Thermoelectric effects

$$f(\vec{k}) \approx f_0(\vec{k}) + \frac{\tau(\vec{k})e\left(\vec{v}\times\vec{B}+\vec{E}\right)\cdot\nabla_k f_0}{\hbar} + \tau(\vec{k})\vec{v}\cdot\left(\frac{\partial f_0}{\partial T}\nabla T + \frac{\partial f_0}{\partial \mu}\nabla\mu\right)$$

Electrical current: $\vec{j}_{elec} = \frac{-e}{4\pi^3}\int v(\vec{k})f(\vec{k})d^3k$

Particle current: $\vec{j}_n = \frac{1}{4\pi^3}\int v(\vec{k})f(\vec{k})d^3k$

Energy current: $\vec{j}_E = \frac{1}{4\pi^3}\int v(\vec{k})E(\vec{k})f(\vec{k})d^3k$

Heat current: $\vec{j}_Q = \frac{1}{4\pi^3}\int v(\vec{k})\left(E(\vec{k})-\mu\right)f(\vec{k})d^3k$

Thermal conductivity

$$\vec{j}_Q = \frac{1}{4\pi^3}\int \vec{v}_{\vec{k}}\left(E(\vec{k})-\mu\right)\left(\tau(\vec{k})\frac{\partial f_0}{\partial\mu}\left(-\frac{e}{\hbar}\left(\vec{v}(\vec{k})\times\vec{B}+\vec{E}\right)\cdot\nabla_k E(\vec{k})+\vec{v}(\vec{k})\cdot\left(\frac{E(\vec{k})-\mu}{T}\nabla T+\nabla\mu\right)\right)\right)d^3k$$

$$\vec{B}=0,\quad \vec{E}=0,\quad \nabla\mu=0$$

$$\vec{j}_Q = \frac{1}{4\pi^3}\int \vec{v}_{\vec{k}}\left(E(\vec{k})-\mu\right)\tau(\vec{k})\frac{\partial f_0}{\partial\mu}\vec{v}(\vec{k})\cdot\frac{E(\vec{k})-\mu}{T}\nabla T d^3k$$

$$\kappa_{mn} = \frac{-j_{Qm}}{\nabla T_n}$$

Thermoelectric effects

$$f(\vec{k}) \approx f_0(\vec{k}) + \frac{\tau e\left(\vec{v} \times \vec{B} + \vec{E}\right) \cdot \nabla_k f_0}{\hbar} - \tau \frac{\partial f_0}{\partial T} \vec{v} \cdot \nabla T$$

Electrical conductivity: $\sigma_{mn} = \frac{j_{em}}{E_n}$ $\nabla T = 0, \vec{B} = 0$

Thermal conductivity: $\kappa_{mn} = \frac{-j_{Qm}}{\nabla T_n}$ $\vec{j}_e = 0, \vec{B} = 0$

Peltier coefficient: $\Pi_{mn} = \frac{j_{Qm}}{j_{en}}$ $\nabla T = 0, \vec{B} = 0$

Thermopower (Seebeck effect): $Q_{mn} = \frac{E_m}{\nabla T_n}$ $\vec{j}_e = 0, \vec{B} = 0$

Thermoelectric effects

$$f(\vec{k}) \approx f_0(\vec{k}) + \frac{\tau e\left(\vec{v} \times \vec{B} + \vec{E}\right) \cdot \nabla_k f_0}{\hbar} - \tau \frac{\partial f_0}{\partial T} \vec{v} \cdot \nabla T$$

Hall effect: $$R_{lmn} = \frac{E_l}{j_{em} B_n} \qquad \nabla T = 0,\ j_{el} = 0$$

Nerst effect: $$N_{lmn} = \frac{E_l}{B_m \nabla T_n} \qquad j_{el} = 0$$

Ettingshausen effect: $$P_{lmn} = \frac{-1}{j_{el} B_m \nabla T_n}$$

Boltzmann equation for phonons

$$\vec{j}_{ph} = \int E(\vec{k})\vec{v}(\vec{k})D(\vec{k})\, f\,(\vec{k})d\vec{k}$$

phonon dispersion — $E(\vec{k})$

phonon group velocity — $\vec{v}(\vec{k})$

mean density of phonon occupation — $f(\vec{k})$

For phonons, there is no external force term.

Student project

Assume that the dispersion relation is $\dfrac{\hbar^2 k^2}{2m^*}$

and that a single relaxation time can be used for all *k*.
Calculate the some transport property.

