

Phonon Spectrum in Solids

LuFe₂O_{4.86} Calculation Details

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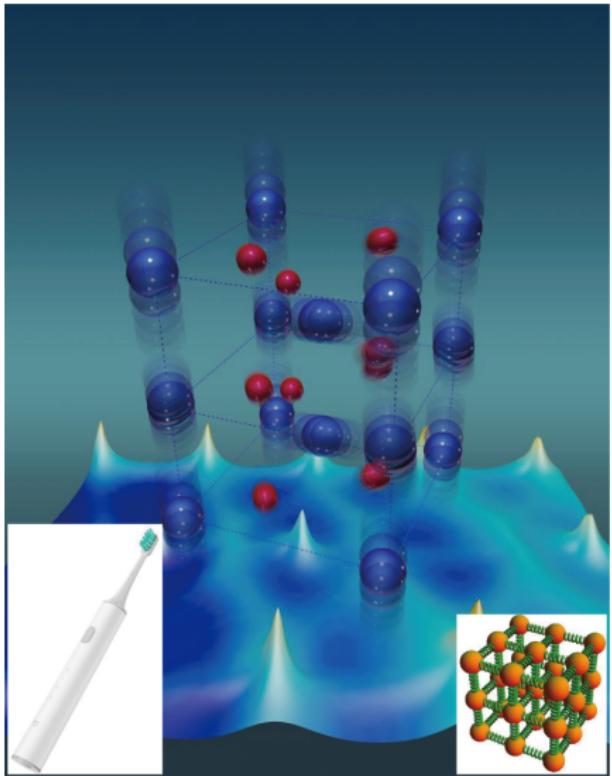
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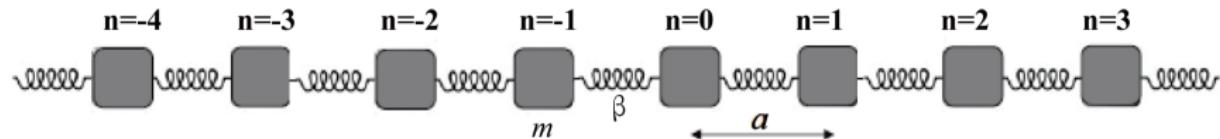
Lattice vibrations



- The atoms in the solid are **jiggling** all the time.
- The vibration amplitude usually far smaller than the atoms radius, e.g., $0.01 \sim 0.1\text{\AA}$.^a
- The speed or frequency of the atoms' movement is usually in $1 \sim 10\text{THz}$ level, much lower than the electrons'.
- That vibration of each atom is **not independent**.
- All of the atoms in the solids **vibrate together**, forming a fantastic picture.

^aL. Cartz, Proc. Phys. Soc. B **68**, 957 (1955).

One dimensional atomic chain: describe



To describe the vibration on this atoms chain, we introduce two kinds of parameters:

- The space frequency $q = 2\pi/\lambda$
- The time frequency $\omega = 2\pi/T$

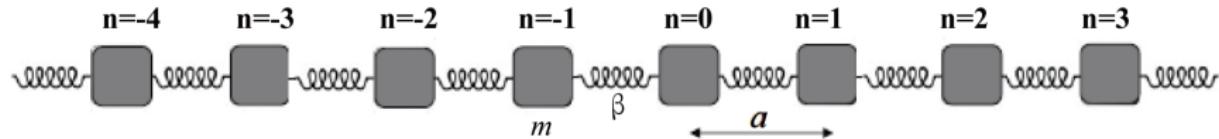
This typical analytical mechanics question has a concise result.

$$u_n = A e^{-i(\omega t - naq)} \quad (1a)$$

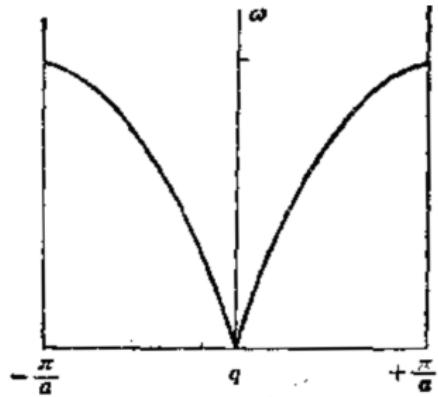
$$\omega^2 = \frac{2\beta}{m} [1 - \cos(qa)] \quad (1b)$$

Where, u_n is the displacement of the n th atom, $\beta = \left. \frac{\partial^2 V}{\partial u_n^2} \right|_{u_n=0}$, V is the potential energy around each atoms.

