Zone-center phonons in polar crystals

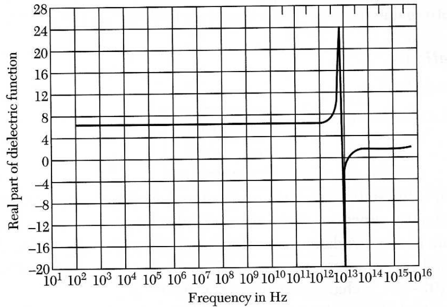
Raffaele Resta

Trieste, 2021

Outline

Outline

From: C. Kittel, Introduction to Solid State Physics

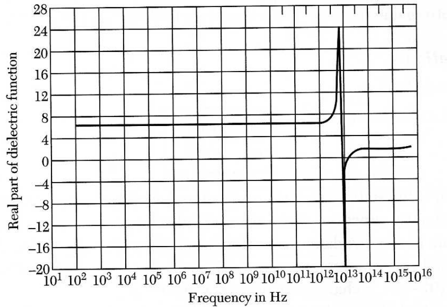


Re $\varepsilon(\omega)$ for SrF_2

Two regimes:

- Re $\varepsilon(\omega) \longrightarrow \varepsilon_0$: static
- Re $\varepsilon(\omega) \longrightarrow \varepsilon_\infty$: "static high frequency"
  a.k.a. clamped ion, a.k.a. electronic
- In a **non**polar crystal $\varepsilon_0 = \varepsilon_\infty$, no pole: why?

From: C. Kittel, Introduction to Solid State Physics

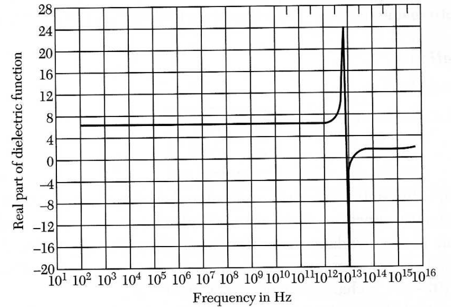


Re $\varepsilon(\omega)$ for SrF_2

Two regimes:

- Re $\varepsilon(\omega) \longrightarrow \varepsilon_0$: static
- Re $\varepsilon(\omega) \longrightarrow \varepsilon_\infty$: "static high frequency"
  a.k.a. clamped ion, a.k.a. electronic
- In a **nonpolar** crystal $\varepsilon_0 = \varepsilon_\infty$, no pole: why?

From: C. Kittel, Introduction to Solid State Physics

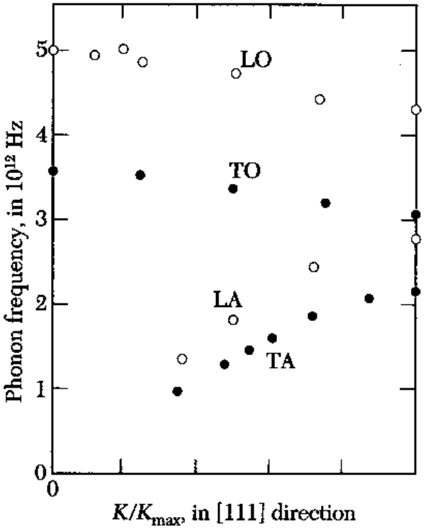


Re $\varepsilon(\omega)$ for SrF_2

Two regimes:

- Re $\varepsilon(\omega) \longrightarrow \varepsilon_0$: static
- Re $\varepsilon(\omega) \longrightarrow \varepsilon_\infty$: "static high frequency"
  a.k.a. clamped ion, a.k.a. electronic
- In a **non**polar crystal $\varepsilon_0 = \varepsilon_\infty$, no pole: why?

From: C. Kittel, Introduction to Solid State Physics

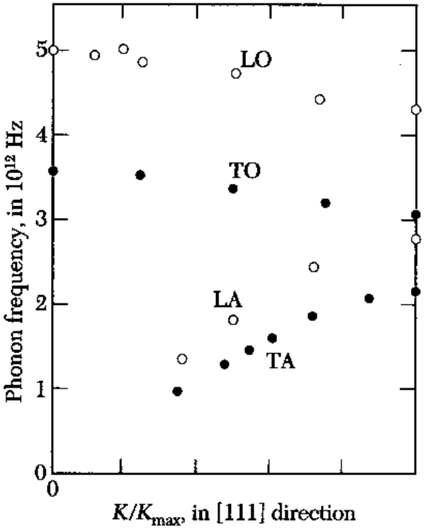


Inelastic neutron scattering in KBr

B.N. Brockhouse et al.