The properties of solids

$$H = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_A \frac{\hbar^2}{2m_A}\nabla_A^2 - \sum_{i,A}\frac{Z_A e^2}{4\pi\varepsilon_0 r_{iA}} + \sum_{i<j}\frac{e^2}{4\pi\varepsilon_0 r_{ij}} + \sum_{A<B}\frac{Z_A Z_B e^2}{4\pi\varepsilon_0 r_{AB}}$$

electronic band structure E vs. k

structure
bond potentials

phonon band structure ω vs. k

density of states

Boltzmann transport

optical
absorption

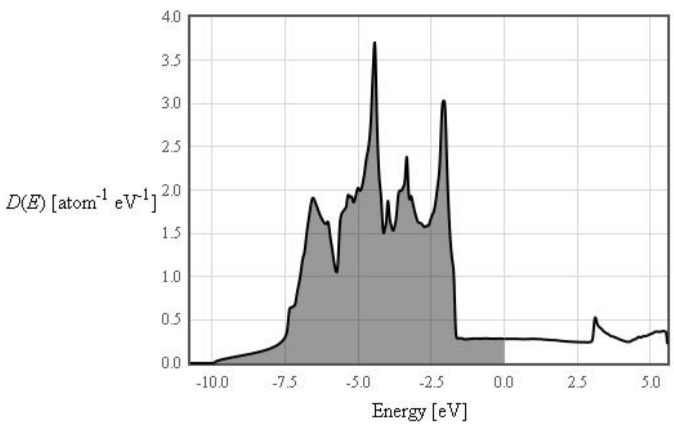
density of states

equilibrium properties
c_v, free energies, bulk modulus,...

optical properties

Calculating free energies

Electronic component

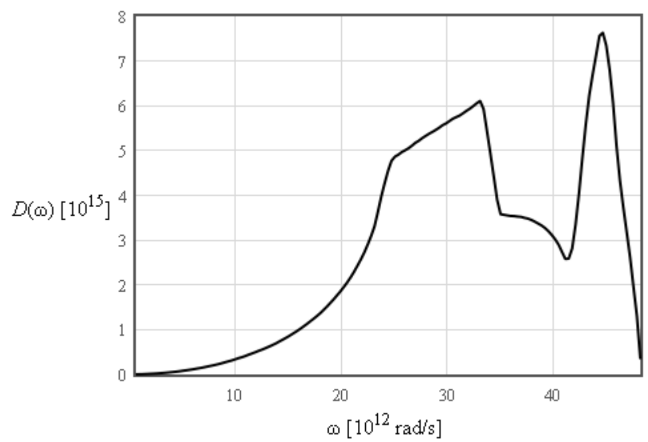


$$n = \int_{-\infty}^{\infty} \frac{D(E)}{1+\exp\left(\frac{E-\mu}{k_B T}\right)} dE$$

$$f = \phi + \mu n = \int_{-\infty}^{\infty} D(E)\left(\frac{\mu}{1+\exp\left(\frac{E-\mu}{k_B T}\right)} - k_B T \ln\left(\exp\left(-\frac{(E-\mu)}{k_B T}\right)+1\right)\right) dE$$

Phonon component

$$f(T) = k_B T \int_0^{\infty} D(\omega) \ln\left(1-\exp\left(\frac{-\hbar\omega}{k_B T}\right)\right) d\omega.$$



Helmholtz free energy

Cannonical ensemble: At constant temperature, make a Legendre transformation to the Helmholtz free energy.

$$F = U - TS$$

$$F(T, N, M, P, \varepsilon)$$

$$dF = dU - TdS - SdT$$

$$dF = -SdT + \mu_i dN_i + \sigma_{ij} d\varepsilon_{ij} + E_k dP_k + H_l dM_l$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{N,M,P,\varepsilon} \qquad \mu_i = \left(\frac{\partial F}{\partial N_i}\right)_{T,M,P,\varepsilon,N_{j\neq i}} \qquad \sigma_{ij} = \left(\frac{\partial F}{\partial \varepsilon_{ij}}\right)_{N,M,P,T}$$

$$E_k = \left(\frac{\partial F}{\partial P_k}\right)_{N,M,T,\varepsilon} \qquad H_l = \left(\frac{\partial F}{\partial M_l}\right)_{N,T,P,\varepsilon}$$

