Crystal Physics

Johann Pototschnig

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1 introduction

1.1 crystal physics

In Crystal Physics you try to describe constrains that arise in the properties of solids due to microscopic symmetries.

1.2 translation, Bravais lattice

Crystals have an ordered structure that repeats itself. In a three - dimensional space you can find three vectors (a_i) to describe this:

$$\mathbf{R} = \sum_{i=1}^{3} n_i a_i \quad n_i \in Z$$

There are 14 Bravais lattice in three dimensions.

1.3 pointgroups

If you have a structure made out of several points or objects, this structure may belong to a certain point group. This means if you perform a certain operation (rotation, inversion, mirroring) the structure stays the same. The points may change the positions but you can not see a difference. These operations can be described by a matrix. These matrices have to fulfill certain conditions:

$$\text{orthogonality:} \qquad A \cdot A^T = E$$

(E ... Einheitsmatrix)

$$\text{normalized:} \qquad |\det(A)| = 1$$

If you multiply the position vector with this matrix you get the new state. In three dimensions you need a three dimensional matrix:

$$A = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix}$$

If you also demand a repeating structure, like it can be found in crystals (the 14 Bravais lattice) out of an infinte nummber of point groups only the 32 crystallographic point groups are possible. As an example you can look at the group C_5. The groups C_n contain all rotations of $\frac{1}{n}^{th}$ of the whole rotation of 360°. So C_5 contains the rotations of 72°, 144°, 216°, 288° and 360°. You can imagine a structure with this symmetry but, as you know no crystal has this symmetry.

If you add the basis to the Bravais lattice some symmetry operations may no longer leave the crystal unchanged, so the point group can be a different one.

1.4 spacegroups

If you add Translations

$$\mathbf{t} = \begin{pmatrix} t_1 \\ t_2 \\ t_3 \end{pmatrix} \qquad \text{(in 3 dimensions)}$$

you get more symmetry operations. If you assume periodic boundary conditions you now get 230 space groups. An additional symmetry operations is for example a rotation and a translation together.

All the operations can be described by a matrix (same conditions as for point groups) and a translation vector: $\{A|\,\mathbf{t}\}$

2 general considerations

2.1 generating matrices

If you want to describe a point group and all the symmetries it contains, it is sufficiant to only give the generating matrices. With them you can calculate all the elements of the group. You have to multiply the element with itself until you get the identity matrix.

Examples for 3 dimensions:

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

The inversion operation leads to the Group:

$$i = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad i^2 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = E$$

$$C_4 = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

This roation gives the group:

$$C_4 = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix};\ C_4^2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = C_2;\ C_4^3 = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix};\ C_4^4 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = E$$

2.2 reduced notation

The reduced Notation is used for symmetric indices ($a_{ij} = a_{ji}\ \forall i, j$) and mostly for 3^{rd} rank tensors or 4^{rd} rank tensors.

$$\begin{gathered} 11 \to 1 \\ 22 \to 2 \\ 33 \to 3 \\ 23 \equiv 32 \to 4 \\ 13 \equiv 31 \to 5 \\ 12 \equiv 21 \to 6 \end{gathered}$$

For example you can look at a 3^{rd} rank tensor:

$$G = \begin{pmatrix} g_{11} & g_{12} & g_{13} & g_{14} & g_{15} & g_{16} \\ g_{21} & g_{22} & g_{23} & g_{24} & g_{25} & g_{26} \\ g_{31} & g_{32} & g_{33} & g_{34} & g_{35} & g_{36} \end{pmatrix} = \begin{pmatrix} g_{111} & g_{122} & g_{133} & g_{123} & g_{113} & g_{112} \\ g_{211} & g_{222} & g_{233} & g_{223} & g_{213} & g_{212} \\ g_{311} & g_{322} & g_{333} & g_{323} & g_{313} & g_{312} \end{pmatrix}$$

2.3 conditions for the tensors of certain materials

If a crystal belongs to a certain point group, has a certain symmetry, the properties of the crystal should have the same symmetry and therfore the crystals tensors.