Experiments: 1950s
Nobel prize: 1994

From: C. Kittel, Introduction to Solid State Physics

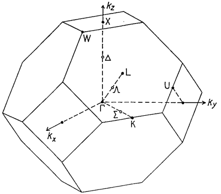


Inelastic neutron scattering in KBr

B.N. Brockhouse et al.

Experiments: 1950s
Nobel prize: 1994

Polar vs. nonpolar: Si & GaAs



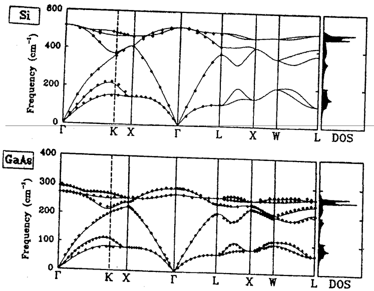


Figure 2. Phonon dispersions for Si (above) and GaAs (below) from *ab initio* calculations

Key message

- Polar crystal (cubic binary)
  - $\varepsilon_0 > \varepsilon_\infty$
  - $\omega_{\mathrm{LO}} > \omega_{\mathrm{TO}}$
  - Zone-center mode **infrared active**
- Nonpolar crystal (cubic binary, e.g. diamond)
  - $\varepsilon_0 = \varepsilon_\infty$
  - $\omega_{\mathrm{LO}} = \omega_{\mathrm{TO}}$
  - Zone-center mode **infrared inactive**

Lyddane-Sachs-Teller (1941)

$$\frac{\omega_{\mathrm{LO}}^2}{\omega_{\mathrm{TO}}^2} = \frac{\varepsilon_0}{\varepsilon_\infty}$$

Beautifully simple and general

Independent of microscopics such as

- masses
- interatomic force constants
- ionic charges
- cell volume.....

Outline

Phenomenological theory: Huang, 1950
(exact within the harmonic approximation)

Free energy **per cell** $\mathcal{F} = V_c \mathscr{F}$
Cubic binary crystal: **independent variables:** E, u
expanded to second order

$$\mathcal{F}(E,u) = \mathcal{F}_0 + \frac{1}{2} M \omega_{\mathrm{TO}}^2 u^2 - \frac{V_c}{8\pi} \varepsilon_\infty E^2 - Z^* u E$$

Equations of motion (M reduced mass):

$$\begin{aligned} f &= -\frac{\partial \mathcal{F}}{\partial u} = -M\omega_{\mathrm{TO}}^2 u + Z^* E \\ D &= -\frac{4\pi}{V_c}\frac{\partial \mathcal{F}}{\partial E} = \varepsilon_\infty E + \frac{4\pi}{V_c} Z^* u \end{aligned}$$

Phenomenological theory: Huang, 1950
(exact within the harmonic approximation)

Free energy **per cell** $\mathcal{F} = V_c \mathscr{F}$
Cubic binary crystal: **independent variables:** E, u
expanded to second order

$$\mathcal{F}(E, u) = \mathcal{F}_0 + \frac{1}{2} M \omega_{\mathrm{TO}}^2 u^2 - \frac{V_c}{8\pi} \varepsilon_\infty E^2 - Z^* uE$$

Equations of motion (M reduced mass):

$$\begin{aligned} f &= -\frac{\partial \mathcal{F}}{\partial u} = -M\omega_{\mathrm{TO}}^2 u + Z^* E \\ D &= -\frac{4\pi}{V_c} \frac{\partial \mathcal{F}}{\partial E} = \varepsilon_\infty E + \frac{4\pi}{V_c} Z^* u \end{aligned}$$

Phenomenological theory: Huang, 1950
(exact within the harmonic approximation)

Free energy **per cell** $\mathcal{F} = V_{\rm c}\mathscr{F}$
Cubic binary crystal: **independent variables:** E, u
expanded to second order

$$\mathcal{F}(E,u) = \mathcal{F}_0 + \frac{1}{2}M\omega_{\rm TO}^2\, u^2 - \frac{V_{\rm c}}{8\pi}\varepsilon_\infty E^2 - Z^* uE$$

Equations of motion (M reduced mass):

$$\begin{aligned} f &= -\frac{\partial\mathcal{F}}{\partial u} = -M\omega_{\rm TO}^2 u + Z^* E \\ D &= -\frac{4\pi}{V_{\rm c}}\frac{\partial\mathcal{F}}{\partial E} = \varepsilon_\infty E + \frac{4\pi}{V_{\rm c}} Z^* u \end{aligned}$$

