CRYSTAL SYMMETRY, X-RAY DIFFRACTION, AND PHYSICAL PROPERTIES

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Lecture 59(A): Third Rank Piezoelectric Property Tensor-I

In the previous lecture, the discussion on second rank property tensors was completed, and several important physical properties that can be represented using second rank tensors were listed. In this lecture, the focus shifts to one specific property; however, before doing so, it is useful to consider a familiar physical example.

One may recognize an ordinary gas lighter, which produces a flame when its trigger is pressed. If such a gas lighter is opened, several components can be observed. On one side, there is a small tank filled with butane. When the trigger is pressed, a valve opens and allows the butane gas to flow out through the tip of the lighter. Simultaneously, the trigger performs another function that is essential for ignition. A specific crystalline component inside the lighter generates a high voltage when mechanical force is applied. When the trigger is pressed, two wires at the tip of the lighter produce a visible spark, which ignites the escaping gas. This is the basic working principle of a simple gas lighter.

The crystalline material responsible for generating this voltage is known as a piezoelectric crystal. The defining property of a piezoelectric material is that when mechanical stress is applied to it, an electric polarization develops, resulting in the generation of a voltage. In a gas lighter, the voltage produced is of the order of several thousand volts, which is sufficient to generate a spark. Despite the high voltage, these devices are safe because the current involved is extremely small, typically of the order of milliamperes. Nevertheless, touching the two exposed wires while pressing the trigger may result in a mild electric shock, and such an experiment is not advisable.

The piezoelectric effect referred to here is known as the direct piezoelectric effect. In this effect, the application of stress to a crystal leads to the development of surface charges, or polarization, with one surface becoming positively charged and the opposite surface

negatively charged. This separation of charge produces the voltage required for applications such as spark generation.

Piezoelectric materials have a wide range of applications, including actuators, sensors, ultrasonic devices, medical ultrasound imaging systems, and everyday devices such as gas lighters. These applications span from low-end consumer products to high-end technological systems.

Some important examples of piezoelectric materials include quartz or silica, SiO_2, which was one of the earliest known piezoelectric materials, lead zirconate titanate, and barium titanate. The chemical formula for lead zirconate titanate is $Pb[Zr_xTi_{1-x}]O_3$, while that for barium titanate is $BaTiO_3$.

Consider barium titanate first. Its crystal structure depends strongly on temperature. Above $120^{\circ}C$, barium titanate has a cubic crystal structure with space group $P\frac{4}{m}\bar{3}\frac{2}{m}$ and point group $\frac{4}{m}\bar{3}\frac{2}{m}$. The point group is particularly important when discussing tensor properties. This point group contains a center of symmetry, which plays a crucial role in determining whether certain tensor properties can exist. In this high-temperature cubic structure, barium ions occupy the corners of the cube, oxygen ions are located at the face centers, and the Ti^{4+} ion is positioned at the body center.

When the temperature falls below $120^{\circ}C$, the structure of barium titanate is no longer cubic. It undergoes a phase transition to a tetragonal structure. In this phase, the Ti^{4+} ion shifts slightly away from the center of the unit cell, and the other ions also undergo small displacements. As a result, the structure loses its center of symmetry. The space group becomes $P4mm$ and the corresponding point group is $4mm$. As discussed in earlier lectures on crystal symmetry, this point group does not possess a center of symmetry.

Lead zirconate titanate has a crystal structure similar to that of tetragonal barium titanate, with space group $P4mm$ and point group $4mm$. This structure is also non-centrosymmetric. Quartz, in contrast, is a rhombohedral crystal with space group $P3_121$ or $P3_221$, depending on specific structural details. These space groups correspond to numbers 152 and 154, respectively, in the International Tables for Crystallography. Quartz is also non-centrosymmetric. The space group $P4mm$ is listed as number 99 in the International Tables. All of these materials exhibit piezoelectric behavior because their crystal structures lack a center of symmetry.

