\ &= 0 \end{aligned}$$

as expected. The other two combinations are left as an exercise for the reader.

For the last part of the question, we are asked to sketch the shape of the surface 1BZ. To do this, it will be necessary first to sketch (fairly accurately) a portion of the surface reciprocal lattice. We have already shown that the two primitive reciprocal lattice vectors are of equal length to one another ($2\pi\sqrt{210}/35$) but it would be useful to obtain the angle between them. Let us, therefore, calculate one last scalar product, namely $\mathbf{b}_1.\mathbf{b}_2 = 4\pi^2\left[(8 \times 13) - (11 \times 4) - (5 \times 5)\right]/35^2 = 4\pi^2/35$. We can therefore write

$$\begin{aligned}\cos\theta' &= \frac{4\pi^2/35}{(2\pi\sqrt{210}/35)^2} \\ &= \frac{1}{6}\end{aligned}$$

and hence $\theta' = 80.4^\circ$ for the angle between the primitive reciprocal lattice vectors (note, in passing, that $\theta + \theta' = 180^\circ$, which must be true in all cases).

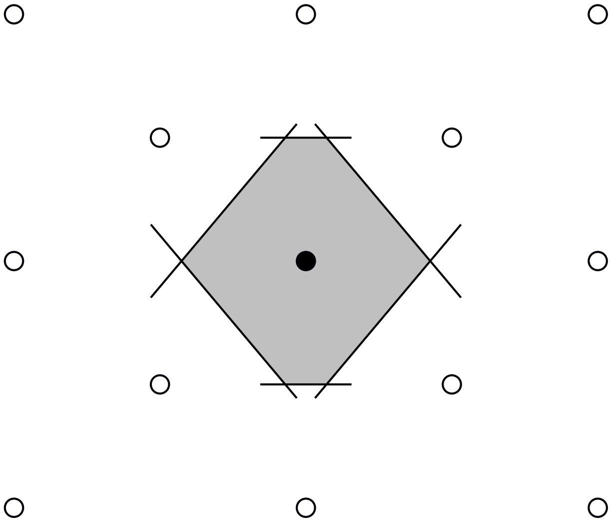

Figure 3: *Scale drawing of the reciprocal lattice, with the 1BZ shaded (and bounded by perpendicular bisectors of reciprocal lattice vectors).*

Now we can make a reasonable scale drawing of the reciprocal lattice (Fig. 3) onto which we may add construction lines perpendicularly bisecting the reciprocal lattice vectors. Once we have drawn enough to identify a region lying closer to the origin than to any other reciprocal lattice point, we will have succeeded in highlighting the 1BZ.