Phenomenological theory: Huang, 1950
(exact within the harmonic approximation)

Free energy **per cell** $\mathcal{F} = V_{\rm c}\mathscr{F}$
Cubic binary crystal: **independent variables:** E, u
expanded to second order

$$\mathcal{F}(E,u) = \mathcal{F}_0 + \frac{1}{2}M\omega_{\rm TO}^2\, u^2 - \frac{V_{\rm c}}{8\pi}\varepsilon_\infty E^2 - Z^* uE$$

Equations of motion (M reduced mass):

$$\begin{aligned} f &= -\frac{\partial \mathcal{F}}{\partial u} = -M\omega_{\rm TO}^2 u + Z^* E \\ D &= -\frac{4\pi}{V_{\rm c}}\frac{\partial \mathcal{F}}{\partial E} = \varepsilon_\infty E + \frac{4\pi}{V_{\rm c}} Z^* u \end{aligned}$$

Phenomenological theory: Huang, 1950
(exact within the harmonic approximation)

Free energy **per cell** $\mathcal{F} = V_c \mathscr{F}$
Cubic binary crystal: **independent variables:** E, u
expanded to second order

$$\mathcal{F}(E,u) = \mathcal{F}_0 + \frac{1}{2} M \omega_{\mathrm{TO}}^2 u^2 - \frac{V_c}{8\pi} \varepsilon_\infty E^2 - Z^* uE$$

Equations of motion (M reduced mass):

$$\begin{aligned} f &= -\frac{\partial \mathcal{F}}{\partial u} = -M\omega_{\mathrm{TO}}^2 u + Z^* E \\ P &= -\frac{4\pi}{V_c}\frac{\partial \mathcal{F}}{\partial E} = \frac{\varepsilon_\infty - 1}{4\pi} E + \frac{1}{V_c} Z^* u \end{aligned}$$

Static response: ε_0

$$
\begin{aligned}
f &= -M\omega_{\mathrm{TO}}^2 u + Z^* E \\
D &= \varepsilon_\infty E + \frac{4\pi}{V_{\mathrm{c}}} Z^* u
\end{aligned}
$$

at equilibrium:

$$
f = 0 \quad \longrightarrow \quad u = \frac{Z^*}{M\omega_{\mathrm{TO}}^2} E
$$

$$
D = \left[\varepsilon_\infty + \frac{4\pi (Z^*)^2}{V_{\mathrm{c}} M\omega_{\mathrm{TO}}^2}\right] E = \varepsilon_0 \, E
$$

Static response: ε_0

$$
\begin{aligned}
f &= -M\omega_{\mathrm{TO}}^2 u + Z^* E \\
D &= \varepsilon_\infty E + \frac{4\pi}{V_\mathrm{c}} Z^* u
\end{aligned}
$$

at equilibrium:

$$
f = 0 \quad \longrightarrow \quad u = \frac{Z^*}{M\omega_{\mathrm{TO}}^2} E
$$

$$
D = \left[\varepsilon_\infty + \frac{4\pi (Z^*)^2}{V_\mathrm{c} M\omega_{\mathrm{TO}}^2} \right] E = \varepsilon_0 \, E
$$

Dynamical response $\varepsilon(\omega)$

$$
\begin{aligned}
f &= -M\omega_{\mathrm{TO}}^2 u + Z^* E \\
D &= \varepsilon_\infty E + \frac{4\pi}{V_{\mathrm{c}}} Z^* u
\end{aligned}
$$

forced oscillations at frequency ω:

$$-M\omega^2 u = -M\omega_{\mathrm{TO}}^2 u + Z^* E$$

$$u = \frac{Z^*}{M(\omega_{\mathrm{TO}}^2 - \omega^2)} E$$

$$D(\omega) = \left[\varepsilon_\infty + \frac{4\pi (Z^*)^2}{V_{\mathrm{c}} M(\omega_{\mathrm{TO}}^2 - \omega^2)}\right] E(\omega) = \mathrm{Re}\ \varepsilon(\omega)\ E(\omega)$$

