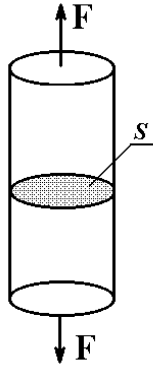


3. Dynamics of a crystalline Lattice

3.1 Elastic properties of solids



Responses of solids to mechanical actions (lengthening, contraction, bending, torsion, and others) are called the mechanical properties. The mechanical properties depend on atomic structure and defects of solids. The dislocations are of great importance.

If external forces act upon a solid, the mechanical strains are produced. The forces of the neighbor regions of the solid undergo an elementary volume of a solid. The total force is proportional to the surface of the volume under investigation. Their ratio is called the mechanical strain. When the body is at rest, the external force F (Fig.3.1) is equal to the intrinsic force:

$$F = \int \sigma dS \quad (3.1)$$

Fig.3.1.

When the strain is uniform:

$$\sigma = F / S \quad (3.2)$$

In the process of deformation, the size of the body changes. Two kinds of strain are distinguished. The ratio of the force to the actual surface of a sample is called the *actual strain*. The ratio of the force to the initial surface is called the *conditional strain*.

To describe the strained state of a body, let us take under consideration an elementary cube (Fig.3.2). The strain acting upon the sides of the elementary cube can be represented as the sum of two tangents and a normal component. Let σ_{ij} be the strain component acting in i -direction upon the cube side, which is perpendicular to j -axis. The strains σ_{11} , σ_{22} и σ_{33} are normal (lengthening or contraction); the strains σ_{12} , σ_{13} , σ_{23} , σ_{21} , σ_{31} , σ_{32} are tangent (breaking off, shearing). Thus, the strained state is

characterized by nine-quantity σ_{ij} , which are the components of a mechanical strain tensor of the second rang:

$$T = \begin{vmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{vmatrix} \quad (3.3)$$

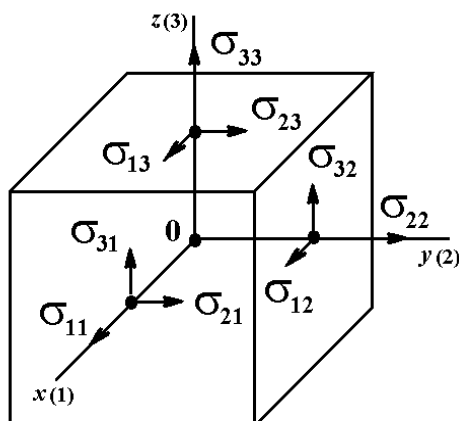


Fig.2.1

The tensor is symmetrical: $\sigma_{12} = \sigma_{21}$, $\sigma_{13} = \sigma_{31}$, $\sigma_{23} = \sigma_{32}$. Thus, only six components are independent: $\sigma_{ij} = \sigma_{ji}$. The deformation and destruction of a body depends on the strained state produced in a body. The plastic deformation is due to the tangent component of strain. The normal components break the atomic bonds and cause the fragile destruction of the solid.

The change of volume or form of a body (the mass is constant) under action of the external force is called the *deformation*. *Lengthening contraction, shearing, torsion, bending* are the basic kinds of deformations. When a longitudinal force is applied, the

length of a cylinder increases and its diameter decreases (Fig.3.3). Deformation is expressed in relative units:

$$\varepsilon = (l_k - l_0)/l_0. \quad (3.4)$$

l_0 is an initial length, l_k is the final length.

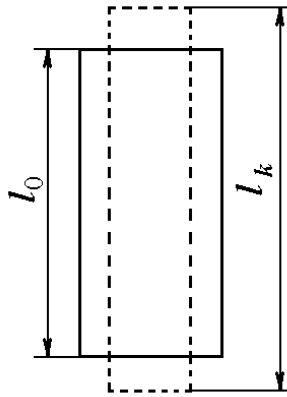


Fig.3.4 Lengthening.

We should distinguish between the conditional (ε) and true (e) deformations. While calculating the true deformations, it is necessary to take into account continuous changing of the length of a sample:

$$e = \int_{l_0}^{l_k} \frac{dl}{l} = \ln \frac{l_k}{l_0}. \quad (3.5)$$

Conditional and true deformations are related. Indeed $\varepsilon = (l_k - l_0)/l_0 = (l_k/l_0) - 1$, $l_k/l_0 = 1 + \varepsilon$, thus

$$e = \ln(l_k/l_0) = \ln(1 + \varepsilon). \quad (3.6)$$

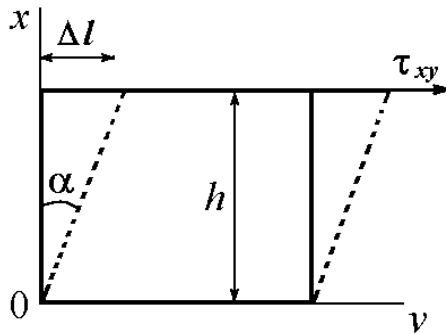


Fig3.5 Shearing under action of a tangent strain.