One dimensional atoms chain: analysis

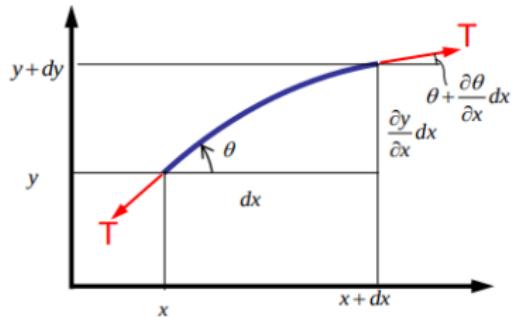


$$u_n = A e^{-i(\omega t - naq)}, \quad \omega = 2 \sqrt{\frac{\beta}{m}} \left| \sin \frac{aq}{2} \right|$$



- The vibration of each atom follows the **simple harmonic motion** format.
- The relation of $\omega(q)$, which also called “**dispersion relation**” or “**phonon spectrum**”, is periodic in q , with the period of $2\pi/a$.
- The ω at $q = 0$ (the Γ point) is zero, for it represent a **constant vibration**, means, no inter vibration.
- The $\omega(q)$ near the Γ point shows a **linear dispersion relation**.

Vibration in continuous medium (Long-wave limit)



Under the **long-wave limit** (the q near the Γ point), the lattice wave can be exactly regarded as spreading in a **continuous medium**.

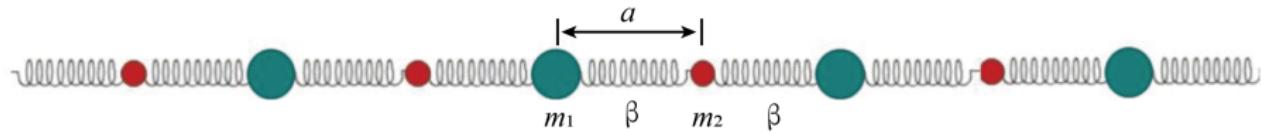
The vibration in the continuous medium is also a typical analytical mechanics problem.

The dispersion relation of $\omega - q$ has a simple **linear relation**,

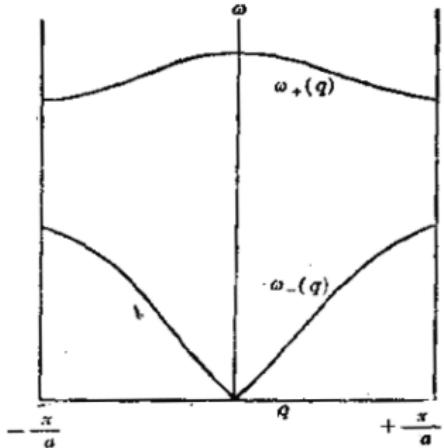
$$\omega = vq \quad (2)$$

Where, v is the group velocity of the wave, a constant.

What if primitive cell contains two atoms?



$$\omega_{\pm}^2 = \beta \frac{m_1 + m_2}{m_1 m_2} \left\{ 1 \pm [1 - \frac{4m_1 m_2}{(m_1 + m_2)^2} \sin^2(aq)]^{1/2} \right\} \quad (3)$$

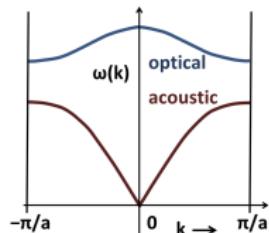


- There are **two kinds of "branches"** in phonon spectrum. Near the Γ point, the lower branch still shows a linear dispersion, but the upper does not.
- We called the lower branch as the **acoustic branch**, and the upper branch as **optical branch**.
- In one dimensional system, the **number of the total branches** is equal to the **number of atoms in one primitive cell**.