Dynamical response $\varepsilon(\omega)$

$$
\begin{aligned}
f &= -M\omega_{\mathrm{TO}}^2 u + Z^* E \\
D &= \varepsilon_\infty E + \frac{4\pi}{V_{\mathrm{c}}} Z^* u
\end{aligned}
$$

forced oscillations at frequency ω:

$$-M\omega^2 u = -M\omega_{\mathrm{TO}}^2 u + Z^* E$$

$$u = \frac{Z^*}{M(\omega_{\mathrm{TO}}^2 - \omega^2)} E$$

$$D(\omega) = \left[\varepsilon_\infty + \frac{4\pi (Z^*)^2}{V_{\mathrm{c}} M(\omega_{\mathrm{TO}}^2 - \omega^2)}\right] E(\omega) = \text{Re}\ \varepsilon(\omega)\ E(\omega)$$

Dynamical response $\varepsilon(\omega)$

$$
\begin{aligned}
f &= -M\omega_{\mathrm{TO}}^2 u + Z^* E \\
D &= \varepsilon_\infty E + \frac{4\pi}{V_{\mathrm{c}}} Z^* u
\end{aligned}
$$

forced oscillations at frequency ω:

$$-M\omega^2 u = -M\omega_{\mathrm{TO}}^2 u + Z^* E$$

$$u = \frac{Z^*}{M(\omega_{\mathrm{TO}}^2 - \omega^2)} E$$

$$D(\omega) = \left[\varepsilon_\infty + \frac{4\pi (Z^*)^2}{V_{\mathrm{c}} M(\omega_{\mathrm{TO}}^2 - \omega^2)}\right] E(\omega) = \mathrm{Re}\ \varepsilon(\omega)\ E(\omega)$$

Dynamical response $\varepsilon(\omega)$

$$\begin{aligned} f &= -M\omega_{\mathrm{TO}}^2 u + Z^* E \\ D &= \varepsilon_\infty E + \frac{4\pi}{V_\mathrm{c}} Z^* u \end{aligned}$$

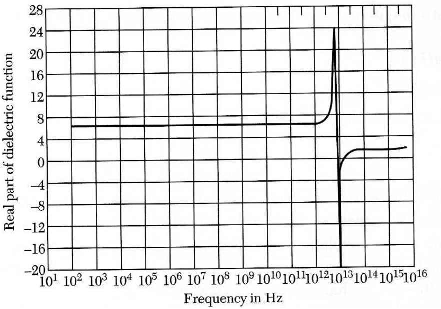
forced oscillations at frequency ω:

$$-M\omega^2 u = -M\omega_{\mathrm{TO}}^2 u + Z^* E$$

$$u = \frac{Z^*}{M(\omega_{\mathrm{TO}}^2 - \omega^2)} E$$

$$D(\omega) = \left[\varepsilon_\infty + \frac{4\pi (Z^*)^2}{V_\mathrm{c} M(\omega_{\mathrm{TO}}^2 - \omega^2)}\right] E(\omega) = \mathrm{Re}\ \varepsilon(\omega)\, E(\omega)$$

From: C. Kittel, Introduction to Solid State Physics



$\varepsilon(\omega)$ for SrF_2 (real part)

$$\mathrm{Re}\ \varepsilon(\omega) = \varepsilon_\infty + \frac{4\pi(Z^*)^2}{V_c M(\omega_{\mathrm{TO}}^2 - \omega^2)}$$

$$\mathrm{Im}\ \varepsilon(\omega) = \frac{2\pi(Z^*)^2}{V_c M \omega_{\mathrm{TO}}}\left[\,\delta(\omega_{\mathrm{TO}} - \omega) - \delta(\omega_{\mathrm{TO}} + \omega)\,\right]$$

E and **D** fields

- In presence of a long wavelength phonon of wave vector **q**:
  - Solid macroscopically homogeneous normal to **q**
  - Macroscopic properties modulated in the of **q** direction

- Ergo:
  - **E** normal to **q** vanish
  - **D** parallel to **q** vanish

  - TO phonon: $\mathbf{E} = 0, \mathbf{D} \neq 0$
  - LO phonon: $\mathbf{D} = 0, \mathbf{E} \neq 0$

$\mathbf{E}$ and $\mathbf{D}$ fields

- In presence of a long wavelength phonon of wave vector $\mathbf{q}$:
  - Solid macroscopically homogeneous normal to $\mathbf{q}$
  - Macroscopic properties modulated in the of $\mathbf{q}$ direction
- Ergo:
  - $\mathbf{E}$ normal to $\mathbf{q}$ vanish
  - $\mathbf{D}$ parallel to $\mathbf{q}$ vanish
  - TO phonon: $\mathbf{E} = 0, \mathbf{D} \neq 0$
  - LO phonon: $\mathbf{D} = 0, \mathbf{E} \neq 0$

