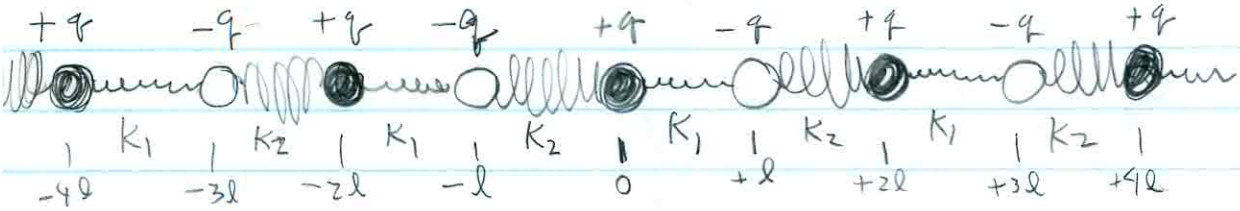
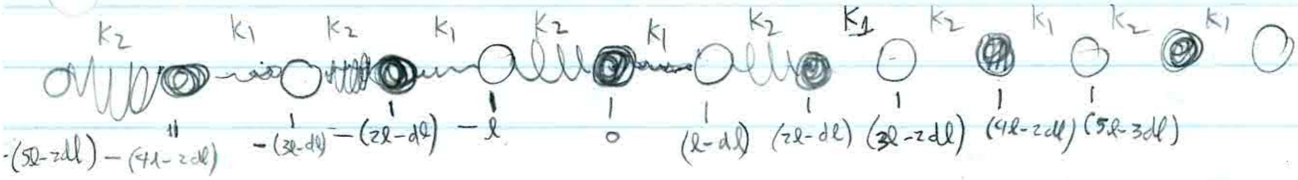
Lecture # 14: Piezoelectric materials, Peierls distortion

Piezoelectric materials

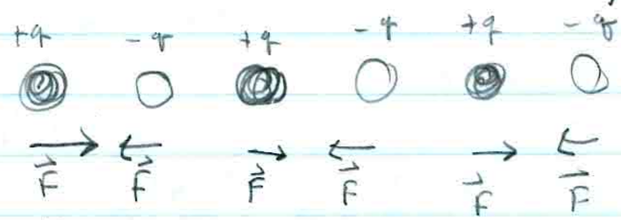
⇒ Acoustic waves can couple to electromagnetic waves: A strain can generate a voltage, and an applied voltage can generate strain (contraction or expansion) of the material.



(a) In equilibrium



(b) Under compressive strain (only K_1 compresses, $K_1 << K_2$)



(c) Under electric field

In equilibrium: $P = \sum_i x_i q_i = 0 + \underbrace{\left[(-q)(-l) + (-q)(+l)\right]}_{=0} + \underbrace{\left[(+q)(-2l) + (+q)(+2l)\right]}_{=0}$

$+ \ldots = 0$

Under compressive strain ($K_1 << K_2$): $P = 0 + \left[\underbrace{(-q)(-l) + (-q)(l-dl)}_{q\,dl}\right] + \left[\underbrace{(+q)(-2l+dl) + (+q)(2l-dl)}_{=0}\right]$

$+ \left[(-q)(3l-2dl) + (-q)(-3l+dl)\right] + \left[(+q)(-4l+2dl) + (+q)(4l-2dl)\right] + \ldots$

Under strain:

$$P = \frac{N}{2} q \, d\lambda \neq 0 \, !$$

Conversely, if an electric field is applied we will have a compression of the spring K_1 (see Fig(c)),

This interaction can be described by the following equations:

$$D_i = \sum_j \epsilon_{ij} E_j + \sum_{jl} e_{jli} \varepsilon_{jl}$$

D_i: Electric displacement, $\vec{D} = \epsilon_0 \vec{E} + \vec{P}$; ϵ_{ij}: dielectric tensor; e_{jli}: Piezoelectric tensor; ε_{jl}: Strain

$$\text{Stress} = \sigma_{ij} = \sum_l e'_{ijl} E_l + \sum_{lm} C_{ijlm} \varepsilon_{lm}$$

e'_{ijl}: Is this related to $\overleftrightarrow{e}$?

