CRYSTAL SYMMETRY, X-RAY DIFFRACTION, AND PHYSICAL PROPERTIES

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Lecture 36: Introduction to Space Groups

In this lecture, we will begin our discussion on space groups in three dimensions. We have already developed all the three-dimensional point groups as well as the fourteen Bravais lattices. These two can now be combined to obtain the three-dimensional space groups. Since there are fourteen Bravais lattices and 32-point groups, their combination leads to a total of 230 space groups. We are not going to discuss all 230 space groups; instead, we will focus only on a small fraction. You will see that the development of space groups follows lines very similar to those used earlier for plane groups.

Let us begin with the triclinic lattice. Consider a triclinic unit cell with no symmetry at all. I will draw only a two-dimensional view of it. This is the a axis, this is the b axis, and the c-axis is coming out of the plane. As you know, for the triclinic system, there are no constraints on a, b, and c, and there are also no constraints on the angles α, β, and γ. If I now place an asymmetric motif, represented by a symbol, and use a plus sign to indicate that the motif lies above the ab plane, then translation by $\bar{b}$ will take it to this position, translation by a will take it here, and translation by $-\bar{b}$ will bring it to this position. This generates the pattern for the first space group, which we will label for now as $P1$.

Now, suppose we add inversion symmetry to this $P1$ space group. Let us introduce inversion centers, denoted by small circles. There will be inversion centers at the corners as well as one at the center of the unit cell, which lies at the body-centered position. If we place an asymmetric motif above the ab plane, inversion will take it below the plane, and this will be designated by a minus sign. In addition, inversion changes handedness, so a small comma is used to indicate that a right-handed motif has transformed into a left-handed one. Translations then generate the full pattern. This space group is denoted as $P\bar{1}$. These are the first two space groups, which are relatively simple and involve very little symmetry. As we already know, inversion does not impose any constraints on the lattice parameters.

Let us now move on to the monoclinic lattice. In the monoclinic system, there are no constraints on a, b, and c, and no constraint on γ, while α and β are constrained to be 90°. There are two monoclinic lattices: the simple monoclinic and the end-centered monoclinic. From the previous lecture, we know that the point groups 2, m, and $2/m$ can be associated with these lattices. If we were to simply multiply, we might expect six space groups; however, the actual number is larger, and in fact, there are thirteen monoclinic space groups.

Let us start with the simple monoclinic lattice with only a twofold rotational symmetry, taken along the c axis, which is therefore the unique axis and is oriented vertically. If a motif is placed above the ab plane, the twofold rotation will rotate it by 180° to this position, and translations will then generate motifs at all corners. You can observe that motifs related by the twofold rotation coincide with one another. This space group is denoted in long notation as $P112$. The capital P indicates a primitive three-dimensional lattice, there is no symmetry along a or b axes, and a twofold rotation along c axis, which is the unique axis.

Consider another example of a simple monoclinic lattice, this time with a mirror plane. Let the ab plane be the mirror plane. In three dimensions, the mirror plane is indicated using a symbol outside the diagram to show that reflection occurs in the ab plane. If we place a motif above the ab plane, the mirror reflects it directly downward. Since the two motifs overlap in projection, the motif is divided into two halves: the right half represents the motif above the plane with a plus sign, and the left half represents the reflected motif below the plane with a minus sign. Because reflection changes handedness, a comma is added to the left half. Translations then generate the complete pattern. This space group is denoted as $P11m$, where again the C axis is the unique axis because it is perpendicular to the mirror plane.

Now let us consider the end-centered monoclinic lattice with only a twofold rotational symmetry. Let the A face be end-centered, and let the centering lattice point be displaced by $c/2$. The twofold axes are introduced, and we begin placing motifs. A motif placed above the ab plane is rotated by 180° to another position, and translations generate additional motifs. However, there is an additional centering translation that must be considered, which moves a motif from the origin to the lattice point at the center of the BC face. Since the c axis is vertical, this centering translation vector is given by $\bar{t} = \bar{b}/2 + \bar{c}/2$. This is indicated by marking the motif as being halfway up relative to the original motif.