Transverse & longitudinal modes

- In a transverse mode $E = 0$:

$$f = -M\omega_{\mathrm{TO}}^2 u + Z^* E$$

- In a longitudinal mode $D = \varepsilon E = 0 \;\Rightarrow\; \varepsilon = 0$:

$$0 = \varepsilon(\omega_{\mathrm{LO}}) = \varepsilon_\infty + \frac{4\pi(Z^*)^2}{V_{\mathrm{c}} M(\omega_{\mathrm{TO}}^2 - \omega_{\mathrm{LO}}^2)}$$

$$\omega_{\mathrm{LO}}^2 = \omega_{\mathrm{TO}}^2 + \frac{4\pi(Z^*)^2}{\varepsilon_\infty V_{\mathrm{c}} M} = \omega_{\mathrm{TO}}^2 + 4\pi\frac{(\text{charge density})^2}{\text{mass density}}$$

$$(\text{charge density})^2 = \frac{(Z^*)^2}{\varepsilon_\infty V_{\mathrm{c}}^2} \qquad \text{reduced mass density} = \frac{M}{V_{\mathrm{c}}}$$

Transverse & longitudinal modes

- In a transverse mode $E = 0$:

$$f = -M\omega_{\mathrm{TO}}^2 u + Z^* E$$

- In a longitudinal mode $D = \varepsilon E = 0 \;\Rightarrow\; \varepsilon = 0$:

$$0 = \varepsilon(\omega_{\mathrm{LO}}) = \varepsilon_\infty + \frac{4\pi (Z^*)^2}{V_c M(\omega_{\mathrm{TO}}^2 - \omega_{\mathrm{LO}}^2)}$$

$$\omega_{\mathrm{LO}}^2 = \omega_{\mathrm{TO}}^2 + \frac{4\pi (Z^*)^2}{\varepsilon_\infty V_c M} = \omega_{\mathrm{TO}}^2 + 4\pi \frac{(\text{charge density})^2}{\text{mass density}}$$

$$(\text{charge density})^2 = \frac{(Z^*)^2}{\varepsilon_\infty V_c^2} \qquad \text{reduced mass density} = \frac{M}{V_c}$$

Transverse & longitudinal modes

- In a transverse mode $E = 0$:

$$f = -M\omega_{\mathrm{TO}}^2 u + Z^* E$$

- In a longitudinal mode $D = \varepsilon E = 0 \;\Rightarrow\; \varepsilon = 0$:

$$0 = \varepsilon(\omega_{\mathrm{LO}}) = \varepsilon_\infty + \frac{4\pi(Z^*)^2}{V_{\mathrm{c}} M(\omega_{\mathrm{TO}}^2 - \omega_{\mathrm{LO}}^2)}$$

$$\omega_{\mathrm{LO}}^2 = \omega_{\mathrm{TO}}^2 + \frac{4\pi(Z^*)^2}{\varepsilon_\infty V_{\mathrm{c}} M} = \omega_{\mathrm{TO}}^2 + 4\pi \frac{(\text{charge density})^2}{\text{mass density}}$$

$$(\text{charge density})^2 = \frac{(Z^*)^2}{\varepsilon_\infty V_{\mathrm{c}}^2} \qquad \text{reduced mass density} = \frac{M}{V_{\mathrm{c}}}$$

Transverse & longitudinal modes

- In a transverse mode $E = 0$:

$$f = -M\omega_{\mathrm{TO}}^2 u + Z^* E$$

- In a longitudinal mode $D = \varepsilon E = 0 \;\Rightarrow\; \varepsilon = 0$:

$$0 = \varepsilon(\omega_{\mathrm{LO}}) = \varepsilon_\infty + \frac{4\pi (Z^*)^2}{V_{\mathrm{c}} M(\omega_{\mathrm{TO}}^2 - \omega_{\mathrm{LO}}^2)}$$

$$\omega_{\mathrm{LO}}^2 = \omega_{\mathrm{TO}}^2 + \frac{4\pi (Z^*)^2}{\varepsilon_\infty V_{\mathrm{c}} M} = \omega_{\mathrm{TO}}^2 + 4\pi \frac{(\text{charge density})^2}{\text{mass density}}$$

$$(\text{charge density})^2 = \frac{(Z^*)^2}{\varepsilon_\infty V_{\mathrm{c}}^2} \qquad \text{reduced mass density} = \frac{M}{V_{\mathrm{c}}}$$