Among these materials, lead zirconate titanate is the most commonly used for piezoelectric applications, primarily because it can operate over a wide temperature range. Its Curie temperature is approximately $350^{\circ}C$, above which it loses its piezoelectric properties. Typical operating temperatures are around $200^{\circ}C$. Barium titanate, on the other hand, has a phase transition at $120^{\circ}C$, with a more practical operating temperature closer to $100^{\circ}C$. This limitation represents a significant disadvantage of barium titanate compared to lead zirconate titanate.

Turning now to the tensorial description of the piezoelectric effect, when stress is applied to a crystal, polarization develops. This relationship can be written in matrix form as

$$P = d\,\sigma,$$

where σ is the stress tensor, P is the polarization vector, and d is the piezoelectric tensor. The stress tensor σ is a second rank tensor and represents the applied mechanical cause, while the polarization P is the response. The piezoelectric tensor d is a third rank tensor.

A third rank tensor has $3^3 = 27$ components. It can be visualized as consisting of three layers of 3×3 matrices, forming a cube-like arrangement. In tensor notation, the piezoelectric relationship can be written as

$$p_i = d_{ijk}\sigma_{jk},$$

where p_i are the components of the polarization vector, d_{ijk} are the components of the third rank piezoelectric tensor, and σ_{jk} are the components of the stress tensor. Here, j and k are dummy indices, while i is a free index.

And now, to be absolutely clear about the stress tensor, let me explicitly write down the form of the stress tensor σ, which has already been described earlier. The components of the stress tensor are σ_{11}, σ_{12}, σ_{13}, σ_{21}, σ_{22}, σ_{23}, σ_{31}, σ_{32}, and σ_{33}.

$$\sigma = \begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{12} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{pmatrix}$$

It should be noted here that the symbol for stress is σ, while the same symbol is also used for electrical conductivity. However, from the context, it should be clear that σ here refers to stress.

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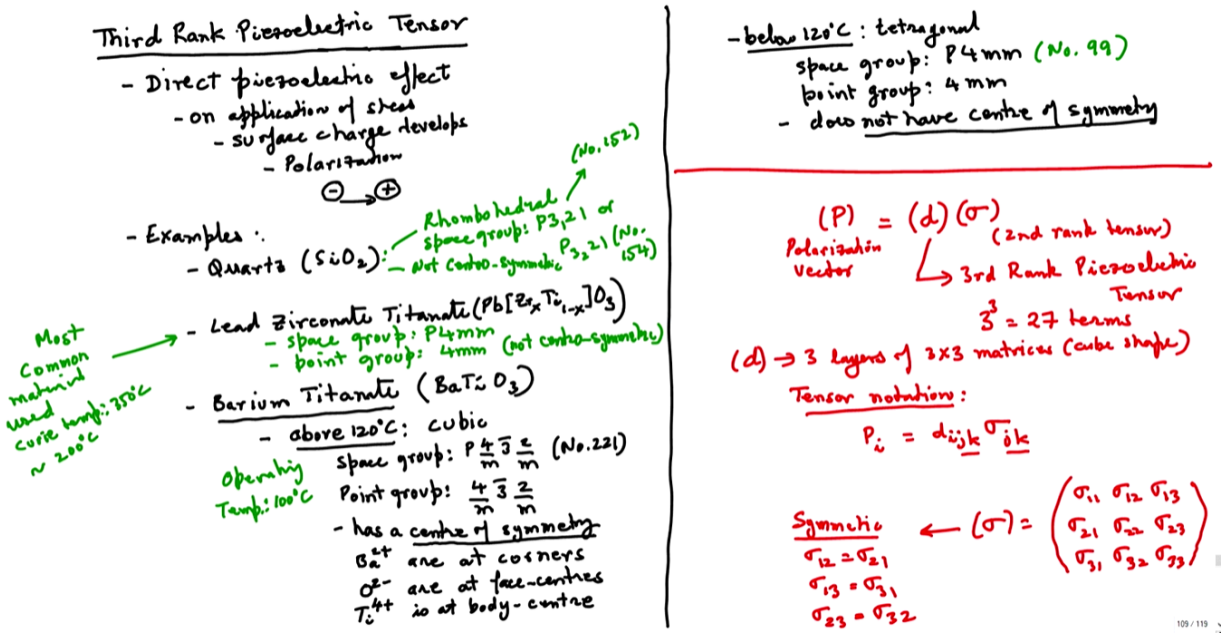