Analyzing this pattern, let us label the original motif as motif 1. A 180° rotation takes it to motif 2, and the centering translation $\bar{b}/2 + \bar{c}/2$ takes motif 2 to motif 3. We now ask how motif 1 is related to motif 3. There is no change in handedness, since neither reflection nor inversion is involved. If we consider a point located one quarter along $\bar{b}$ from the origin, a rotation of motif 1 by 180° about this point brings it to a position directly below motif 3. A subsequent translation upward by $\bar{c}/2$ brings it into coincidence with motif 3.

This combined operation, consisting of a rotation followed by a translation, is known as a screw operation. Since the rotation involved is 180°, this symmetry element is called a twofold screw axis. To visualize this, consider a twofold screw axis and an asymmetric motif. A rotation of 180° moves the motif to a new position, followed by a translation of $\bar{c}/2$ along the axis. Repeating this operation moves the motif again by 180° and another translation of $\bar{c}/2$. After two such operations, the net effect is a translation by $\bar{c}$. Thus, for a twofold screw axis, the translational component is exactly half the lattice translation. This property is specific to the twofold case and will not generally hold for threefold, fourfold, or sixfold screw axes, which we will discuss later.

Now, another point concerns the symbol used for the screw axis. The symbol starts out like a twofold axis, but we add small markers to indicate that this is a twofold screw rotational symmetry. Going back to the previous diagram, we now insert the screw axis into this space-group diagram. Thus, there will be a screw axis located here, and similarly another one located here. The translational symmetry will also reproduce the screw axis at this location. If we now examine the relation between points 1 and 4, we ask how we go from 1 to 4 and from 4 back to 1. There will be a screw axis located here and another screw axis located here. With this, the diagram for this particular space group is complete.

Now, what notation should be used for this diagram? First, the initial letter must indicate whether the lattice is primitive or non-primitive. In this case, it is end-centered, and the centering face is the A face. Therefore, the symbol starts with A. Again, there is no symmetry along the A and B directions, so we write 1 1, and we have introduced a twofold symmetry along the unique axis c. Hence, the notation for this space group is A112.

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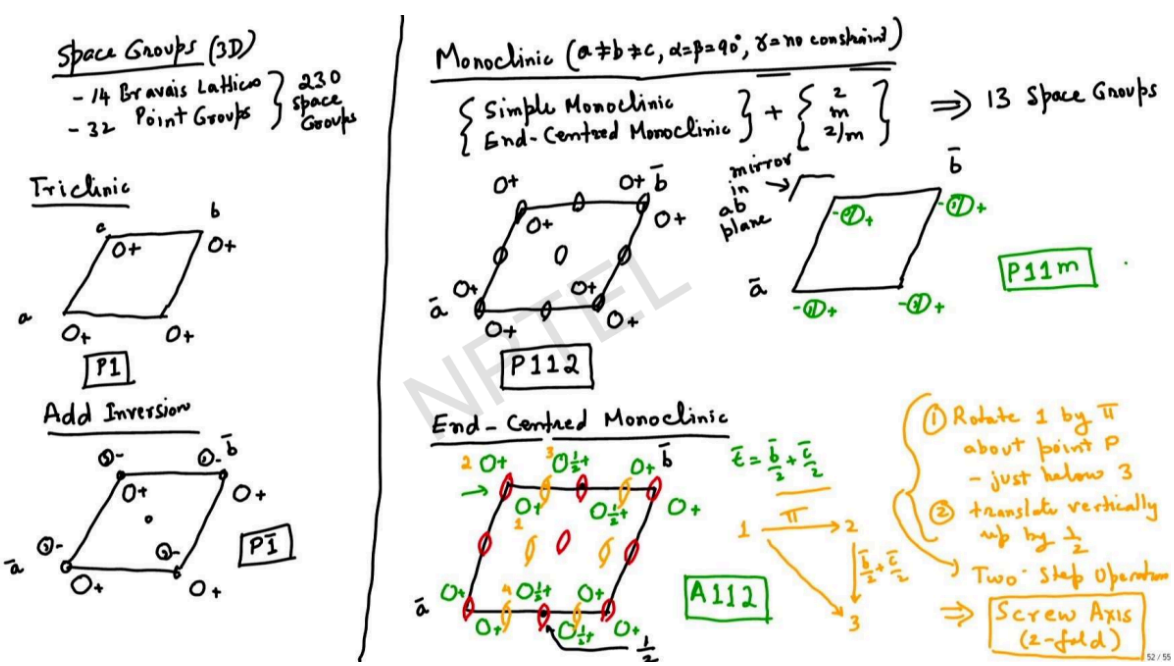

Before discussing the screw axis further, let us consider another space group based on the monoclinic system, specifically the end-centered monoclinic system. End-centered monoclinic means that we again have a lattice point at the center of the A face. This time, instead of a twofold axis, there is a mirror plane in the ab plane. We have already seen this situation for the primitive case. If it were primitive, the notation would be $P11m$. Here, it is end-centered, and the mirror plane is still in the ab plane.