Gibbs free energy

$$G(T, \mu, H, E, \sigma)$$

$$G = U - TS - \mu_i N_i - \sigma_{ij}\varepsilon_{ij} - E_k P_K - H_l M_l$$

$$dU = TdS + \mu_i dN_i + \sigma_{ij} d\varepsilon_{ij} + E_k dP_K + H_l dM_l$$

$$dG = -SdT - N_i d\mu_i - \varepsilon_{ij} d\sigma_{ij} - P_k dE_k - M_l dH_l$$

$$dG = \left(\frac{\partial G}{\partial T}\right) dT + \left(\frac{\partial G}{\partial \mu_i}\right) d\mu_i + \left(\frac{\partial G}{\partial \sigma_{ij}}\right) d\sigma_{ij} + \left(\frac{\partial G}{\partial E_k}\right) dE_k + \left(\frac{\partial G}{\partial H_l}\right) dH_l$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{\sigma,E,H,\mu} \qquad N_i = -\left(\frac{\partial G}{\partial \mu_i}\right)_{T,E,H,\sigma} \qquad \varepsilon_{ij} = -\left(\frac{\partial G}{\partial \sigma_{ij}}\right)_{T,E,H,\mu}$$

$$P_k = -\left(\frac{\partial G}{\partial E_k}\right)_{T,\mu,H,\sigma} \qquad M_l = -\left(\frac{\partial G}{\partial H_l}\right)_{T,\mu,E,\sigma}$$

$$d\varepsilon_{ij} = \left(\frac{\partial \varepsilon_{ij}}{\partial \sigma_{kl}}\right)_{1} d\sigma_{kl} + \left(\frac{\partial \varepsilon_{ij}}{\partial E_k}\right)_{2} dE_k + \left(\frac{\partial \varepsilon_{ij}}{\partial H_l}\right)_{3} dH_l + \left(\frac{\partial \varepsilon_{ij}}{\partial T}\right)_{4} dT$$

$$dP_i = \left(\frac{\partial P_i}{\partial \sigma_{kl}}\right)_{5} d\sigma_{kl} + \left(\frac{\partial P_i}{\partial E_k}\right)_{6} dE_k + \left(\frac{\partial P_i}{\partial H_l}\right)_{7} dH_l + \left(\frac{\partial P_i}{\partial T}\right)_{8} dT$$

$$dM_i = \left(\frac{\partial M_i}{\partial \sigma_{kl}}\right)_{9} d\sigma_{kl} + \left(\frac{\partial M_i}{\partial E_k}\right)_{10} dE_k + \left(\frac{\partial M_i}{\partial H_l}\right)_{11} dH_l + \left(\frac{\partial M_i}{\partial T}\right)_{12} dT$$

$$dS = \left(\frac{\partial S}{\partial \sigma_{kl}}\right)_{13} d\sigma_{kl} + \left(\frac{\partial S}{\partial E_k}\right)_{14} dE_k + \left(\frac{\partial S}{\partial H_l}\right)_{15} dH_l + \left(\frac{\partial S}{\partial T}\right)_{16} dT$$

1. Elastic deformation.
2. Reciprocal (or converse) piezo-electric effect.
3. Reciprocal (or converse) piezo-magnetic effect.
4. Thermal dilatation.
5. Piezo-electric effect.
6. Electric polarization.
7. Magneto-electric polarization.
8. Pyroelectricity.
9. Piezo-magnetic effect.
10. Reciprocal (or converse) magneto-electric polarization.
11. Magnetic polarization.
12. Pyromagnetism.
13. Piezo-caloric effect.
14. Electro-caloric effect.
15. Magneto-caloric effect.
16. Heat transmission.

http://www.iucr.org/education/pamphlets/18

http://it.iucr.org

2006 edition available through TU Graz library

International Tables for Crystallography
Volume D: Physical properties of crystals

Second online edition (2013) ISBN: 978-1-118-76229-5 doi: 10.1107/97809553602060000113

Edited by A. Authier

Contents

Groups

Crystals can have symmetries: translation, rotation, reflection, inversion,...