Transverse & longitudinal modes

- In a transverse mode $E = 0$:

$$f = -M\omega_{\rm TO}^2 u + Z^* E$$

- In a longitudinal mode $D = \varepsilon E = 0 \;\Rightarrow\; \varepsilon = 0$:

$$0 = \varepsilon(\omega_{\rm LO}) = \varepsilon_\infty + \frac{4\pi(Z^*)^2}{V_c M(\omega_{\rm TO}^2 - \omega_{\rm LO}^2)}$$

$$\omega_{\rm LO}^2 = \omega_{\rm TO}^2 + \frac{4\pi(Z^*)^2}{\varepsilon_\infty V_c M} = \omega_{\rm TO}^2 + 4\pi\frac{(\text{charge density})^2}{\text{mass density}}$$

$$(\text{charge density})^2 = \frac{(Z^*)^2}{\varepsilon_\infty V_c^2} \qquad \text{reduced mass density} = \frac{M}{V_c}$$

Bottom line: Lyddane-Sachs-Teller

$$\frac{\omega_{\mathrm{LO}}^2}{\omega_{\mathrm{TO}}^2} = 1 + \frac{4\pi(Z^*)^2}{\varepsilon_\infty V_{\mathrm{c}} M \omega_{\mathrm{TO}}^2}$$

$$\frac{\varepsilon_0}{\varepsilon_\infty} = \text{the same}$$

- All microscopic parameters disappear (Z^*, M, V_{c})
- LST is **exact** (within the harmonic approx.)
- Both members of LST measure the field-lattice coupling

- Can be generalized to more complex crystals, and beyond (anharmonic solids, amorphous materials....)

Bottom line: Lyddane-Sachs-Teller

$$\frac{\omega_{\mathrm{LO}}^2}{\omega_{\mathrm{TO}}^2} = 1 + \frac{4\pi(Z^*)^2}{\varepsilon_\infty V_{\mathrm{c}} M \omega_{\mathrm{TO}}^2}$$

$$\frac{\varepsilon_0}{\varepsilon_\infty} = \text{the same}$$

- All microscopic parameters disappear (Z^*, M, V_{c})
- LST is **exact** (within the harmonic approx.)
- Both members of LST measure the field-lattice coupling

- Can be generalized to more complex crystals, and beyond (anharmonic solids, amorphous materials....)

Bottom line: Lyddane-Sachs-Teller

$$\frac{\omega_{\mathrm{LO}}^2}{\omega_{\mathrm{TO}}^2} = 1 + \frac{4\pi(Z^*)^2}{\varepsilon_\infty V_{\mathrm{c}} M \omega_{\mathrm{TO}}^2}$$

$$\frac{\varepsilon_0}{\varepsilon_\infty} = \text{the same}$$

- All microscopic parameters disappear (Z^*, M, V_{c})
- LST is **exact** (within the harmonic approx.)
- Both members of LST measure the field-lattice coupling
- Can be generalized to more complex crystals, and beyond (anharmonic solids, amorphous materials....)

Bottom line: Lyddane-Sachs-Teller

$$\frac{\omega_{\mathrm{LO}}^2}{\omega_{\mathrm{TO}}^2} = 1 + \frac{4\pi (Z^*)^2}{\varepsilon_\infty V_\mathrm{c} M \omega_{\mathrm{TO}}^2}$$

$$\frac{\varepsilon_0}{\varepsilon_\infty} = \text{the same}$$

- All microscopic parameters disappear (Z^*, M, V_c)
- LST is **exact** (within the harmonic approx.)
- Both members of LST measure the field-lattice coupling

- Can be generalized to more complex crystals, and beyond (anharmonic solids, amorphous materials....)

Bottom line: Lyddane-Sachs-Teller

$$\frac{\omega_{\mathrm{LO}}^2}{\omega_{\mathrm{TO}}^2} = 1 + \frac{4\pi (Z^*)^2}{\varepsilon_\infty V_{\mathrm{c}} M \omega_{\mathrm{TO}}^2}$$

$$\frac{\varepsilon_0}{\varepsilon_\infty} = \text{the same}$$

- All microscopic parameters disappear (Z^*, M, V_{c})
- LST is **exact** (within the harmonic approx.)
- Both members of LST measure the field-lattice coupling
- Can be generalized to more complex crystals, and beyond (anharmonic solids, amorphous materials....)

