# PHY 745 Group Theory
# 11-11:50 AM MWF Olin 102

## Plan for Lecture 21:

### Symmetry of lattice vibrations

### Chapter 11 in DDJ

1. **Review of vibrations in a one-dimensional lattice**
2. **Vibrations in a three-dimensional lattice**
3. **Lattice modes and "molecular" modes**

Some materials taken from DDJ and also Solid State Physics text by Grosso and Parravicini (2014)



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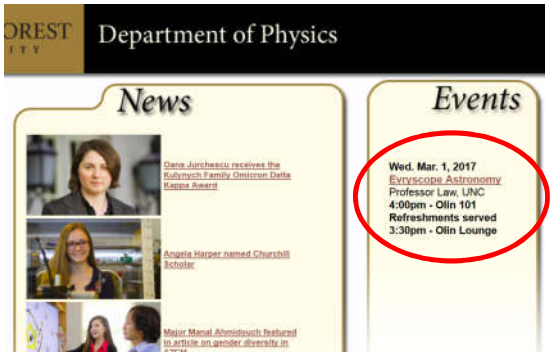
|---|---|---|---|---|---|
| 13 | Fri: 02/10/2017 | Chap. 5 | Atomic orbitals | #11 | 02/13/2017 |
| 14 | Mon: 02/13/2017 | Chap. 6 | Direct product groups | #12 | 02/15/2017 |
| 15 | Wed: 02/15/2017 | Chap. 7 | Molecular orbital | #13 | 02/17/2017 |
| 16 | Fri: 02/17/2017 | Chap. 9 | Introduction to Space Groups | #14 | 02/20/2017 |
| 17 | Mon: 02/20/2017 | Chap. 10 | Group theory for the periodic lattice | | |
| 18 | Wed: 02/22/2017 | Chap. 10 | Group theory for the periodic lattice | | |
| 19 | Fri: 02/24/2017 | Chap. 1-10 | Review -- Distribute take-home exam | | |
| 20 | Mon: 02/27/2017 | Chap. 10 | Space group representations | | Exam |
| 21 | Wed: 03/01/2017 | Chap. 11 | Symmetry of vibrations | | Exam |
| 22 | Fri: 03/03/2017 | Chap. 11 | Symmetry of vibrations | | Exam Due |
| | Mon: 03/06/2017 | | *Spring break - no class* | | |
| | Wed: 03/08/2017 | | *Spring break - no class* | | |
| | Fri: 03/10/2017 | | *Spring break - no class* | | |
| | Mon: 03/13/2017 | | *APS Meeting - no class* | | |
| | Wed: 03/15/2017 | | *APS Meeting - no class* | | |
| | Fri: 03/17/2017 | | *APS Meeting - no class* | | |
| 23 | Mon: 03/20/2017 | | | | |
| 24 | Wed: 03/22/2017 | | | | |





Thanks to the Born-Oppenheimer approximation, the nuclei of a material in equilibrium move in the potential field provided by the ground electronic state of the system

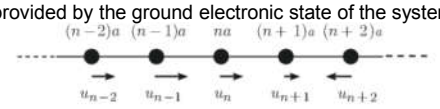
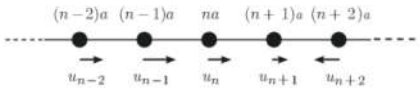



**Figure 9.1** Longitudinal displacements in a one-dimensional monoatomic lattice. The equilibrium positions $t_n = na$ are indicated by circles; the displacements $u_n$ at a given instant are indicated by arrows.