For example you can have a crystal that is symmetric under the rotation of $90°$ around the z - axis. $C_4 = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ Then the results of experiments, the crystals properties should not change under this rotations. For a three dimensional crystal this leads to following conditions for the tensors:

2.3.1 1^{st} rank

$$G = \begin{pmatrix} g_1 \\ g_2 \\ g_3 \end{pmatrix} \qquad T(G) = \begin{pmatrix} -g_2 \\ g_1 \\ g_3 \end{pmatrix} =^! \begin{pmatrix} g_1 \\ g_2 \\ g_3 \end{pmatrix}$$

This gives the conditions: $g_1 = -g_2, g_2 = g_1$, which can only be satisfied by $g_2 = g_1 = 0$. So only the following form of tensors is allowed:

$$G = \begin{pmatrix} 0 \\ 0 \\ g_3 \end{pmatrix}$$

2.3.2 2^{nd} rank

$$G = \begin{pmatrix} g_{11} & g_{12} & g_{13} \\ g_{21} & g_{22} & g_{23} \\ g_{31} & g_{32} & g_{33} \end{pmatrix}$$

You can write the transformation as a matrix multiplication:

$$T(G) = C_4^T \cdot G \cdot C_4 = \begin{pmatrix} g_{22} & -g_{21} & g_{23} \\ -g_{12} & g_{11} & -g_{13} \\ g_{32} & -g_{31} & g_{33} \end{pmatrix} =^! G$$

This leads to the conditons: $g_{22} = g_{11}$; $g_{31} = g_{32} = 0$; $g_{13} = g_{23} = 0$; $g_{12} = -g_{21}$. For symmetric tensors you get additionaly: $g_{12} = g_{21} = 0$.

2.3.3 3^{rd} rank

For

$$G = \begin{pmatrix} g_{111} & g_{121} & g_{131} & g_{112} & g_{122} & g_{132} & g_{113} & g_{123} & g_{133} \\ g_{211} & g_{221} & g_{231} & g_{212} & g_{222} & g_{232} & g_{213} & g_{223} & g_{233} \\ g_{311} & g_{321} & g_{331} & g_{312} & g_{322} & g_{332} & g_{313} & g_{323} & g_{333} \end{pmatrix}$$

$$G' = \begin{pmatrix} -g_{211} & -g_{221} & -g_{231} & -g_{212} & -g_{222} & -g_{232} & -g_{213} & -g_{223} & -g_{233} \\ g_{111} & g_{121} & g_{131} & g_{112} & g_{122} & g_{132} & g_{113} & g_{123} & g_{133} \\ g_{311} & g_{321} & g_{331} & g_{312} & g_{322} & g_{332} & g_{313} & g_{323} & g_{333} \end{pmatrix}$$

$$G'' = \begin{pmatrix} g_{221} & -g_{211} & -g_{231} & g_{222} & -g_{212} & -g_{232} & g_{223} & -g_{213} & -g_{233} \\ -g_{121} & g_{111} & g_{131} & -g_{122} & g_{112} & g_{132} & -g_{123} & g_{113} & g_{133} \\ -g_{321} & g_{311} & g_{331} & -g_{322} & g_{312} & g_{332} & -g_{323} & g_{313} & g_{333} \end{pmatrix}$$

$$G''' = \begin{pmatrix} -g_{222} & g_{212} & g_{232} & g_{221} & -g_{211} & -g_{231} & g_{223} & -g_{213} & -g_{233} \\ g_{122} & -g_{112} & -g_{132} & -g_{121} & g_{111} & g_{131} & -g_{123} & g_{113} & g_{133} \\ g_{322} & -g_{312} & -g_{332} & -g_{321} & g_{311} & g_{331} & -g_{323} & g_{313} & g_{333} \end{pmatrix} =^! G$$

After fulfilling these conditions you have to include the symmetry in the last two indices and this gives the result in table.

Similar calculations can be made for 4^{th} rank tensors.

3 examples

For the following descriptions I use the einstein notation. If on one side of the equal sign an index appears twice you have to sum over it.

3.1 inversion symmetry

If you have inversions symmetry you have to multiply with -1 for each rank of the tensor (look above), everything else stay the same. So all tensors with an odd number of ranks have to be zero (1^{st}, 3^{rd} 5^{th}).

Properties that need tensors of this form can not be observed in crystals with inversion symmetrie. For example piezoelectricity or piezomagnetism.