One of the important properties of the second-rank stress tensor is that it is symmetric. This implies that $\sigma_{12} = \sigma_{21}$, $\sigma_{13} = \sigma_{31}$, and $\sigma_{23} = \sigma_{32}$. As a consequence of this symmetry, the stress tensor has only six independent components.

At first glance, the twenty-seven components of the piezoelectric tensor may appear daunting. However, several terms can be reduced immediately. Just as the stress tensor is symmetric, the piezoelectric tensor d also exhibits symmetry. The question then arises as to what symmetry means for a tensor with three indices. In this case, each layer, that is, each 3×3 matrix corresponding to a fixed value of i, is itself symmetric. This means that $d_{ijk} = d_{ikj}$. Here, the index i identifies the particular layer of the 3×3 matrix, while j and k denote the indices within that matrix. Due to this symmetry, the total number of independent components of the piezoelectric tensor reduces from twenty-seven to eighteen.

Incidentally, it is also worth noting that any component d_{ijk} of the piezoelectric tensor is referred to as a piezoelectric modulus. To illustrate the expansion explicitly, consider the case $i = 1$. The polarization component P_1 can be written as

$$P_1 = d_{1jk}\sigma_{jk}.$$

Here, summation is implied over $j = 1$ to 3 and $k = 1$ to 3. This results in a sum of nine terms, analogous to what is encountered in the case of a second-rank tensor.

Writing out all the components of this three-dimensional tensor in the form of layers is cumbersome. Therefore, a commonly used approach is to reduce the number of indices. Instead of working with three indices for d_{ijk}, we attempt to represent it using only two indices. Correspondingly, the stress tensor will be written using a single index.

Let us begin with the stress tensor. The components $\sigma_{11}, \sigma_{12}, \sigma_{13}, \sigma_{21}, \sigma_{22}, \sigma_{23}, \sigma_{31}, \sigma_{32}, \sigma_{33}$ are considered.

$$\sigma = \begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{12} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{pmatrix}$$

The procedure is as follows. Starting from σ_{11}, we move to σ_{22}, then to σ_{33}. From there, we move to σ_{23}, followed by σ_{13}, and finally to σ_{12}. In this manner, instead of writing σ_{11} we denote it as σ_1, instead of σ_{22} as σ_2, and instead of σ_{33} as σ_3. Continuing along this sequence, σ_{23} is written as σ_4, σ_{13} as σ_5, and σ_{12} as σ_6.

With this notation, the stress tensor can be written with diagonal elements $\sigma_1, \sigma_2, \sigma_3$, and off-diagonal elements $\sigma_4, \sigma_5, \sigma_6$. Since the stress tensor is symmetric, the corresponding symmetric positions are filled by σ_6, σ_5, and σ_4. In this way, the stress tensor indices are reduced from two to one.

$$\sigma = \begin{pmatrix} \sigma_1 & \sigma_6 & \sigma_5 \\ \sigma_6 & \sigma_2 & \sigma_4 \\ \sigma_5 & \sigma_4 & \sigma_3 \end{pmatrix}$$

The same reduction can be applied to the indices j and k of the piezoelectric tensor. Thus, the tensor d_{ijk} can be rewritten as d_{in}, where n runs from 1 to 6. For $n = 1, 2, 3$, these correspond to the diagonal terms of the matrix. For $n = 4, 5, 6$, the components are written as $2d_{in}$. The factor of two appears because the off-diagonal terms in the stress matrix occur in pairs, and the corresponding terms in the piezoelectric tensor add together. In the sum over nine terms, not all terms are independent; six are independent, while the remaining terms combine, leading to this factor of two for the off-diagonal components.

