CRYSTAL SYMMETRY, X-RAY DIFFRACTION, AND PHYSICAL PROPERTIES

Prof. Sandeep Sangal
IIT Kanpur

Lecture 59(B): Third Rank Piezoelectric Property Tensor-II

Now, let us consider a tetragonal crystal. The reason for choosing a tetragonal crystal is that some of the examples of materials exhibiting piezoelectric behavior, such as barium titanate and lead zirconate titanate, possess a tetragonal crystal structure with the space group $P4mm$. Thus, we focus on the tetragonal crystal system.

Let us place the fourfold rotation axis parallel to the x_3 axis. Accordingly, we have the coordinate axes x_1, x_2, and x_3, with a fourfold rotation axis along x_3. A fourfold rotation corresponds to a rotation by 90°. As a result of this rotation, x'_1 coincides with x_2, x'_2 points in the direction opposite to x_1, and x'_3 coincides with x_3. This transformation has already been discussed in the context of second-rank tensors, and therefore the derivation of the corresponding direction cosine matrix will not be repeated here. The direction cosine matrix for this operation is

$$\begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

Let us now examine how the piezoelectric tensor transforms under this symmetry operation. The transformation rule is given by

$$d'_{ijk} = a_{il}a_{jm}a_{kn}d_{lmn}.$$

We evaluate a few components explicitly. Consider, for example, the component d'_{111}. From the direction cosine matrix, the only nonzero contribution arises from the product $a_{12}a_{12}a_{12}d_{222}$. Since $a_{12} = 1$, this gives

$$d'_{111} = d_{222}.$$

Next, consider how d_{222} transforms. The transformed component is

$$d'_{222} = a_{21}a_{21}a_{21}d_{111}.$$

Here, $a_{21} =- 1$, and therefore

$$d'_{222} = (-1)(-1)(-1)\, d_{111} =- d_{111}.$$

For a 90° rotation to be a symmetry operation, the tensor must remain unchanged. The only way this condition can be satisfied is if

$$d_{111} = d_{222} = 0.$$

Now consider the component d'_{333}. This transforms as

$$d'_{333} = a_{33}a_{33}a_{33}d_{333}.$$

Since $a_{33} = 1$, this gives

$$d'_{333} = d_{333},$$

and therefore this component is nonzero and survives the symmetry operation.

Similarly, consider the component d'_{123}. This transforms as

$$d'_{123} = a_{12}a_{21}a_{33}d_{213}.$$

Using $a_{12} = 1$, $a_{21} =- 1$, and $a_{33} = 1$, we obtain

$$d'_{123} =- d_{213}.$$

Proceeding in this manner, without explicitly writing all components, one finds that $d_{113} = d_{223}$ and $d_{311} = d_{322}$, while all other components vanish.

We now express these results using the reduced index notation. For reference, d_1 in the reduced matrix corresponds to d_{11}, d_2 corresponds to d_{22}, and d_3 corresponds to d_{33}. Similarly, the component d_{123} corresponds to a reduced-index component, and $-d_{213}$ corresponds to another reduced-index component. The mapping between full indices and reduced indices follows directly from the index-reduction scheme discussed earlier.

At this stage, it is convenient to adopt a compact notation commonly used in standard textbooks. Instead of writing numerical values explicitly, a symbolic matrix is used. In this notation, a dot indicates that the corresponding component is zero. A filled circle indicates a nonzero component. If two filled circles of the same color are connected, the corresponding components are equal. If two filled circles of different colors are connected, the corresponding components are equal in magnitude but opposite in sign.

Now, suppose that in addition to the fourfold rotation axis, a vertical mirror plane is introduced. Referring back to the point group discussion, a vertical mirror plane is one that contains the fourfold axis. In this case, the x_2x_3 plane acts as a mirror plane. When this mirror symmetry is added, the resulting point group is $4mm$.

Let us examine the effect of this mirror operation. The mirror reflects the x_1 axis, so that x_1 transforms to $x'_1 = -x_1$, while x_2 and x_3, being in the mirror plane, remain unchanged. The corresponding direction cosine matrix is

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

Consider a specific component, for example d'_{123}. In reduced notation, this corresponds to d'_{14}. The transformation of d_{123} is given by

$$d'_{123} = a_{11}a_{22}a_{33}d_{123}.$$

Substituting the values from the direction cosine matrix, we obtain

$$d'_{123} = (-1)(1)(1)\,d_{123} = -d_{123}.$$

For the tensor to remain invariant under reflection in the x_2x_3 plane, this component must therefore satisfy

$$d_{123} = 0.$$

From the fourfold rotation symmetry, we already had $d_{123} = d_{213}$. Consequently, d_{213} must also vanish. In reduced notation, these correspond to the components d_{14} and d_{25}, and both of these components become zero. Performing a similar analysis for the remaining components shows that all other allowed components remain unchanged.

The resulting piezoelectric tensor then contains only the components d_{311}, d_{322}, and d_{333}, along with d_{113} and d_{223}. Furthermore, symmetry requires that

$$d_{311} = d_{322},$$

and the remaining two off-diagonal components are also equal. Thus, only three independent components remain.

Among these, the component d_{333}, or equivalently d_{33} in reduced notation, is the most important piezoelectric modulus. This is because, in practical applications such as a gas lighter, pulling the trigger compresses the piezoelectric crystal uniaxially along the x_3 direction. As a result, the response is dominated by the d_{33} modulus, while the other two components are less significant.

Therefore, for materials belonging to the space group or point group $4mm$, it is essential to examine the magnitude of the d_{33} modulus when assessing their suitability for a given application. With this, the discussion is concluded.

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