3.1.1 callculations

Now lets show the conditon that arrise for inversion $i = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$

In first rank:

$$T(G) = \begin{pmatrix} -g_1 \\ -g_2 \\ -g_3 \end{pmatrix} \stackrel{!}{=} \begin{pmatrix} g_1 \\ g_2 \\ g_3 \end{pmatrix} \Rightarrow \text{all elements have to be zero}$$

In second rank:

$$T(G) = \begin{pmatrix} g_{11} & g_{12} & g_{13} \\ g_{21} & g_{22} & g_{23} \\ g_{31} & g_{32} & g_{33} \end{pmatrix} = G \Rightarrow \text{no conditions}$$

In third rank:

$$T(G) = \begin{pmatrix} -g_{111} & -g_{121} & -g_{131} & -g_{112} & -g_{122} & -g_{132} & -g_{113} & -g_{123} & -g_{133} \\ -g_{211} & -g_{221} & -g_{231} & -g_{212} & -g_{222} & -g_{232} & -g_{213} & -g_{223} & -g_{233} \\ -g_{311} & -g_{321} & -g_{331} & -g_{312} & -g_{322} & -g_{332} & -g_{313} & -g_{323} & -g_{333} \end{pmatrix} = -G$$

$\Rightarrow$ all elements have to be zero

3.2 0^{th} rank tensors

This simply is a constant. You have 1 independent element.

3.2.1 density ρ

It is independent of any tensors.

$$\Delta m = \rho \cdot \Delta V$$

3.2.2 specific heat c

$$\Delta Q = c \cdot \Delta T$$

3.3 1^{st} rank tensors

You have 3 independent elements. As already described this tensor is zero for all groups with inversion symmetry.

3.3.1 pyroelectricity p_i

$$\Delta P_i = p_i \cdot \Delta T$$

3.3.2 electrocaloric effect p_l

$$\Delta S = p_l \cdot \Delta E_l$$

3.4 symmetric 2^{nd} rank tensor

You have 6 independent elements. ($g_{ij} = g_{ji}$)

3.4.1 electrical conductivity σ_{ik}

$$j_i = \sigma_{ik} E_k$$

3.4.2 electrical resistivity ρ_{ki}

$$E_k = \rho_{ki} j_i$$

3.4.3 thermal conductivity k_{ij}

$$\dot{Q}_i = -k_{ij} (\nabla T)_j$$

3.4.4 dielectric permitivity ϵ_{ij}

$$D_i = \epsilon_{ij} E_j$$

3.4.5 magnetic permitivity μ_{ij}

$$B_i = \mu_{ij} H_j$$

3.4.6 thermal expansion α_{ij}

$$\epsilon_{ij} = \alpha_{ij} \Delta T$$

3.4.7 optical rotation

3.5 asymmetric 2^{nd} rank tensor

You have 9 independent elements.

3.5.1 Seebeck - effect β_{ik}

$$E_i = -\beta_{ik} \left(\nabla T\right)_k$$

3.5.2 Peltier - effect π_{ik}

$$\dot{Q}_i = \pi_{ik} j_k$$

3.5.3 Hall - effect

In general you would describe the Hall - effect with a tensor of 3^{rd} rank:

$$E_i = a^H_{ikl} j_k B_l$$

But as already explained then the effect would only occur in materials without inversion symmetrie. As most of you know something similar to the Hall - effect occurs in vacuum. A ray of electrons can be diverted by a magnetic field.

So the question arrises, what role does the material and its properties play in the Hall - effect.

A possibility to describe the Hall - effect is to use a 2^{nd} rank tensor that depends on the magnetic field and the symmetries of the crystal:

$$E_i = \rho_{ik} \left(\mathbf{B}\right) j_k$$

The 2^{nd} rank tensor has to fulfill following conditions:

$$\rho_{ik} \left(\mathbf{B}\right) = -\rho_{ki} \left(\mathbf{B}\right) = \rho_{ki} \left(-\mathbf{B}\right)$$

So this tensor is antisymmetric.

If you look at asymmetric 2^{nd} rank tensors for certain materials, you see, that an antisymmetric form is not possible, unless you take into acount, that the magnetic field destroys certain symmetries.

So the symmetries of the crystal and the magnetic field together form a new symmetry class. Within this point group the Hall effect can be described with a second rank tensor (antisymmetric).

3.6 symmetric 3^{nd} rank tensor

You have 9 independent elements.($g_{ijk} = g_{jik} = g_{kij} = \ldots$) As already described this tensor is zero for all groups with inversion symmetry.

