## Chapter 4: Phonons I Crystal Vibrations

## Major Elementary Excitation in Solids

<u>с</u>	Name	Field
· · · · · · · · · · · · · · · · · · ·	Electron	
~~~~~	Photon	Electromagnetic wave
<b>→</b> <i>M</i> →	Phonon	Elastic wave
·	Plasmon	Collective electron wave
-lle-	Magnon	Magnetization wave
- ( - ) - () - () - () - () - () - () -	Polaron	Electron + elastic deformation
_	Exciton	Polarization wave

Figure 1 Important elementary excitations in solids.

## Displacement of Planes of Atoms in a Longitudinal Wave

 $U_s$  is defined as the displacement for the plane s from its equilibrium position





#### Hooke's Law

- We assume the elastic response of the crystal is a linear function of the forces.
- The elastic energy is a quadratic function of the relative displacement of any two points in the crystal.
- Hooke's Law : The force exerted on the plane *s* as caused by the displacement of the plane *s+p* is directly proportional to the difference of the displacement *u<sub>s+p</sub> u<sub>s</sub>*. For nearest neighbor interaction, *p = ± 1* Hence, the total force on plane *s* from planes *s+1*, and *s-1* is

$$F_s = C(u_{s+1} - u_s) + C(u_{s-1} - u_s)$$

The equation of motion of the plane s is

$$M\frac{d^2u_s}{dt^2} = C(u_{s+1} + u_{s-1} - 2u_s) ,$$

(1) C: force constant between nearest neighbor planes for one atom in the plane

With time dependence,  $u = u \exp(-i\omega t)$ 

$$-M\omega^2 u_s = C(u_{s+1} + u_{s-1} - 2u_s) \tag{3}$$

By the traveling wave solution for a periodic set of atomic planes with a spacing of "a",  $u_s = u \exp(iska)$ 

$$u_{s\pm 1} = u \exp(isKa) \exp(\pm iKa)$$

$$-\omega^{2}Mu \exp(isKa)$$

$$= Cu\{\exp[i(s+1)Ka] + \exp[i(s-1)Ka] - 2\exp(isKa)\} . (5)$$

$$\omega^{2}M = -C[\exp(iKa) + \exp(-iKa) - 2] . (6)$$

$$\omega^{2} = (2C/M)(1 - \cos Ka) . (7)$$

At the first Brillouin zone boundary,  $K = \pi/a$ , and  $-\pi/a$ ,

$$d\omega^2/dK = (2Ca/M)\sin Ka = 0 \tag{8}$$

(9)

 $\omega^2 = (4C/M) \sin^2 \frac{1}{2} Ka$ ;  $\omega = (4C/M)^{1/2} |\sin \frac{1}{2} Ka|$ .

#### $\omega$ vs $\kappa$ Dispersion for Monoatomic Lattice



**Figure 4** Plot of  $\omega$  versus *K*. The region of  $K \ll 1/a$  or  $\lambda \ge a$  corresponds to the continuum approximation; here  $\omega$  is directly proportional to *K*.

$$\frac{u_{s+1}}{u_s} = \frac{u \exp[i(s+1)Ka]}{u \exp(isKa)} = \exp(iKa) \quad \begin{aligned} -\pi < K a < \pi \\ -\pi/a < K < \pi/a \end{aligned}$$
(10)

The meaningful range of K is only inside the first Brillouin Zone of the linear lattice.

$$u_{s+1}/u_s = \exp(iKa) \equiv \exp(i2\pi n) \exp[i(Ka - 2\pi n)] \equiv \exp(iK'a) , \quad (11)$$
$$K' = K - 2 \operatorname{n} \pi/a = K - \operatorname{n} G$$

We can always subtract a reciprocal lattice vector **G** from **K** to become **K**', to be inside the first Brillouin zone. "**Reduced zone scheme !**"

At the zone boundary, 
$$K_{max} = \pi/a$$
, and  $-\pi/a$   
 $u_s = u \exp(\pm is\pi) = u (-1)^s$ . (12)

This is not a traveling wave, but **a standing wave**; alternating atoms oscillate in opposite phases.  $U_s$  equals to u or -u, depending on s is an even, or odd integer.

#### **Reciprocal Lattice Vector**

To proceed further with the Fourier analysis of the electron concentration we must find the vectors **G** of the Fourier sum  $\sum n_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r})$  as in (9).