The ground electronic state depends on the nuclear positions

$E_0\left(\left\{\mathbf{R}^a\right\}\right)$ Suppose $\mathbf{R}^a = \mathbf{R}^{a0} + \mathbf{u}^a$






For one-dimensional case:

$$E_0(\{u_n\}) = E_0(0) + \frac{1}{2}\sum_{nn'}\left(\frac{\partial^2 E_0}{\partial u_n \partial u_{n'}}\right)_0 u_n u_{n'} + \frac{1}{3!}\sum_{nn'n''}\left(\frac{\partial^3 E_0}{\partial u_n \partial u_{n'} \partial u_{n''}}\right)_0 u_n u_{n'} u_{n''} + \cdots$$

$$E_0^{(\text{harm})}(\{u_n\}) = E_0(0) + \frac{1}{2}\sum_{nn'} D_{nn'} u_n u_{n'}, \qquad D_{nn'} = \left(\frac{\partial^2 E_0}{\partial u_n \partial u_{n'}}\right)_0$$

Relationships:

$$D_{nn'} = D_{n'n}. \qquad D_{nn'} = D_{mm'} \text{ if } t_n - t_{n'} = t_m - t_{m'}.$$

$$\sum_{n'} D_{nn'} = 0 \quad \text{for any} \quad n;$$



Classical equations of motion:

$$M\ddot{u}_n = -\sum_{n'} D_{nn'} u_{n'}$$

Solution

$$u_n(t) = A\, e^{i(qna - \omega t)}$$

$$-M\omega^2 A = -\sum_{n'} D_{nn'} e^{-iq(na - n'a)} A.$$

$$\boxed{M\omega^2(q) = D(q)},$$

where

$$\boxed{D(q) = \sum_{n'} D_{nn'} e^{-iq(na - n'a)}};$$

Analytic result for monoatomic chain with only nearest neighbor interactions

$$D_{nn} = 2C, \quad D_{n\,n+1} = D_{n-1\,n} = -C, \quad D_{nn'} = 0 \quad \text{if} \mid \ n' - n \mid > 1$$

$$D(q) = \sum_{n'} D_{nn'} e^{iqa(n-n')} = C\left(2 - e^{iqa} - e^{-iqa}\right) = 4C\sin^2\left(qa/2\right)$$

➔ $$\omega = \sqrt{\frac{4C}{M}}\left|\sin\frac{1}{2}qa\right|$$

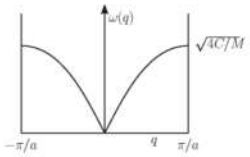



**Figure 9.2** Phonon dispersion curve for a monoatomic linear lattice with nearest neighbor interactions only; the Brillouin zone is the segment between $-\pi/a$ and $+\pi/a$.



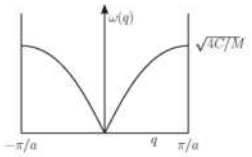



**Figure 9.2** Phonon dispersion curve for a monoatomic linear lattice with nearest neighbor interactions only; the Brillouin zone is the segment between $-\pi/a$ and $+\pi/a$.

$$\omega = \sqrt{\frac{C}{M}}aq \equiv v_s q \quad (qa \ll 1);$$

velocity of sound in the material



One-dimensional diatomic lattice

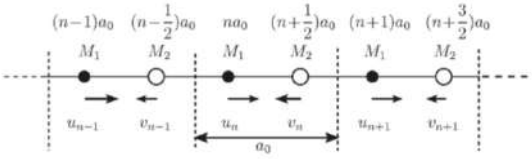
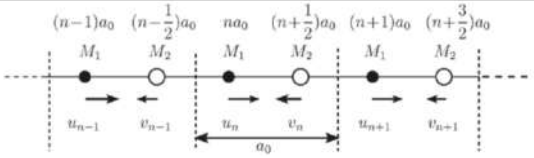



**Figure 9.3** Longitudinal displacements in a one-dimensional diatomic lattice. The equilibrium positions of the two sublattices of atoms, of mass $M_1$ and $M_2$, are indicated by black and white circles, respectively; the displacements $u_n$ and $v_n$ at a given instant are indicated by arrows.