Acoustic branch and optical branch



黃昆 (Kun Huang)



- There are two kinds of branches in the phonon spectrum, **acoustic branch** and **optical branch**.
- The **acoustic branch** described the **vibration of the center of mass** for the whole primitive cell.
- The **optical branch** described the vibration of atoms in each primitive cell. In the optical mode, the primitive cell's **center of mass DOES NOT move**.
- There will be d **acoustic branch** and $(n - 1)d$ **optical branch**, where d is the space dimension, and n is the atoms number in one primitive cell.
- As prof. Huang points, the energy or frequency of optical modes is higher than the acoustic modes, and the optical branch near the Γ point do not satisfied the linear dispersion, are all caused by the **electric forces between atoms**.

Phonon spectrum in solids: calculation equation

The Hamiltonian of the phonon system is,

$$H = C_0 + \frac{1}{2} \sum_{\mu\alpha i} M_\alpha \dot{u}_{\mu\alpha i}^2 + \frac{1}{2} \sum_{\mu\alpha i, \nu\beta j} C_{\mu\alpha i}^{\nu\beta j} u_{\mu\alpha i} u_{\nu\beta j} \quad (4)$$

So we get its motion equation,

$$M_\alpha \ddot{u}_{\mu\alpha i} = - \sum_{\nu\beta j} C_{\mu\alpha i}^{\nu\beta j} u_{\nu\beta j} \quad (5)$$

Let,

$$D_{\alpha\beta,ij}(\mathbf{q}) = D_{\alpha\beta,ij}(\mathbf{q}, \mu) = \sum_{\nu} \frac{1}{\sqrt{M_\alpha M_\beta}} C_{\mu\alpha i}^{\nu\beta j} e^{i\mathbf{k}\cdot(\mathbf{R}_\nu - \mathbf{R}_\mu)} \quad (6)$$

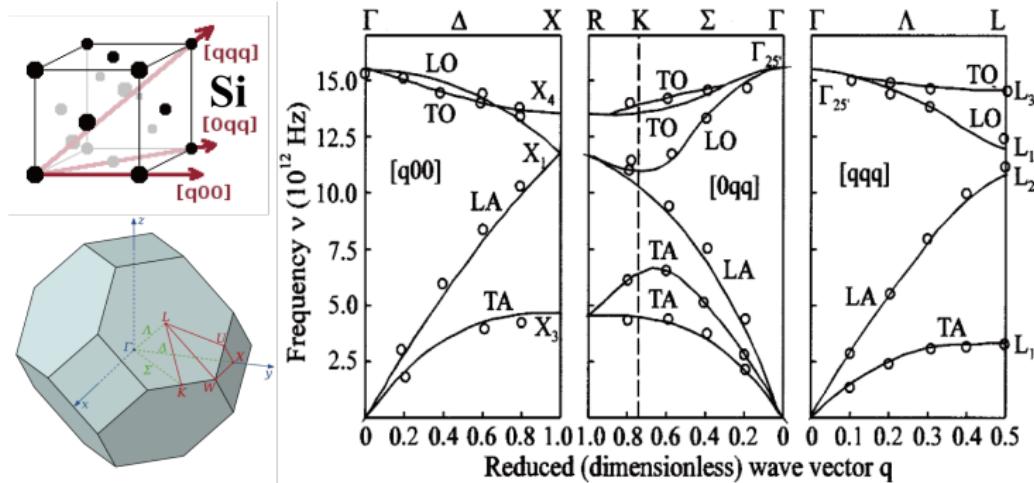
And the phonon spectrum $\omega(\mathbf{q})$ can be calculated as,

$$\det|\omega^2 \delta_{\alpha\beta} \delta_{ij} - D_{\alpha\beta,ij}(\mathbf{q})| = 0 \quad (7)$$

Where μ, ν are the index of primitive cells, α, β are the index of atoms in each primitive cell, and i, j are the index of directions.

The key parameters we need for calculate the phonon spectrum is the **force constant matrix** $\mathbf{C} = [C_{\mu\alpha i}^{\nu\beta j}]$. $C_{\mu\alpha i}^{\nu\beta j}$ means that, if the β th atom in ν th cell move a unit length in j direction, what forces will the α th atom in μ th cell in i direction fell.