Actually $\overleftrightarrow{e}'$ and $\overleftrightarrow{e}$ are related by thermodynamics.

<u>Digression on thermodynamics of a dielectric</u>

To find the relationship, Consider the energy density of a dielectric $U(\vec{D}, S)$, and the Work necessary to change its state (i.e., to change the polarization or its entropy):

$$dU = TdS + \vec{E} \cdot d\vec{D}$$

(Because the energy density of a dielectric is $\vec{E} \cdot \vec{D}$, see §10 of Landau & Lifshitz Vol 8)

$$\Rightarrow \vec{E} = \left(\frac{\partial U}{\partial \vec{D}} \right)_S$$

To derive a similar relationship at constant T (instead of constant S), do a Legendre transformation and define the Free energy $F(\vec{D}, T)$:

$$F = U - TS \Rightarrow dF = dU - TdS - SdT = \vec{E} \cdot d\vec{D} - SdT$$

$$\Rightarrow \vec{E} = \left(\frac{\partial F}{\partial \vec{D}}\right)_T .$$

It's convenient to do another Legendre transformation to $F(\vec{D},T)$ in order to get $\tilde{F}(\vec{E},T)$:

$$\tilde{F} = F - \vec{E}\cdot\vec{D}$$

$$d\tilde{F} = dF - d\vec{E}\cdot\vec{D} - \vec{E}\cdot d\vec{D} = -S\,dT - \vec{D}\cdot d\vec{E}$$

$$\Rightarrow \quad (*) \quad \boxed{\vec{D} = -\left(\frac{\partial \tilde{F}}{\partial \vec{E}}\right)_T} \quad \text{(Note the } - \text{!)}$$

From $D_i = \sum_j \epsilon_{ij} E_j$ we see that $\epsilon_{ij} = \left(\frac{\partial D_i}{\partial E_j}\right)_T = -\left(\frac{\partial^2 \tilde{F}}{\partial E_j \partial E_i}\right)$.

swap

$$= -\left(\frac{\partial^2 \tilde{F}}{\partial E_i \partial E_j}\right) = \epsilon_{ji}$$

$\Rightarrow$ Hence $\overleftrightarrow{\epsilon}$ is a symmetric tensor.

This shows the power of thermodynamics.

We can also relate stress to energy:

$$\sigma_{ij} = +\left(\frac{\partial U}{\partial \varepsilon_{ij}}\right)_{T,\vec{E}}$$ (just like $\vec{F} = -\left(\frac{\partial U}{\partial \vec{r}}\right)$, but no $\ominus$ because positive strain (stretch) increases energy...)

$$(**) \quad \boxed{\sigma_{ij} = +\left(\frac{\partial \tilde{F}}{\partial \varepsilon_{ij}}\right)_{T,\vec{E}}}$$

Using $(*)$ and $(**)$, we can find a relationship between $\overleftrightarrow{e}$ and $\overleftrightarrow{e}'$:

$$e'_{ijl} = \left(\frac{\partial \sigma_{ij}}{\partial E_l}\right)_{T,\overleftrightarrow{\varepsilon}} = +\left(\frac{\partial^2 \tilde{F}}{\partial E_l \, \partial \varepsilon_{ij}}\right)_T$$

But

$$e_{jli} = \left(\frac{\partial D_i}{\partial \varepsilon_{jl}}\right)_{T,\vec{E}} = -\left(\frac{\partial^2 \tilde{F}}{\partial \varepsilon_{jl} \, \partial E_i}\right)_T = -e'_{jli}$$

Swap

$$\Rightarrow \boxed{\begin{aligned} D_i &= \sum_j \epsilon_{ij} E_j + \sum_{jl} e_{jli} \varepsilon_{jl} \\ \sigma_{ij} &= -\sum_l e_{ijl} E_l + \sum_{l,m} C_{ijlm} \varepsilon_{lm} \end{aligned}}$$

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This kind of "dependence" occurs frequently in "cross coupling" phenomena.

For a cubic crystal (T or T_d symmetry):

$$\overleftrightarrow{e} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ e_{41} & 0 & 0 \\ 0 & e_{41} & 0 \\ 0 & 0 & e_{41} \end{pmatrix}$$ with $e_{41} = 0$ if there is inversion symmetry.

