CRYSTAL SYMMETRY, X-RAY DIFFRACTION, AND PHYSICAL PROPERTIES

Prof. Sandeep Sangal

IIT Kanpur

Lecture 58(C): Effect of Crystal Symmetry on Second Rank Property Tensor-III

In this lecture, we continue the discussion on second rank property tensors, building on the earlier analysis of how such tensors transform under symmetry operations for different crystal structure systems. For a given crystal, one is often interested in determining the value of a physical property in a specific direction, based on the known tensor representation of that property for the crystal.

For example, consider a monoclinic crystal and suppose we wish to determine the value of a property along the crystallographic direction $[1\ 1\ 1]$. The question is how to extract the property along this direction from the known second rank tensor associated with the crystal. To address this, we consider the general problem of evaluating a property in a given direction and illustrate the method using electrical conductivity as a specific example.

Electrical conductivity is a second rank tensor. When an electric field is applied in a particular direction in an anisotropic crystal, the resulting current density, which is the flux vector, does not generally lie in the same direction as the applied electric field. This situation contrasts with isotropic crystals, in which the electric field and the flux vectors are always parallel.

Consider a crystal with electrical contacts made on two opposite faces, such that an electric potential is applied to produce an electric field in a specified direction. The resulting current density can be measured. In anisotropic crystals, since the current density vector J need not be parallel to the electric field vector E, one must consider the component of the flux along the direction of the electric field. Let this component be denoted by $J_{\parallel}$. The conductivity in the given direction is then defined as the ratio of this parallel flux component to the magnitude of the electric field.

Let n be a unit vector along the direction of the electric field. The component of the flux parallel to the electric field is given by the dot product

$$J_{\|} = J \cdot n.$$

The unit vector n is obtained by normalizing the electric field vector,

$$n = \frac{E}{|E|}.$$

Hence,

$$J_{\|} = \frac{J \cdot E}{|E|}.$$

In tensor notation, this expression can be written as

$$J_{\|} = \frac{J_i E_i}{|E|},$$

where J_i and E_i are the components of the flux and electric field vectors, respectively. Expanding the summation explicitly,

$$J_{\|} = \frac{J_1 E_1 + J_2 E_2 + J_3 E_3}{|E|}.$$

The flux components are related to the electric field components through the conductivity tensor σ_{ij} as

$$J_i = \sigma_{ij} E_j,$$

where summation over the repeated index j is implied. Substituting this relation into the previous expression yields the conductivity in the direction of n as

$$\sigma(n) = \frac{\sigma_{ij} E_i E_j}{|E|^2}.$$

Recognizing that $E_i/|E| = n_i$, the components of the unit vector n, this expression can be written compactly as

$$\sigma(n) = \sigma_{ij} n_i n_j.$$

Expanding the summation over i and j from 1 to 3 gives

$$\sigma(n) = \sigma_{11} n_1^2 + \sigma_{12} n_1 n_2 + \sigma_{13} n_1 n_3 + \sigma_{21} n_2 n_1 + \sigma_{22} n_2^2 + \sigma_{23} n_2 n_3 + \sigma_{31} n_3 n_1 + \sigma_{32} n_3 n_2 + \sigma_{33} n_3^2.$$

Consider first an orthorhombic crystal. From the previous lecture, the conductivity tensor for an orthorhombic crystal has only diagonal components,

$$\begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix}.$$

All off-diagonal components are zero. Substituting this form into the general expression for $\sigma(n)$, all terms involving off-diagonal components vanish, and only the diagonal terms remain. Thus,

$$\sigma(n) = \sigma_{11} n_1^2 + \sigma_{22} n_2^2 + \sigma_{33} n_3^2.$$

Next, consider a tetragonal crystal. In this case, the conductivity tensor has the form

$$\begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{11} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix}.$$