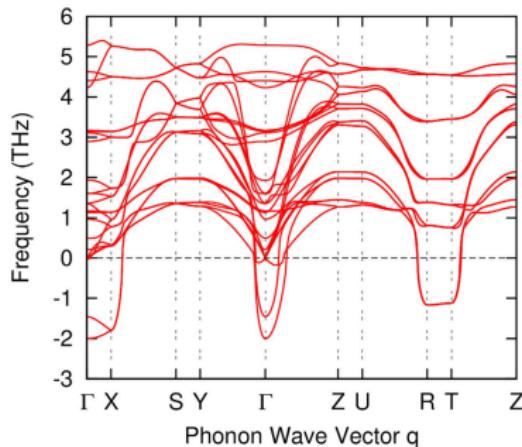
Phonon spectrum in solids: LA, LO, TA, TO



R. Tubino, et. al., J. Chem. Phys. 56, 1022 (1972).

- For each direction, there are **acoustic** and **optical branches**.
- Both kinds of branches split into **longitudinal** and **transversal** modes (longitudinal acoustic (LA) and optical (LO) and transversal acoustic (TA) and optical (TO)).
- In some cases, the transversal branches **split further**.

Imaginary frequency in phonon spectrum



- In some cases, we may get this kind of phonon spectrum in calculation, which has the “negative” valued ω .
- But actually, the $\omega(\mathbf{q})$ in the calculation cannot be negative, since we can only get the ω^2 from Eq. (7), and then choice the positive ω .
- The “negative” values here actually represent the **imaginary part** of the ω . In order to express more easily and directly, we **bend them into the real negative plane**.
- The appearance of the imaginary part indicates the structure's **dynamic instability**. Because,

$$u_{\mu\alpha i}(\mathbf{q}, t) = \frac{e_{\alpha i}(\mathbf{q})}{\sqrt{M_\alpha}} e^{-i(\omega t - \mathbf{q} \cdot \mathbf{R}_\mu)} = \mathbf{A}_{\mu\alpha i} e^{-i\omega t} \quad (8)$$

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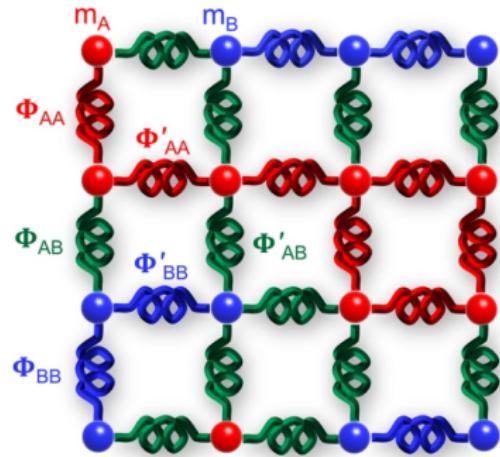
Force constant matrix in solid

As we mention before, the key parameters we need for calculating the phonon spectrum is the **force constant matrix** $C = [C_{\mu\alpha i}^{\nu\beta j}]$ (Φ in the figure). The C has at least two different meaning,

- The **forces** that other atoms might feel if we move one atom.
- The **second derivative of potential energy** about position.

$$C_{\mu\alpha i}^{\nu\beta j} = \left. \frac{\partial^2 V}{\partial u_{\mu\alpha i} \partial u_{\nu\beta j}} \right|_{u=0}$$

In order to get C , rather than using the empirical potential or simple Coulomb forces between atoms, we need to use **density functional theory (DFT)** to get precise value of the **forces** or **energies**.



“Frozen phonon method”

The algorithm that the “frozen phonon method” use is as follow:

- Read in a target atomic structure, S .
- Slightly change the position of one atom in S , get a new atomic structure, S'_1 .
- Use DFT method calculate S'_1 , and obtain the forces on all of the atoms.
- Slightly change the position of another atom in S , get another new atomic structure, S'_2 . Repeat steps above.
- Summarize all of the forces in all of the structures, calculate the phonon spectrum.