Accordingly, the motifs are distributed in this manner. What we see initially is only the primitive part, but now we must also consider the centering translation of $\bar{b}/2 + \bar{c}/2$. As a result, this motif moves to this position. It undergoes a half translation, with a change in handedness, and appears at a half-minus position. Similarly, translation along b will bring another motif here, again with half-plus and half-minus positions. This is how the overall pattern appears.

Next, we analyze this pattern to determine whether any additional symmetry is present. Consider motif number 1, which is right-handed and located above the ab plane. The mirror plane takes it to motif number 2, which is left-handed and located below the ab plane. Motif 2 is taken to motif 3 by the centering translation of $\bar{b}/2 + \bar{c}/2$. The handedness remains the same, namely left-handed, and the motif moves to a half-minus position.

Summarizing these operations, the transformation from 1 to 2 is a mirror operation σ, and the transformation from 2 to 3 is the translation $\bar{b}/2 + \bar{c}/2$. We now ask how we go directly from 1 to 3. This is something you may be able to infer by thinking about it carefully.

In going from 1 to 3, there is a change in handedness as well as a translation. Clearly, this corresponds to a glide plane, similar to what we have seen earlier. The operation consists of two steps: reflection followed by translation. The motif is first reflected to the negative position, and then the centering translation moves it to position 3, where it lies at a half-minus height.

Thus, there is a glide plane present. The location of this glide plane must be between motifs 1 and 3. In fact, it lies exactly one quarter along the c axis above the ab plane. We represent this glide plane graphically in this way, and we explicitly indicate its position by writing $1/4$, signifying that the glide plane is located one-fourth of the unit cell along the c axis above the ab plane. The arrow drawn on the plane indicates the direction of the glide translation, which is along the B direction and has a magnitude of $\bar{b}/2$.

Now, let us determine the notation for this space group. First, it is an A-centered lattice. There is no symmetry along $\bar{a}$ or $\bar{b}$, and there is a mirror plane. Therefore, the notation is $A11m$. In this construction, we have introduced centering and mirror symmetry, and the analysis reveals the presence of glide symmetry as well.

When we say that many space groups arise from the monoclinic system, what we mean is that we can systematically generate them by adding screw axes or glide planes to simpler monoclinic lattices. For example, we can add a screw axis to a primitive monoclinic lattice, or we can add a glide plane to a primitive monoclinic lattice, thereby generating additional space groups.

Let us briefly illustrate this. Consider a primitive monoclinic lattice and replace the twofold axis with a screw axis. There will also be a screw axis at the center. Thus, only a twofold screw axis is present, and no pure twofold rotational axis exists. If we place motifs in this lattice, a motif above the ab plane is taken to a half-plus position, and translations reproduce the motif at all corners of the cell.

What should we call this space group? Since it is primitive, we start with P. There is no symmetry along $\bar{a}$ or $\bar{b}$, so we write 1 1. Along the unique axis $\bar{c}$, however, there is a twofold rotational symmetry of the screw type. The appropriate symbol for this is 2_1. The logic behind this notation will be explained in more detail when we discuss screw axes explicitly in the next lecture.

Finally, let us add a glide plane to a primitive monoclinic lattice. In this case, since no numerical subscript is written, the glide plane lies in the ab plane. A motif above the plane is translated to all corners of the cell, and we must also apply the glide translation. Starting with the motif in the top left, we reflect it so that it moves downward and then translate it by $\overline{b}/2$. It becomes left-handed and lies below the ab plane. Applying the same operations elsewhere produces the full pattern.

The notation for this space group is $P11b$. We cannot write m because this is not a simple mirror plane but a glide plane. The lowercase letter b indicates that the glide translation is along the b direction. In general, lowercase letters such as a, b, or c indicate glide translations along the corresponding crystallographic directions. Other symbols, such as n are also used, and we will discuss all of these in subsequent lectures.

With this, I conclude the lecture. We will continue this discussion in the next lecture.

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