Equations of motion for this case:

$$M_1\ddot{u}_n = -C(2u_n - v_{n-1} - v_n)$$
$$M_2\ddot{v}_n = -C(2v_n - u_n - u_{n+1})$$




Solution: $u_n(t) = A_1 e^{i(qna_0-\omega t)}$ and $v_n(t) = A_2 e^{i(qna_0+qa_0/2-\omega t)}$

$$-M_1\omega^2 A_1 = -C(2A_1 - A_2 e^{-iqa_0/2} - A_2 e^{iqa_0/2}),$$
$$-M_2\omega^2 A_2 = -C(2A_2 - A_1 e^{-iqa_0/2} - A_1 e^{iqa_0/2}).$$

convenient constant

Necessary condition for non-trivial solution:

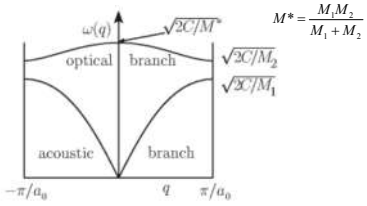
$$\begin{vmatrix} 2C - M_1\omega^2 & -2C\cos(qa_0/2) \\ -2C\cos(qa_0/2) & 2C - M_2\omega^2 \end{vmatrix} = 0.$$



One-dimensional diatomic lattice -- continued

Normal modes

$$\omega^2 = C\left(\frac{1}{M_1}+\frac{1}{M_2}\right) \pm C\sqrt{\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^2 - \frac{4\sin^2(qa_0/2)}{M_1 M_2}}.$$




$$M^* = \frac{M_1 M_2}{M_1 + M_2}$$

**Figure 9.4** Phonon dispersion curves of a diatomic linear chain, with nearest neighbor atoms interacting with spring constant $C$. The masses of the atoms are $M_1$ and $M_2$ (with $M_1 > M_2$); $M^*$ is the reduced mass.



Lattice modes of general three-dimensional crystals

$$E_0^{(\text{harm})}(\{\mathbf{u}_{n\nu}\}) = E_0(0) + \frac{1}{2}\sum_{n\nu\alpha,n'\nu'\alpha'} D_{n\nu\alpha,n'\nu'\alpha'} u_{n\nu\alpha} u_{n'\nu'\alpha'}$$

$$D_{n\nu\alpha,n'\nu'\alpha'} = \left(\frac{\partial^2 E_0}{\partial u_{n\nu\alpha}\partial u_{n'\nu'\alpha'}}\right)_0.$$

Relationships:

$$D_{n\nu\alpha,n'\nu'\alpha'} = D_{n'\nu'\alpha',n\nu\alpha},$$

$$D_{n\nu\alpha,n'\nu'\alpha'} = D_{m\nu\alpha,m'\nu'\alpha'} \quad \text{if} \quad \mathbf{t}_n - \mathbf{t}_{n'} = \mathbf{t}_m - \mathbf{t}_{m'}$$

$$\sum_{n'\nu'} D_{n\nu\alpha,n'\nu'\alpha'} \equiv 0,$$

Lattice modes of general three-dimensional crystals -- continued

Equations of motion

$$M_\nu \ddot{u}_{n\nu\alpha} = -\sum_{n'\nu'\alpha'} D_{n\nu\alpha,n'\nu'\alpha'} u_{n'\nu'\alpha'},$$

Solution

$$\mathbf{u}_{n\nu}(t) = \mathbf{A}_\nu(\mathbf{q},\omega)e^{i(\mathbf{q}\cdot\mathbf{t}_n-\omega t)}$$

$$-M_\nu\omega^2 A_{\nu\alpha} = -\sum_{n'\nu'\alpha'} D_{n\nu\alpha,n'\nu'\alpha'} e^{-i\mathbf{q}\cdot(\mathbf{t}_n-\mathbf{t}_{n'})} A_{\nu'\alpha'}$$

$$D_{\nu\alpha,\nu'\alpha'}(\mathbf{q}) = \sum_{n'} D_{n\nu\alpha,n'\nu'\alpha'} e^{-i\mathbf{q}\cdot(\mathbf{t}_n-\mathbf{t}_{n'})},$$

$$\left\| D_{\nu\alpha,\nu'\alpha'}(\mathbf{q}) - M_\nu\omega^2\delta_{\alpha\alpha'}\delta_{\nu,\nu'} \right\| = 0,$$