(reduced notation: $e_{ijl} \rightarrow e_{\underbrace{(ij)}_{I}\underbrace{l}_{L}}$)

$e_{41} \neq 0$ when there is no inversion symmetry. For example, acoustic phonons in GaAs generate an electric field $\Rightarrow$ Piezophonons. This fact greatly changes the way phonons couple to electrons in GaAs.

Peierls instability

A one dimensional material without an inversion center such as in Fig (a) is unstable. It can lower its energy by "dimerization", i.e.:

dimerization

Coulomb energy per particle of Fig (b):

$$\frac{U_{Coulomb}}{N} = \left(-\frac{q^2}{l} - \frac{q^2}{l-dl}\right) + \left(\frac{q^2}{2l-dl} + \frac{q^2}{2l-dl}\right) + \left(\frac{-q^2}{3l-dl} - \frac{q^2}{3l-2dl}\right)$$

$$+ \left(\frac{q^2}{4l-2dl} + \frac{q^2}{4l-2dl}\right) + \cdots$$

$$\frac{U_{Coulomb}}{N} = -\frac{q^2}{l}\left\{\left(1 + \frac{1}{1-d}\right) - \left(\frac{1}{1-\frac{d}{2}}\right) + \left(\frac{1}{3-d} + \frac{1}{3-2d}\right) - \left(\frac{1}{2-d}\right) + \cdots\right\}$$

$$= -\frac{q^2}{l}\left\{\left[1 + 1 + d + O(d^2)\right] - \left[1 + \frac{d}{2} + O(d^2)\right] + \frac{1}{3}\left[1 + \frac{d}{3} + 1 + \frac{2}{3}d + O(d^2)\right] - \frac{1}{2}\left[1 + \frac{d}{2} + O(d^2)\right] + \cdots\right\}$$

$$= -\frac{q^2}{l}\left\{\left(1 - \frac{1}{2} + \frac{1}{3} - \cdots\right) + d\left(1 - \frac{1}{2} + \frac{1}{3} - \cdots\right)\right\}$$

$$= -\frac{q^2}{l}\left\{\underbrace{\left(1 - \frac{1}{2} + \frac{1}{3} - \cdots\right)}_{\ln(2) = \left(1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \frac{1}{5} - \frac{1}{6} + \cdots\right)}\left(1 + d\right) + O(d^2)\right\}$$

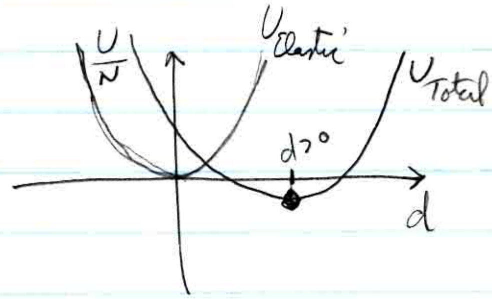
(6)

$$U_{\text{Coulomb}} = -\frac{Nq^2}{\ell} \ln(2) \left(1 + d\right)$$ (N is # of unit cells)

Note: Coulomb energy is lowered by $d > 0$!

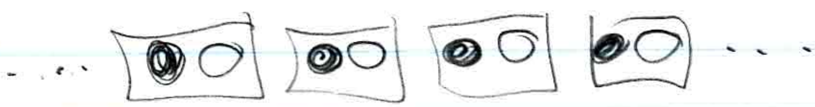
Elastic energy:

$$U_{\text{Elastic}} = \frac{1}{2} K_1 (d\ell)^2 N$$



$$\frac{U_{\text{Total}}}{N} = \left(\frac{1}{2} K_1 \ell^2\right) d^2 - \ln(2) \frac{q^2}{\ell} \left(1 + d\right)$$

$$\frac{dU_T}{dd} = K_1 \ell^2 d - \frac{\ln(2) q^2}{\ell} = 0 \Rightarrow d_{eq} = \frac{\ln(2) q^2}{\ell} \frac{1}{K_1 \ell^2} = \frac{\ln(2) q^2}{K_1 \ell^3}$$



dimerization.

Peierls distortion.

Note: Peierls distortion occurs even when there is inversion symmetry!