Again, all off-diagonal terms are zero, but now the first two diagonal components are equal. The conductivity in the direction of n becomes

$$\sigma(n) = \sigma_{11}(n_1^2 + n_2^2) + \sigma_{33} n_3^2.$$

The components n_1, n_2, and n_3 are the direction cosines of the unit vector n, and hence they satisfy

$$n_1^2 + n_2^2 + n_3^2 = 1.$$

Using this relation, the expression for conductivity can be rewritten as

$$\sigma(n) = \sigma_{11}(1 - n_3^2) + \sigma_{33}n_3^2.$$

Let the unit vector n make an angle θ with the x_3 axis. Then $n_3 = cos\theta$, and the conductivity in the direction n can be expressed as

$$\sigma(n) = \sigma_{11}sin^2\theta + \sigma_{33}cos^2\theta.$$

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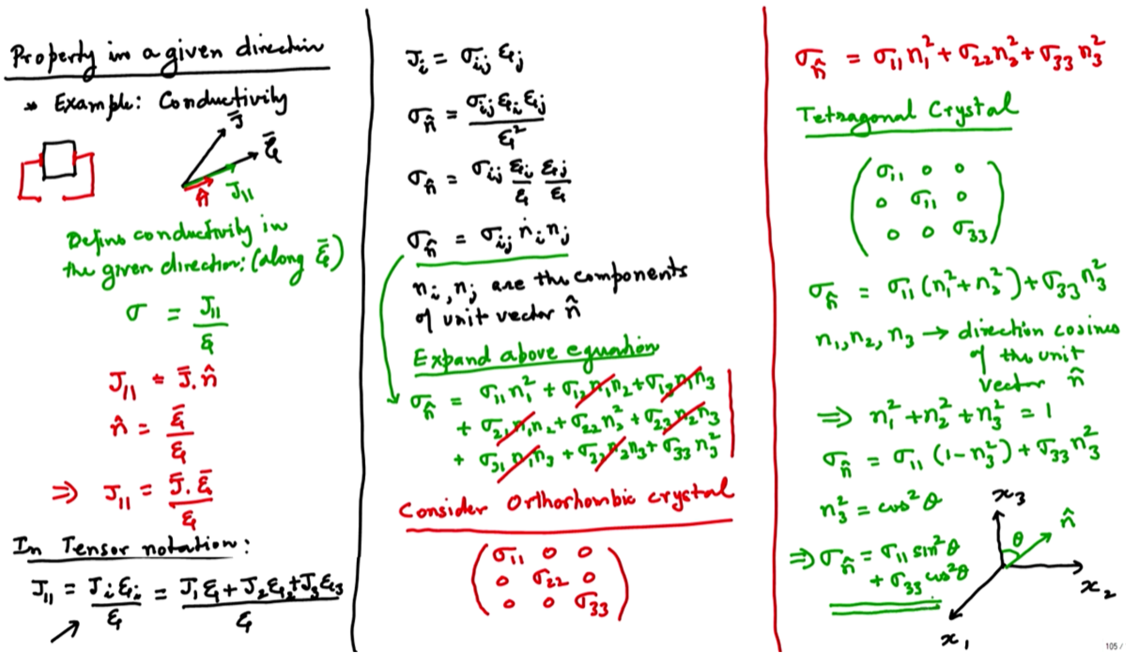

Now consider directions lying in the x_1x_2 plane of a tetragonal crystal. This plane is perpendicular to the fourfold rotation axis, which lies along x_3, and is therefore referred to as the basal plane. For any direction in the basal plane, the unit vector is perpendicular to x_3, implying $\theta = \pi/2$. Substituting this value,

$$\sigma(n) = \sigma_{11},$$

since $sin^2(\pi/2) = 1$ and $cos^2(\pi/2) = 0$. Thus, within the basal plane, the conductivity is independent of direction, and the conductivity is isotropic in the x_1x_2 plane for all tetragonal crystal systems.

Finally, consider cubic crystals. For cubic symmetry, the conductivity tensor reduces to

$$\begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{11} & 0 \\ 0 & 0 & \sigma_{11} \end{pmatrix}.$$

In this case, all diagonal components are equal. Substituting into the general expression for conductivity yields

$$\sigma(n) = \sigma_{11},$$

independent of the direction of n. This demonstrates that cubic crystals are isotropic with respect to electrical conductivity, and the same conductivity is measured regardless of the direction of the applied electric field.