We construct the axis vectors  $\mathbf{b}_1$ ,  $\mathbf{b}_2$ ,  $\mathbf{b}_3$  of the **reciprocal lattice**: 倒晶格

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} ; \qquad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} ; \qquad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3} . \tag{13}$$

If  $\mathbf{a}_1$ ,  $\mathbf{a}_2$ ,  $\mathbf{a}_3$  are primitive vectors of the crystal lattice, then  $\mathbf{b}_1$ ,  $\mathbf{b}_2$ ,  $\mathbf{b}_3$  are **primitive vectors of the reciprocal lattice**. Each vector defined by (13) is orthogonal to two axis vectors of the crystal lattice. Thus  $\mathbf{b}_1$ ,  $\mathbf{b}_2$ ,  $\mathbf{b}_3$  have the property  $\mathbf{b}_1 = 2\pi \delta$ .

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij} , \qquad (14)$$

where  $\delta_{ij} = 1$  if i = j and  $\delta_{ij} = 0$  if  $i \neq j$ .

Points in the reciprocal lattice are mapped by the set of vectors

$$\mathbf{G} = v_1 \mathbf{b}_1 + v_2 \mathbf{b}_2 + v_3 \mathbf{b}_3 \quad , \tag{15}$$

#### **Reciprocal Lattice to sc Lattice**

#### **Simple Cubic**

The primitive translation vectors of a <u>simple cubic lattice</u> may be taken as the set

$$\mathbf{a}_1 = a\hat{\mathbf{x}}$$
;  $\mathbf{a}_2 = a\hat{\mathbf{y}}$ ;  $\mathbf{a}_3 = a\hat{\mathbf{z}}$ . (27a)

Here  $\hat{\mathbf{x}}$ ,  $\hat{\mathbf{y}}$ ,  $\hat{\mathbf{z}}$  are orthogonal vectors of unit length. The volume of the cell is  $\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3 = a^3$ . The primitive translation vectors of the reciprocal lattice are found from the standard prescription (13):

$$\mathbf{b}_1 = (2\pi/a)\hat{\mathbf{x}}$$
;  $\mathbf{b}_2 = (2\pi/a)\hat{\mathbf{y}}$ ;  $\mathbf{b}_3 = (2\pi/a)\hat{\mathbf{z}}$ . (27b)

Here the reciprocal lattice is itself a simple cubic lattice, now of lattice constant  $2\pi/a$ .

The boundaries of the first Brillouin zones are the planes normal to the six reciprocal lattice vectors  $\pm \mathbf{b}_1$ ,  $\pm \mathbf{b}_2$ ,  $\pm \mathbf{b}_3$  at their midpoints:

$$\pm \frac{1}{2} \mathbf{b}_1 = \pm (\pi/a) \hat{\mathbf{x}} \; ; \qquad \pm \frac{1}{2} \mathbf{b}_2 = \pm (\pi/a) \hat{\mathbf{y}} \; ; \qquad \pm \frac{1}{2} \mathbf{b}_3 = \pm (\pi/a) \hat{\mathbf{z}} \; . \tag{28}$$

The six planes bound a cube of edge  $2\pi/a$  and of volume  $(2\pi/a)^3$ ; this cube is the first Brillouin zone of the sc crystal lattice.

## **Group Velocity**



At zone boundary,  $K = \pi/a$ ,  $V_g = 0$  for standing wave At the zone center, Ka << 1, the continuum approximation

$$\omega^2 = (C/M)K^2a^2 \quad (15)$$
$$\mathbf{v}_g = (C/M)^{1/2}a \quad V_g \sim \text{ is nearly a constant}$$

See Figure 6

## The Traveling Wave Description of the Atomic Displacement in a linear lattice



Figure 5 The wave represented by the solid curve conveys no information not given by the dashed curve. Only wavelengths longer than 2a are needed to represent the motion.

a: lattice spacing

#### Group Velocity Vg vs K of Mono Atomic Lattice



Figure 6 Group velocity  $v_g$  versus K, for model of Fig. 4. At the zone boundary  $K = \pi/a$  the group velocity is zero.