Outline

Born effective charge (cubic binary crystal)

$$\mathcal{F}(E,u) = \mathcal{F}_0 + \frac{1}{2}M\omega_{\mathrm{TO}}^2\, u^2 - \frac{V_{\mathrm{c}}}{8\pi}\varepsilon_\infty E^2 - Z^* uE$$

$$\begin{aligned} f &= -\frac{\partial \mathcal{F}}{\partial u} = -M\omega_{\mathrm{TO}}^2 u + Z^* E \\ P &= -\frac{1}{V_{\mathrm{c}}}\frac{\partial \mathcal{F}}{\partial E} = \frac{\varepsilon_\infty - 1}{4\pi}E + \frac{1}{V_{\mathrm{c}}} Z^* u \end{aligned}$$

- Dual interpretation of $Z^* = \dfrac{\partial^2 \mathcal{F}}{\partial u \partial E}$
  - Force exerted on the **clamped** nuclei by E: $\dfrac{\partial f}{\partial E}$
  - Polarization due to the ionic displacement at $E = 0$: $\dfrac{1}{V_{\mathrm{c}}}\dfrac{\partial P}{\partial u}$

Born effective charge (generic crystal)

- Generalization to a low-symmetry lattice with $\ell = 1, 2.....n$ sublattices:
  - Effective mass tensor:

$$Z^*_{\ell,\alpha\beta} = \frac{\partial^2 \mathcal{F}}{\partial u_{\ell,\alpha} \partial E_\beta}$$

  - Sum rule: $\sum_\ell Z^*_{\ell,\alpha\beta} = 0$
  - In general, **not** a symmetric tensor
  - It could be strongly **counterintuitive**

Born effective charge (generic crystal)

- Generalization to a low-symmetry lattice with $\ell = 1, 2.....n$ sublattices:
  - Effective mass tensor:

$$Z^*_{\ell,\alpha\beta} = \frac{\partial^2 \mathcal{F}}{\partial u_{\ell,\alpha} \partial E_\beta}$$

  - Sum rule: $\sum_\ell Z^*_{\ell,\alpha\beta} = 0$
  - In general, **not** a symmetric tensor
  - It could be strongly **counterintuitive**

Macroscopic current

- In a cubic binary crystal:

$$P = \frac{1}{V_{\mathrm{c}}} Z^* u, \qquad E = 0$$

- **Harmonic:** The sublattices oscillate at frequency ω_{TO}:

$$\begin{aligned} P(t) &= \frac{1}{V_{\mathrm{c}}} Z^* u(t) \\ j(t) &= \frac{d}{dt} P(t) = \frac{1}{V_{\mathrm{c}}} Z^* \frac{d}{dt} u(t) = \frac{1}{V_{\mathrm{c}}} Z^* v(t) \end{aligned}$$

Total current (a.k.a. charge flux): electronic and nuclear

- Generic, anharmonic system (e.g. liquid):

$$j_\alpha(t) = \frac{e}{V} \sum_{\ell=1}^{N} Z^*_{\ell,\alpha\beta}(t)\, v_{\ell,\beta}(t)$$

Macroscopic current

- In a cubic binary crystal:

$$P = \frac{1}{V_\mathrm{c}} Z^* u, \qquad E = 0$$

- **Harmonic:** The sublattices oscillate at frequency ω_TO:

$$\begin{aligned} P(t) &= \frac{1}{V_\mathrm{c}} Z^* u(t) \\ j(t) &= \frac{d}{dt} P(t) = \frac{1}{V_\mathrm{c}} Z^* \frac{d}{dt} u(t) = \frac{1}{V_\mathrm{c}} Z^* v(t) \end{aligned}$$

Total current (a.k.a. charge flux): electronic and nuclear

- Generic, anharmonic system (e.g. liquid):

$$j_\alpha(t) = \frac{e}{V} \sum_{\ell=1}^{N} Z^*_{\ell,\alpha\beta}(t)\, v_{\ell,\beta}(t)$$

Macroscopic vs. microscopic field

$\mathbf{E}^{(\mathrm{micro})}(\mathbf{r})$ is the "real" electric field inside the material:

$$
\begin{aligned}
\mathbf{f}_\ell &= Z_\ell\, \mathbf{E}^{(\mathrm{micro})}(\mathbf{r}_\ell) && Z_\ell \text{ bare nuclear charge} \\
\mathbf{f}_{\ell,\alpha} &= Z^*_{\ell,\alpha\beta}\, E_\beta && \text{force induced by } \textbf{macroscopic E} \text{ field}
\end{aligned}
$$

$$Z^*_{\ell,\alpha\beta} = \frac{E^{(\mathrm{micro})}_\alpha(\mathbf{r}_\ell)}{E_\beta} Z_\ell$$

$$Z^*_{\mathrm{cation}} > 0 \qquad\qquad Z^*_{\mathrm{anion}} < 0$$

CAVEAT: No pseudopotentials here!