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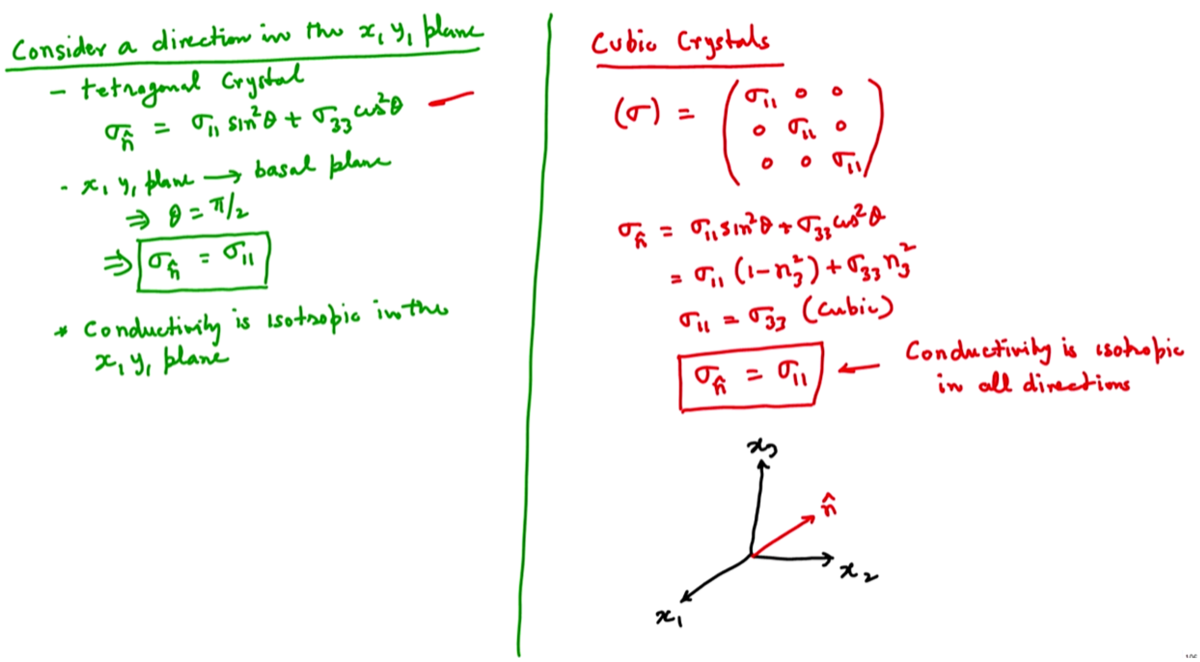

Before concluding, it is useful to list some examples of second rank property tensors. One example is Fourier's law of heat conduction, given by

$$q = - k \cdot \nabla T,$$

where ∇T is the temperature gradient, q is the heat flux vector, and k is the thermal conductivity tensor, which is a symmetric second rank tensor. Consequently, heat flow in tetragonal crystals is isotropic within the basal plane, and in cubic crystals it is isotropic in all directions.

Another example is the diffusion tensor, where the flux is given by

$$J =- D\cdot\nabla C,$$

with ∇C being the concentration gradient and D the diffusion tensor, again a second rank tensor.

Magnetic susceptibility provides another example, with magnetization related to the applied magnetic field by

$$M = \chi \cdot H,$$

where χ is the susceptibility tensor of rank two.

Thermal expansion is also described by a second rank tensor. Consider a bar of initial length L at temperature T. If the temperature increases by ΔT, the length changes by ΔL. The linear expansion coefficient is defined as

$$\alpha = \frac{1}{L}\frac{\Delta L}{\Delta T}.$$

Since expansion occurs in all directions, α is a second rank tensor. A temperature change produces a strain tensor ε_{ij}, related to the thermal expansion tensor by

$$\varepsilon_{ij} = \alpha_{ij}\Delta T.$$

Here, ΔT is a scalar, while α_{ij} and ε_{ij} are symmetric second rank tensors. The strain tensor has components ε_{11}, ε_{12}, ε_{13}, ε_{21}, ε_{22}, ε_{23}, ε_{31}, ε_{32}, and ε_{33}, and its symmetry implies the symmetry of the thermal expansion tensor.