Lattice modes of general three-dimensional crystals -- continued

Some special values

$$\sum_{\nu'} D_{\nu\alpha,\nu'\alpha'}(\mathbf{q}=0) \equiv 0;$$

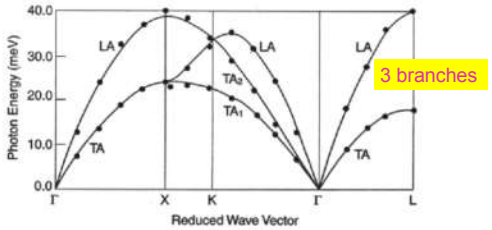
$$\sum_{\nu'\alpha'} D_{\nu\alpha,\nu'\alpha'}(\mathbf{q}=0)A_{\alpha'} \equiv 0.$$

Orthogonality of normal modes

$$\sum_{\nu\alpha} M_\nu A^*_{\nu\alpha}(\mathbf{q},p)A_{\nu\alpha}(\mathbf{q},p') = \delta_{p,p'}.$$



Example for fcc Al lattice




3 branches

**Figure 9.5** Phonon dispersion curves of aluminum along symmetry directions. The solid lines represents the calculations of Fig. 1, Phys. Rev. B *46*, 10734 (1992). Longitudinal and transverse acoustic branchesare indicated by LA and TA (or $TA_1$ and $TA_2$), respectively. The experimental points are from the papers of G. Gilat and R. M. Nicklow, Phys. Rev. *143*, 487 (1966) and R. Stedman, S. Almqvist and G. Nilsson, Phys. Rev. *162*, 549 (1967).

Example for Si and Ge lattices

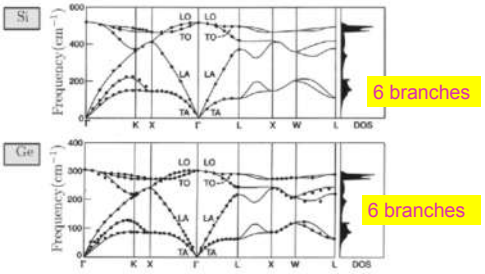



**Figure 9.6** Phonon dispersion curves and density-of-states of Si and Ge calculated by Figs. 1, 2, Phys. Rev. B *43*, 7231 (1991). Longitudinal and transverse acoustic (or optical) modes are indicated by LA and TA (LO and TO), respectively. The experimental points are from G. Dolling, in "Inelastic Scattering of Neutrons in Solids and Liquids" edited by S. Ekland (IAEA, Vienna, 1963) Vol. II, p. 37; G. Nilsson and G. Nelin, Phys. Rev. B *3*, 364 (1971) and Phys. Rev. B *6*, 3777 (1972). Conversion to meV units can be done noting that $1\ \text{cm}^{-1} = 0.124$ meV.



Example for LiF

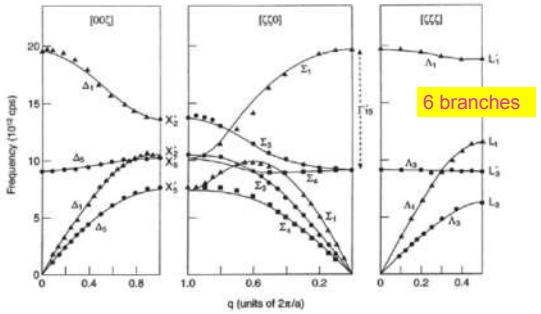



**Figure 9.8** Measured phonon dispersion curves along three directions of high symmetry in LiF; the solid curves are a best least-squares fit of a parameter model [With permission from Fig. 4, Phys. Rev. *168*, 970 (1968)]. Notice that $10^{12}$ Hz = 4.137 meV.



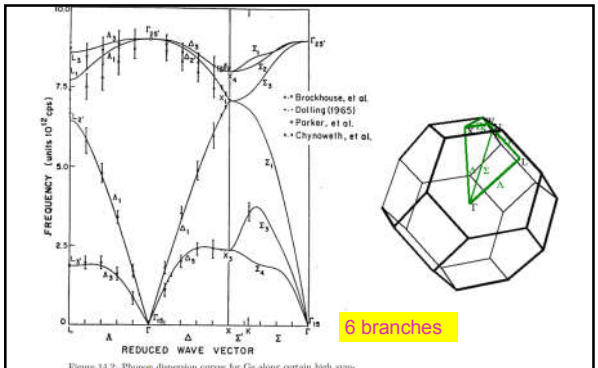



Figure 14.2: Phonon dispersion curves for Ge along certain high symmetry axes in the Brillouin zone. The data at the Γ point are from Raman scattering measurements and the data elsewhere in the zone are from neutron scattering experiments.