#### Derivation of Force Constant from Experiment

For longer range force, we include p nearest planes of contributions to  $\omega$ 

$$\omega^2 = (2/M) \sum_{p>0} C_p (1 - \cos p Ka) \quad . \tag{16a}$$

We times *M* cos rKa term on both sides, and integrate over K

$$M \int_{-\pi/a}^{\pi/a} dK \,\omega_K^2 \cos rKa = 2 \sum_{p>0} C_p \int_{-\pi/a}^{\pi/a} dK \,(1 - \cos pKa) \cos rKa$$
$$= -2\pi C_r/a \quad . \tag{16b}$$

Note the integral vanishes, except for p = r

$$C_p = -\frac{Ma}{2\pi} \int_{-\pi/a}^{\pi/a} dK \,\omega_K^2 \cos pKa$$

From experimentally measured  $\omega_{\kappa}$  we will derive  $C_{\rho}$ 



**Figure 9** A diatomic crystal structure with masses  $M_1$ ,  $M_2$  connected by force constant C between adjacent planes. The displacements of atoms  $M_1$  are denoted by  $u_{s-1}$ ,  $u_s$ ,  $u_{s+1}$ , ..., and of atoms  $M_2$  by  $v_{s-1}$ ,  $v_s$ ,  $v_{s+1}$ . The repeat distance is a in the direction of the wavevector K. The atoms are shown in their undisplaced positions.

Considering only nearest neighbor interaction, force constant *C* are identical between all pairs of near-neighbor planes.

## Equation of Motion for a Diatomic Linear Crystal

$$M_{1}\frac{d^{2}u_{s}}{dt^{2}} = C(v_{s} + v_{s-1} - 2u_{s}) ;$$

$$M_{2}\frac{d^{2}v_{s}}{dt^{2}} = C(u_{s+1} + u_{s} - 2v_{s}) .$$

$$Traveling wave solution$$

$$\begin{cases} u_{s} = u \exp(isKa) \exp(-i\omega t) ; \\ v_{s} = v \exp(isKa) \exp(-i\omega t) . \end{cases} (19)$$

*a* as the distance between nearest identical planes, but not nearest neighbor planes.

$$-\omega^2 M_1 u = Cv[1 + \exp(-iKa)] - 2Cu ;$$
  
$$-\omega^2 M_2 v = Cu[\exp(iKa) + 1] - 2Cv .$$

#### *ω* vs K for a Diatomic Linear Crystal

Solution exists only if the determinant of the coefficients vanishes

$$\frac{2C - M_1 \omega^2}{-C[1 + \exp(iKa)]} = 0 , \qquad (21)$$

$$M_1 M_2 \omega^4 - 2C(M_1 + M_2)\omega^2 + 2C^2(1 - \cos Ka) = 0 \quad . \tag{22}$$

At Ka << 1, at the zone center

$$\omega^{2} \cong 2C \left( \frac{1}{M_{1}} + \frac{1}{M_{2}} \right) \qquad (\text{optical branch}) ; \qquad (23)$$

$$\mathbf{W}^{2} \cong \frac{\frac{1}{2}C}{M_{1} + M_{2}} \mathbf{K}^{2} a^{2} \qquad (\text{acoustical branch}) . \qquad (24)$$

$$\mathbf{W}^{2} \cong \frac{1}{2}C \mathbf{K}^{2} a^{2} \qquad (\text{acoustical branch}) . \qquad (24)$$

$$\mathbf{W}^{2} = \frac{1}{2}C \mathbf{K}^{2} \mathbf{M}_{1} ; \qquad \omega^{2} = \frac{1}{2}C \mathbf{M}_{2} . \qquad (25)$$

# Optical and Acoustic Branches of the Dispersion for a Diatomic Linear Lattice

Optical phonon branch  $\left[2C\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\right]$  $(2C/M_{2})^{1/2}$  $M_1 > M_2$  $(2C/M_1)^{1/2}$ Acoustical phonon branch ·K  $\pi$ 0 a

**Figure 7** Optical and acoustical branches of the dispersion relation for a diatomic linear lattice, showing the limiting frequencies at K = 0 and  $K = K_{\text{max}} = \pi/a$ . The lattice constant is a.



 $K/K_{\text{max}}$ , in [111] direction

**Figure 8a** Phonon dispersion relations in the [111] direction in germanium at 80 K. The two **TA** + **LA** phonon branches are horizontal at the zone boundary position,  $K_{\text{max}} = (2\pi/a)(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ . The LO and TO branches coincide at K = 0; this also is a consequence of the crystal symmetry of Ge. The results were obtained with neutron inelastic scattering by G. Nilsson and G. Nelin.