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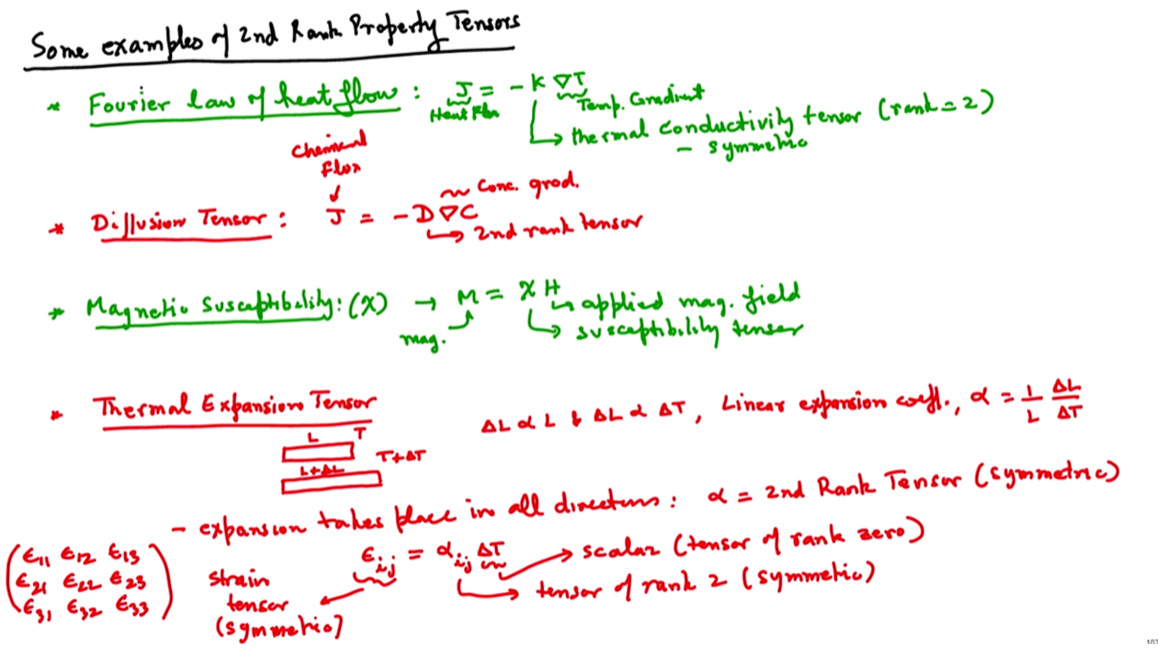

A final example is the Seebeck tensor associated with thermoelectric effects. When heat conduction and electrical conduction occur simultaneously, their interaction gives rise to thermoelectricity. In this case, the electric field is related to the temperature gradient by

$$E =- S \cdot \nabla T,$$

where S is the Seebeck tensor, a second rank tensor. This effect occurs when two dissimilar materials are joined to form a hot junction and a cold junction, producing an electromotive force proportional to the temperature difference. Devices based on this principle are called thermocouples and are widely used for accurate temperature measurements over a broad range. Unlike many second rank property tensors discussed earlier, the Seebeck tensor is generally not symmetric and therefore has nine independent components. The reverse phenomenon is known as the Peltier effect, in which an applied electromotive force produces a temperature difference, a principle used in Peltier coolers.

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* Seebeck effect

- when conduction of heat and electricity occur together
  - interference of these two processes result in "thermoelectricity"

$$E_q = -S \nabla T$$

2nd Rank Tensor (Not symmetric)

- 9 independent components

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Measuring wide range of temperatures

- thermocouple

- Reverse effect: Peltier effect

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Peltier coolers