Macroscopic vs. microscopic field

$\mathbf{E}^{(\mathrm{micro})}(\mathbf{r})$ is the "real" electric field inside the material:

$$\mathbf{f}_\ell = Z_\ell \, \mathbf{E}^{(\mathrm{micro})}(\mathbf{r}_\ell) \qquad Z_\ell \text{ bare nuclear charge}$$

$$\mathbf{f}_{\ell,\alpha} = Z^*_{\ell,\alpha\beta} \, E_\beta \qquad \text{force induced by } \textbf{macroscopic } \mathbf{E} \text{ field}$$

$$Z^*_{\ell,\alpha\beta} = \frac{E^{(\mathrm{micro})}_\alpha(\mathbf{r}_\ell)}{E_\beta} \, Z_\ell$$

$$Z^*_{\mathrm{cation}} > 0 \qquad Z^*_{\mathrm{anion}} < 0$$

CAVEAT: No pseudopotentials here!

Macroscopic vs. microscopic field

$\mathbf{E}^{(\mathrm{micro})}(\mathbf{r})$ is the "real" electric field inside the material:

$$\begin{aligned} \mathbf{f}_\ell &= Z_\ell \, \mathbf{E}^{(\mathrm{micro})}(\mathbf{r}_\ell) && Z_\ell \text{ bare nuclear charge} \\ \mathbf{f}_{\ell,\alpha} &= Z^*_{\ell,\alpha\beta} \, E_\beta && \text{force induced by } \textbf{macroscopic } \mathbf{E} \text{ field} \end{aligned}$$

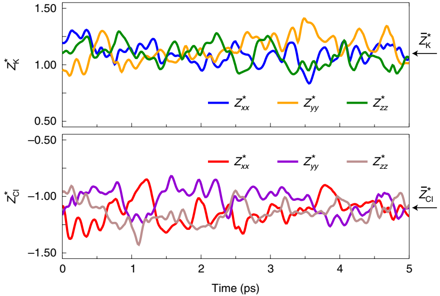
$$Z^*_{\ell,\alpha\beta} = \frac{E^{(\mathrm{micro})}_\alpha(\mathbf{r}_\ell)}{E_\beta} Z_\ell$$

$$Z^*_{\mathrm{cation}} > 0 \qquad\qquad Z^*_{\mathrm{anion}} < 0$$

CAVEAT: No pseudopotentials here!

Z^* tensors in molten KCl

$$j_\alpha(t) = \frac{e}{V} \sum_{\ell=1}^{N} Z^*_{\ell,\alpha\beta}(t)\, v_{\ell,\beta}(t)$$



Instantaneous $\overleftrightarrow{Z}^*_\ell(t)$ (after Grasselli & Baroni, Nature Phys. 2019)

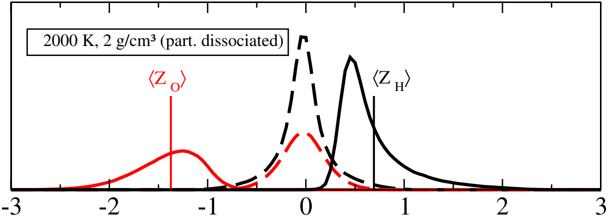
Scalar in average, $\langle \overleftrightarrow{Z}^*_{\mathrm{K}} \rangle = 1.1$, $\langle \overleftrightarrow{Z}^*_{\mathrm{Cl}} \rangle = -1.1$

Z^* tensors in partially dissociated water

54 O atoms and 108 H atoms in a PBCs simulation cell of volume V: **anharmonic** thermal motion in zero **E** field

$$j_\alpha(t) = \frac{e}{V} \sum_{\ell=1}^{N} Z^*_{\ell,\alpha\beta}(t)\, v_{\ell,\beta}(t)$$

Distribution of the Z^*_ℓ tensors: diagonal (solid) & off-diagonal (dashed)



French, Hamel, & Redmer, Phys. Rev. Lett. **107**, 185901 (2011)

Ionic conductivity

Fluctuation-dissipation theorem (Green-Kubo) for ionic conductivity:

$$\sigma = \frac{V\beta}{3} \int_0^\infty dt \, \langle \, \mathbf{j}(t) \cdot \mathbf{j}(0) \, \rangle$$