**Figure 8b** Dispersion curves in the [111] direction in KBr at 90 K, after A. D. B. Woods, B. N. Brockhouse, R. A. Cowley, and W. Cochran. The extrapolation to K = 0 of the TO, LO branches are called  $\omega_T$ ,  $\omega_L$ .

#### Transverse Optical and Transverse Acoustic Waves of a Diatomic Linear Lattice



#### Quantization of Elastic Waves

The quantum of lattice vibration energy is called phonon, and the quantum number is denoted as *n*. The elastic waves in crystals are made of phonons.

 $\boldsymbol{\epsilon} = (n + \frac{1}{2})\hbar\boldsymbol{\omega}$ 

*u* = *u*<sub>o</sub> cos *Kx* cos *wt* for a standing wave

The time average kinetic energy is

$$\frac{1}{8}\rho V\omega^2 u_0^2 = \frac{1}{2}(n+\frac{1}{2})\hbar\omega \quad , \tag{28}$$

$$u_0^2 = 4(n + \frac{1}{2})\hbar/\rho V\omega$$
 (29)

The sign of  $\omega$  is usually positive; for imaginary  $\omega$ , the crystal is unstable. An optical mode with  $\omega$  close to zero is called a soft mode. **Phonon Momentum** 

Physical momentum of a crystal is

$$\boldsymbol{p} = M \left( \frac{d}{dt} \right) \sum u_s \tag{30}$$

$$\boldsymbol{p} = M \left( \frac{du}{dt} \right) \sum_{s} \exp(is\boldsymbol{K}a) = M \left( \frac{du}{dt} \right) \left[ 1 - \exp(iN\boldsymbol{K}a) \right] / \left[ 1 - \exp(i\boldsymbol{K}a) \right]$$
(31)

$$\sum_{s=0}^{N-1} x^s = (1-x^N) / (1-x)$$
(32)

For 
$$\mathbf{K} = +2\pi r/Na$$
,  $Exp(iN\mathbf{K}a) = exp(+i2\pi r) = 1$   
 $\mathbf{p} = M (du/dt) \sum_{s} exp(is\mathbf{K}a) = 0$  (33)

The physical momentum of a crystal is zero.

## **Phonon Momentum**

- $\mathbf{k}' = \mathbf{k} + \mathbf{G}$ , (34) Elastic scattering of photons by a crystal
- $\mathbf{k}' + \mathbf{K} = \mathbf{k} + \mathbf{G}$ . For inelastic photon scattering, (35) it creates a phonon momentum  $\mathbf{K}$
- $\mathbf{k}' = \mathbf{k} + \mathbf{K} + \mathbf{G}$ . For absorption of a phonon  $\mathbf{K}$  (36)

Inelastic neutron scattering by phonons to obtain  $\omega$  (K)

$$\mathbf{k} + \mathbf{G} = \mathbf{k}' \pm \mathbf{K} \quad (37)$$

$$\frac{\hbar^2 k^2}{2M_n} = \frac{\hbar^2 k'^2}{2M_n} \pm \hbar \omega \quad , \tag{38}$$

#### Phonon Dispersions of Na in 3-D



Wavevector, in units  $2\pi/a$ 

Figure 11 The dispersion curves of sodium for phonons propagating in the [001], [110], and [111] directions at 90 K, as determined by inelastic scattering of neutrons, by Woods, Brockhouse, March and Bowers.

#### **SUMMARY**

- The quantum unit of a crystal vibration is a phonon. If the angular frequency is  $\omega$ , the energy of the phonon is  $\hbar\omega$ .
- When a phonon of wavevector **K** is created by the inelastic scattering of a photon or neutron from wavevector **k** to  $\mathbf{k}'$ , the wavevector selection rule that governs the process is

$$\mathbf{k} = \mathbf{k}' + \mathbf{K} + \mathbf{G} ,$$

where **G** is a reciprocal lattice vector.

- All elastic waves can be described by wavevectors that lie within the first Brillouin zone in reciprocal space.
- If there are p atoms in the primitive cell, the phonon dispersion relation will have 3 acoustical phonon branches and 3p 3 optical phonon branches.

Chapter 4

Problem setNo. 1, 3, and 4.