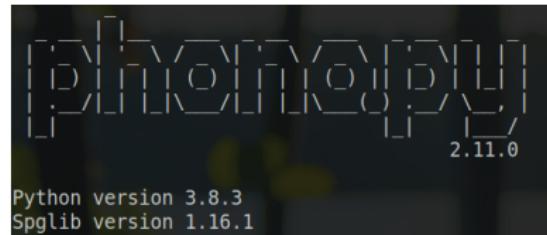


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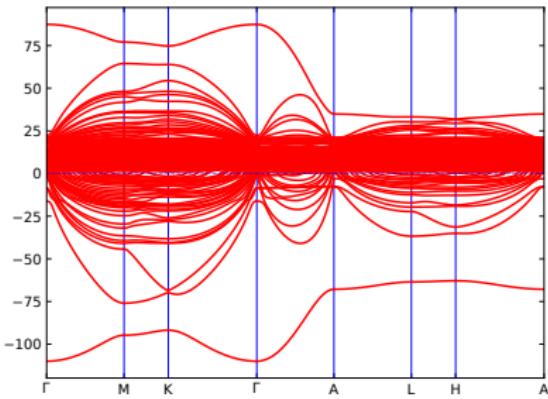
Difficulties in complex magnetic system

In the **complex magnetic system**, obtain the **stable phonon spectrum** using “frozen phonon method” may **face some challenges**,

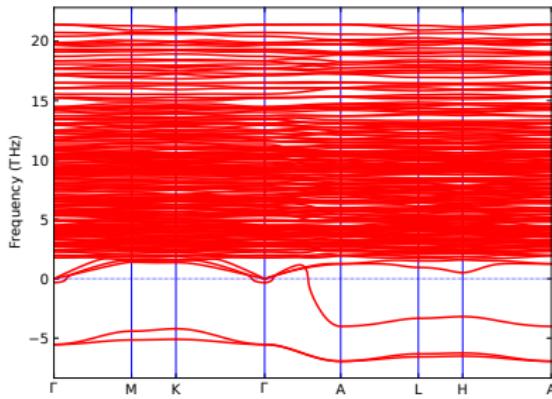
- The slight movement of atoms may let the DFT calculation fall into a **meta-stable state**, especially when the system is magnetic or extremely complex.
- Even worse, in a large system, randomly move one atom may cause the DFT calculation **hard to converge**.
- The phonon spectrum is **extremely expensive** in time and resources when we try to calculate a huge system, for it may contain hundreds of calculation tasks.

$\text{LuFe}_2\text{O}_{4.86}$ without electron/hole doping

Frequency (THz)



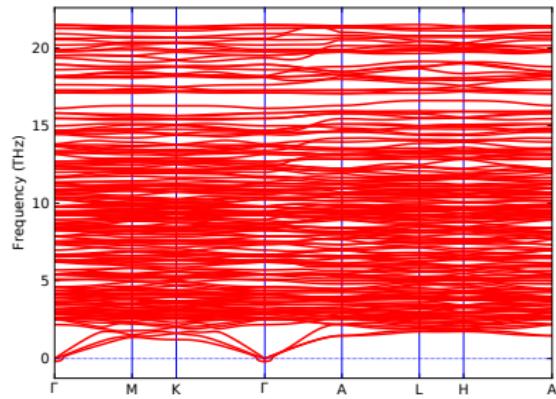
With inversion without hole doping



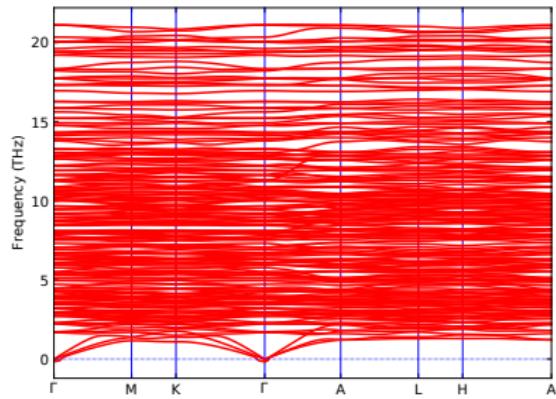
Without inversion without electron doping

Without any electron or hole doping, the phonon spectrum is **unstable**.

$\text{LuFe}_2\text{O}_{4.86}$ with electron/hole doping



With inversion with one-hole doping



Without inversion with one-electron doping

With electron or hole doping, the phonon spectrum is **stable**. The tiny imaginary parts near the Γ point is some numerical error, which are usually ignored.