3.7 asymmetric 3^{nd} rank tensor

You have 18 independent elements.($g_{kij} = g_{kji} \neq g_{jki}$, symmetric in the last two indices)

(piezoelectric and elektrooptical tensors)

As already described this tensor is zero for all groups with inversion symmetry.

3.7.1 piezoelectric effect d_{ijk}

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

3.7.2 innverse piezoelectric effect t_{ijk}

$$\epsilon_{jk} = t_{ijk}E_i$$

3.7.3 Piezomagnetic effect q_{lij}

$$M_l = q_{lij}\sigma_{ij}$$

3.7.4 second harmonic generation d_{kij}

$$P\left(2\omega\right)_k = d_{kij}E_iE_j$$

3.7.5 electrooptic effect q_{ijk}

$$\Delta a_{ij} = R_{ijkl}E_k$$

3.8 symmetric 4^{nd} rank tensor

You have 21 independent elements.($g_{ijlk} = g_{jilk} = g_{jikl} = g_{lkij} = \ldots$) (mostly elastic constants)

3.8.1 elastic stiffness c_{ijkl}

$$\sigma_{ij} = c_{ijkl}\epsilon_{kl}$$

3.8.2 elasitc compliance s_{ijkl}

$$\epsilon_{ij} = c_{ijkl}\sigma_{kl}$$

3.9 asymmetric 4^{nd} rank tensor

You have 36 independent elements.($g_{ijlk} = g_{jilk} = g_{jikl} \neq g_{lkij}$, symmetric in the first two and last two indices)

3.9.1 piezooptic effect π_{ijkl}

$$\Delta a_{ij} = \pi_{ijkl}\sigma_{kl}$$

3.9.2 photoelastic effect

3.9.3 electrostriction μ_{lmjk}

$$\epsilon_{jk} = \mu_{lmjk}E_l E_m$$

3.9.4 piezoresistivity R_{ijkl}

$$\rho_{ij} = R_{ijkl}\sigma_{kl}$$

3.10 symmetric - asymmetric tensors

3.10.1 symmetric

You get an symmetric tensor if the vector components are connected by a derivation of a thermodynamical potential. If this is true one variable can be described as the derivation after the other and the derivations can be exchanged:

For example stiffness (4^{th} rank tensor):

$$\frac{\partial G}{\partial \sigma_{ij}} = -\epsilon_{ij}$$

$$s_{ijkl} = \frac{\partial \epsilon_{ij}}{\partial \sigma_{kl}} = -\frac{\partial^2 G}{\partial \sigma_{ij}\partial \sigma_{kl}} = \frac{\partial \epsilon_{kl}}{\partial \sigma_{ij}} = s_{klij}$$

(You can use Schwarz's theorem, that states that if the derivatives exist they can be exchanged.)

3.10.2 asymmetric

For an asymmetric tensor on the other hand you get different derivations and they can not be exchanged: For example the piezoelectic coefficent (3^{rd} rank tensor):

$$d_{ijk} = \frac{\partial P_i}{\partial \sigma_{jk}} = -\frac{\partial^2 G}{\partial \sigma_{jk} \partial E_i} = -\frac{\partial^2 G}{\partial E_i \partial \sigma_{jk}} = \frac{\partial \epsilon_{jk}}{\partial E_i} = t_{ijk}$$

As you can see this time you get no condition for symmetry, but a relation between the coefficents of the piezoelectric effect and the inverse piezoelectric effect.

For example the electrostriction (4^{th} rank tensor):

$$\mu_{lmjk} = \frac{\partial^2 \epsilon_{jk}}{\partial E_l \partial E_m} = -\frac{\partial^3 G}{\partial \sigma_{jk} \partial E_l \partial E_m} = -\frac{\partial^3 G}{\partial E_l \partial E_m \partial \sigma_{jk}} = \frac{\partial^2 P_l}{\partial E_m \partial \sigma_{jk}}$$

As you see you get also the coefficent for some kind of inverse effect, although I do not know, if it has any physical meaning.

3.11 variables

- T ... temperature
- E ... electric field
- j ... current density
- ρ ... resistivity
- V ... volume
- m ... mass
- $\dot{Q}$ ... heat flux
- S ... entropy
- D ... dielectric displacement
- P ... electric polarisation
- H ... magnetic field
- B ... magnetic induction
- M ... magnetisation
- ϵ ... strain (Verformung)
- σ ... stress (Belastung)
- Δa ... dielectric impermeability (direction depnding refractive index)