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\alpha & \sin\alpha \\ 0 & -\sin\alpha & \cos\alpha \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Symmetries can be represented by matrices.
All such matrices that bring the crystal into itself form the group of the crystal.

$$AB \in G \text{ for } A, B \in G$$

32 point groups (one point remains fixed during transformation)
230 space groups

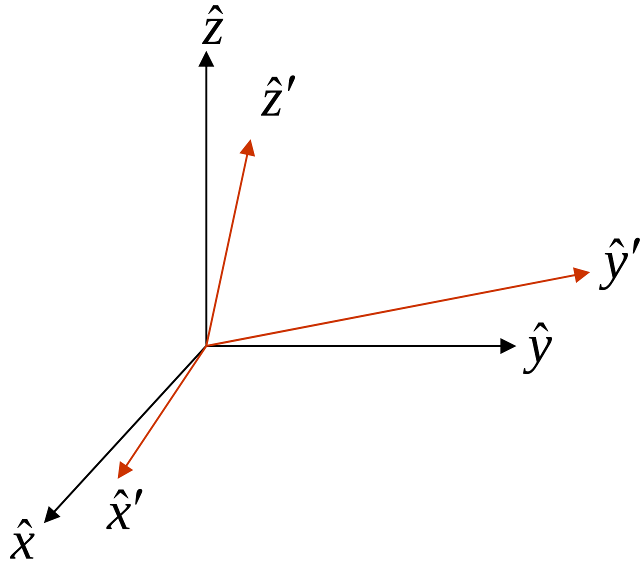
Strain

A distortion of a material is described by the strain matrix

$$x' = (1 + \varepsilon_{xx})\hat{x} + \varepsilon_{xy}\hat{y} + \varepsilon_{xz}\hat{z}$$

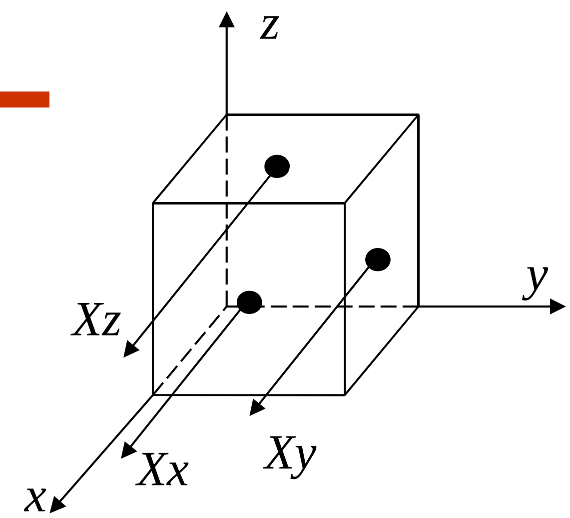
$$y' = \varepsilon_{yx}\hat{x} + (1 + \varepsilon_{yy})\hat{y} + \varepsilon_{yz}\hat{z}$$

$$z' = \varepsilon_{zx}\hat{x} + \varepsilon_{zy}\hat{y} + (1 + \varepsilon_{zz})\hat{z}$$



Strain is dimensionless $\Delta L/L$

Stress



9 forces describe the stress

Xx, Xy, Xz, Yx, Yy, Yz, Zx, Zy, Zz

Xx is a force applied in the *x*-direction to the plane normal to *x*

Xy is a sheer force applied in the *x*-direction to the plane normal to *y*

stress tensor:

$$\sigma = \begin{bmatrix} \frac{X_x}{A_x} & \frac{X_y}{A_y} & \frac{X_z}{A_z} \\ \frac{Y_x}{A_x} & \frac{Y_y}{A_y} & \frac{Y_z}{A_z} \\ \frac{Z_x}{A_x} & \frac{Z_y}{A_y} & \frac{Z_z}{A_z} \end{bmatrix}$$

Stress is force/m^2

Stress and Strain

$$\varepsilon_{ij} = s_{ijkl}\sigma_{kl}$$

The stress - strain relationship is described by a rank 4 stiffness tensor. The inverse of the stiffness tensor is the compliance tensor.

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

Einstein convention: sum over repeated indices.

$$\varepsilon_{xx} = s_{xxxx}\sigma_{xx} + s_{xxxy}\sigma_{xy} + s_{xxxz}\sigma_{xz} + s_{xxyx}\sigma_{yx} + s_{xxyy}\sigma_{yy}$$
$$+ s_{xxyz}\sigma_{yz} + s_{xxzx}\sigma_{zx} + s_{xxzy}\sigma_{zy} + s_{xxzz}\sigma_{zz}$$

Pyroelectricity

Pyroelectricity is described by a rank 1 tensor

$$\pi_i = \frac{\partial P_i}{\partial T}$$

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} \pi_x \\ \pi_y \\ \pi_z \end{bmatrix} = \begin{bmatrix} \pi_x \\ \pi_y \\ -\pi_z \end{bmatrix} \Rightarrow \begin{bmatrix} \pi_x \\ \pi_y \\ 0 \end{bmatrix}$$

rank 1: pyroelectric effect, pyromagnetic effect, electrocaloric effect, magnetocaloric effect