Using this notation, the polarization vector can be written in matrix form as

$$\begin{pmatrix} P_1 \\ P_2 \\ P_3 \end{pmatrix} = \begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{pmatrix} \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{pmatrix}.$$

It is evident from this representation that the two matrices can be multiplied to yield the polarization vector.

The terms d_{11}, d_{22}, and d_{33} correspond, in the full index notation, to d_{111}, d_{222}, and d_{333}, respectively. This representation is useful because it allows the components of the piezoelectric tensor to be expressed in a two-dimensional matrix form. However, it must be emphasized that this object is no longer a tensor; it is merely a matrix of numbers.

The implication of this is important. A true tensor must obey specific transformation rules when the coordinate system changes from x_1, x_2, x_3 to x'_1, x'_2, x'_3. The reduced matrix form does not satisfy these transformation rules. Therefore, when considering symmetry transformations, one must work with the full piezoelectric tensor containing all three indices. The correct tensorial relation is

$$P_i = d_{ijk}\,\sigma_{jk}.$$

The transformation rule for a second-rank tensor is given, for reference, by

$$T'_{ij} = A_{im}A_{jn}T_{mn}.$$

In an analogous manner, the transformation rule for the piezoelectric tensor is

$$d'_{ijk} = A_{il}A_{jm}A_{kn}d_{lmn},$$

when transforming from x_1, x_2, x_3 to x'_1, x'_2, x'_3.

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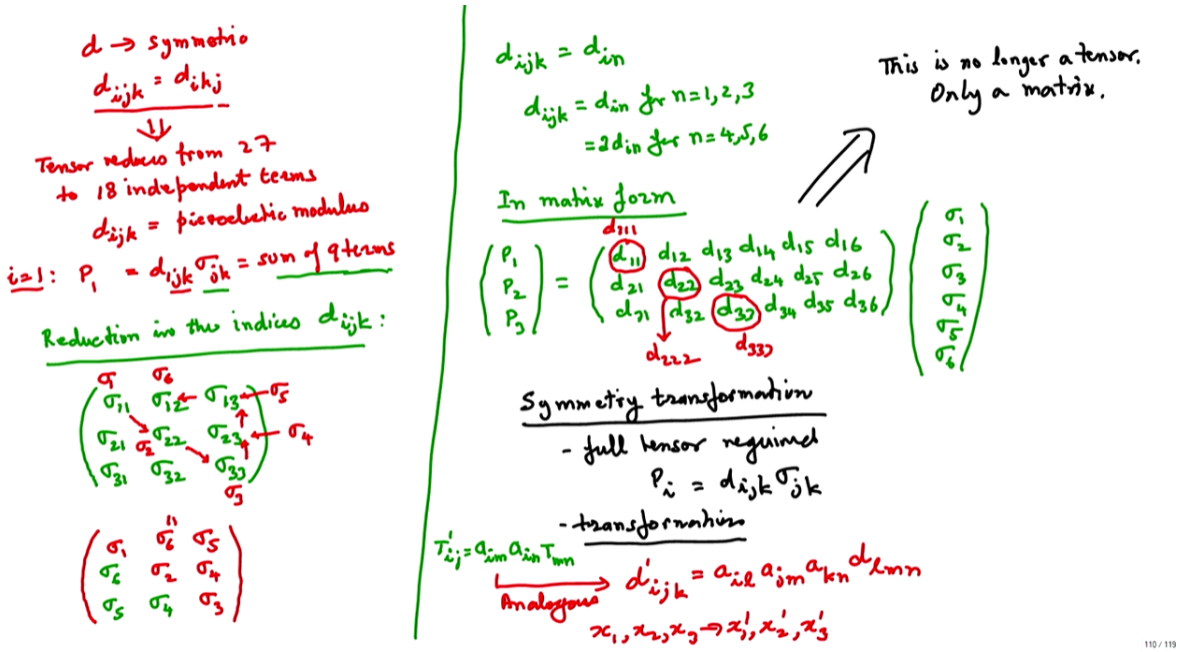