The **general outline** for discussing lattice modes in solids is:

1. Find the symmetry operations for the group of the wave vector $\vec{k} = 0$, the appropriate character table and irreducible representations.
2. Find $\chi_{\text{lattice modes}} = \chi_{\text{atom sites}} \otimes \chi_{\text{vector}}$. The meaning of this relation is discussed below (item #3 in §14.2).
3. Find the irreducible representations of $\chi_{\text{lattice modes}}$. The characters for the lattice mode representation express the symmetry types and degeneracies of the lattice modes.
4. Find the normal mode patterns.
5. Which modes are IR-active?
6. Which modes are Raman-active?
7. Are there any polarization effects?
8. Find the lattice modes at other points in the Brillouin zone.
9. Using the compatibility relations, connect up the lattice modes at neighboring $\vec{k}$ points to form a phonon branch.



Notation for $O_h$ symmetry

| BSW | Molecular |
|---|---|
| $\Gamma_1$ | $A_{1g}$ |
| $\Gamma_2$ | $A_{2g}$ |
| $\Gamma_{12}$ | $E_g$ |
| $\Gamma_{15}'$ | $T_{1g}$ |
| $\Gamma_{25}'$ | $T_{2g}$ |
| $\Gamma_1'$ | $A_{1u}$ |
| $\Gamma_2'$ | $A_{2u}$ |
| $\Gamma_{12}'$ | $E_u$ |
| $\Gamma_{15}$ | $T_{1u}$ |
| $\Gamma_{25}$ | $T_{2u}$ |



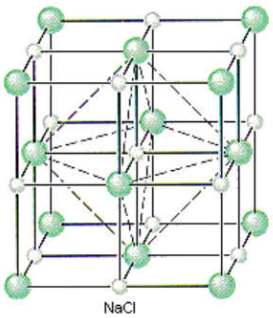
How many phonon branches?

# atoms in unit cell x dimension of lattice

Example -- NaCl

2 atoms per primitive cell

➔ 6 phonon branches



NaCl

Symmetry associated with k=0 phonons $O_h$ symmetry

| O(432) | | | $E$ | $8C_3$ | $3C_2 = 3C_4^2$ | $6C_2$ | $6C_4$ |
|---|---|---|---|---|---|---|---|
| $\Gamma_1$ | | $A_1$ | 1 | 1 | 1 | 1 | 1 |
| $\Gamma_2$ | | $A_2$ | 1 | 1 | 1 | −1 | −1 |
| $\Gamma_{12}$ | $(x^2-y^2, 3z^2-r^2)$ | $E$ | 2 | −1 | 2 | 0 | 0 |
| $\Gamma_{15}$ | $(R_x, R_y, R_z)$ / $(x, y, z)$ | $T_1$ | 3 | 0 | −1 | −1 | 1 |
| $\Gamma_{25}$ | $yz, zx, xy$ | $T_2$ | 3 | 0 | −1 | 1 | −1 |

$O_h = O \times i \quad (m3m)$

Under all symmetry operations of $O_h$ each Na and Cl atom site is transformed either into itself or into an equivalent atom site separated by a lattice vector $\vec{R}_m$. Thus,

$$\chi_{\text{atom sites}} = 2A_{1g} \tag{14.4}$$

For $O_h$ symmetry, $\chi_{\text{vector}} = T_{1u}$, so that at $\vec{k} = 0$

$$\chi_{\text{lattice modes}} = 2A_{1g} \otimes T_{1u} = 2T_{1u}. \tag{14.5}$$



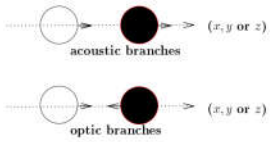



Figure 14.4: In-phase and out-of-phase normal modes at $\vec{k} = 0$ for NaCl.