With this clarified, let us now examine the effect of a center of inversion, which was mentioned earlier. Consider a coordinate system with axes x_1, x_2, x_3. If there is a center of inversion at the origin, then x_1 transforms to $x'_1 = -x_1$, x_2 transforms to $x'_2 = -x_2$, and x_3 transforms to $x'_3 = -x_3$. The corresponding direction cosine matrix is

$$A = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix},$$

as discussed previously for second-rank tensors.

Now consider the transformation

$$d'_{ijk} = A_{im}A_{jn}A_{kp}d_{mnp}.$$

The transformed component d'_{ijk} will be nonzero only if the product $A_{im}A_{jn}A_{kp}$ is nonzero. From the form of the direction cosine matrix, only the diagonal terms are nonzero. Therefore, for each index, only the term with matching indices survives, giving

$$d'_{ijk} = A_{ii}A_{jj}A_{kk}d_{ijk}.$$

Since each diagonal element $A_{ii} = -1$, this yields

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

Thus, $d'_{ijk} = -d_{ijk}$. For the center of inversion to be a symmetry operation, the tensor must remain unchanged under this transformation. The only way this condition can be satisfied is if

$$d_{ijk} = 0$$

for all i, j, k. Hence, all twenty-seven components of the piezoelectric tensor must vanish.

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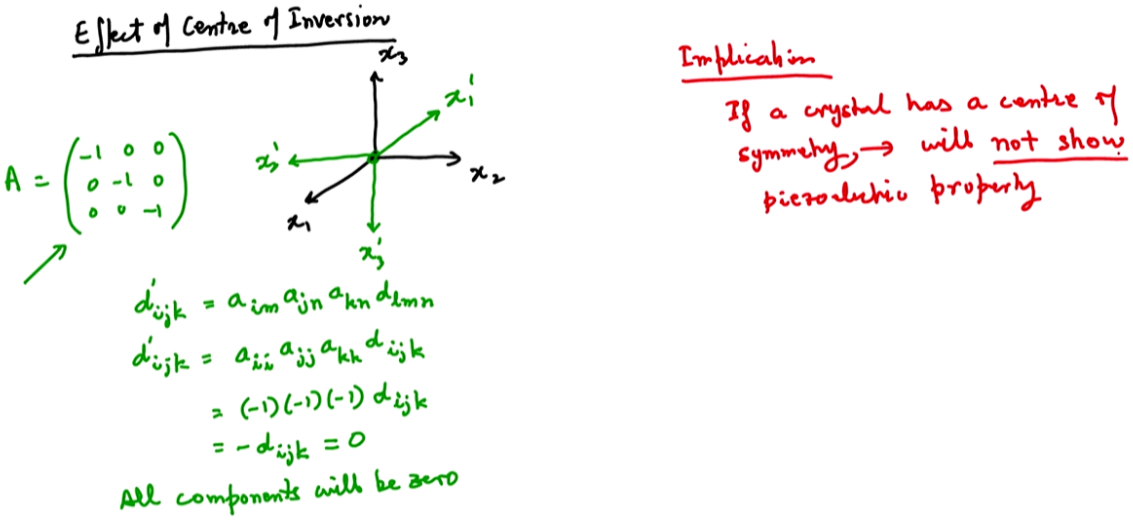

The implication of this result is that if a crystal possesses a center of inversion, it cannot exhibit piezoelectricity. Therefore, when searching for piezoelectric materials, one must examine the point groups of the crystals. Any material that has a center of inversion should be excluded from consideration, as it will not display the piezoelectric effect.