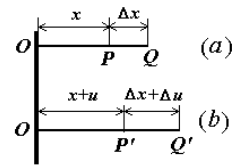


Fig.3.6 Lengthening of a string ;
a) before lengthening;
b) after lengthening.

When ε is small, $\ln(1 + \varepsilon) = \varepsilon - \frac{\varepsilon^2}{2} + \frac{\varepsilon^3}{3} - \dots$. We get in the first approximation: $e \approx \varepsilon$.

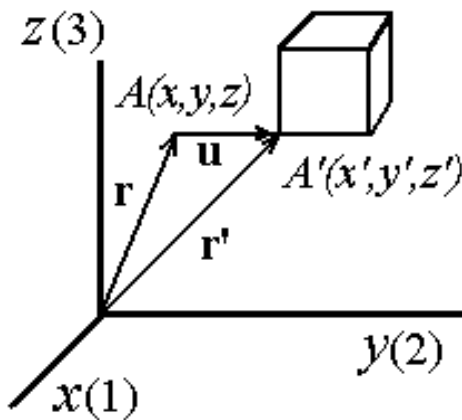


Fig.3.7.

The true deformations are additive, the conditional deformations are not additive.

The tangential strains produce shearing, which is characterized by the *shearing angle* α . $\gamma = \tan \alpha$ is called the *relative shearing*. The changing of the body form under action of tangent forces is shown in Fig.3.3. It follows that $\gamma = \Delta l/h = \tan \alpha$. When deformations are small, $\tan \alpha \approx \alpha = \gamma$. We will discuss the uniform small deformations.

The string with fixed left end is shown in Fig.3.6. $PQ = \Delta x$. After deformation, P

transforms in P' , Q in Q' ; u – displacement; $P'Q' = \Delta x + \Delta u$. Deformation of the segment PQ is: $\frac{|P'Q'| - |PQ|}{|PQ|} = \frac{\Delta u}{\Delta x}$, deformation at the point P :

$$e = \lim_{\Delta x \rightarrow 0} \frac{\Delta u}{\Delta x} = \frac{du}{dx}, \quad (3.7)$$

Thus, deformation at any point is a derivative of displacement relative the coordinate. It follows from Eq.(3.7) that displacement is a linear function of coordinate: $u = ex$.

Fig.3.7 shows the volume deformation of a solid. After deformation, the position of the point O does not change; the positions of other points are changed.

The initial position of point $A(x,y,z)$ is determined by the radius vector \mathbf{r} . After deformation, the point $A(x,y,z)$ transforms in the point $A'(x',y',z')$, which is characterized by the radius vector \mathbf{r}' . The quantity $\mathbf{u} = \mathbf{r}' - \mathbf{r}$ is a *displacement vector* with components u , v , and w . Thus, $x' = x + u$, $y' = y + v$, $z' = z + w$.

The components of a displacement vector are the linear functions of coordinates. Thus:

$$\begin{aligned} \Delta u &= \frac{\partial u}{\partial x} \Delta x + \frac{\partial u}{\partial y} \Delta y + \frac{\partial u}{\partial z} \Delta z = e_{11} \Delta x + e_{12} \Delta y + e_{13} \Delta z \\ \Delta v &= \frac{\partial v}{\partial x} \Delta x + \frac{\partial v}{\partial y} \Delta y + \frac{\partial v}{\partial z} \Delta z = e_{21} \Delta x + e_{22} \Delta y + e_{23} \Delta z \\ \Delta w &= \frac{\partial w}{\partial x} \Delta x + \frac{\partial w}{\partial y} \Delta y + \frac{\partial w}{\partial z} \Delta z = e_{31} \Delta x + e_{32} \Delta y + e_{33} \Delta z \end{aligned} \quad (3.8)$$

Nine quantities e_{ij} are components of a tensor of the second rank, which is called the *deformation tensor*.

If $\Delta y = \Delta z = 0$,

$$\Delta u = \frac{\partial u}{\partial x} \Delta x = e_{11} \Delta x; \quad \Delta v = \frac{\partial v}{\partial x} \Delta x = e_{21} \Delta x; \quad \Delta w = \frac{\partial w}{\partial x} \Delta x = e_{31} \Delta x. \quad (3.9)$$

Thus, $e_{11} = \partial u / \partial x$ is the increment of the segment Δx , which is projected upon x-axis.

In analogues way:

$$e_{22} = \partial v / \partial y; \quad e_{33} = \partial w / \partial z \quad (3.10)$$

The components $e_{21} = \partial v / \partial x$ и $e_{31} = \partial w / \partial x$ determine the rotation of the linear element that is parallel to the x-axis: in the first case, it rotates about z-axis clockwise; in the second case, its rotation about y-axis is in an opposite direction. In accordance with equation (3.9) $\Delta v = (\partial v / \Delta x) \Delta x = e_{21} \Delta x$. Taking into account that the lengthening of the segment Δx is Δu , we get that $e_{21} = \Delta v / (\Delta x + \Delta u) = \text{tg} \theta$; θ is the angle of rotation of the linear element.

The quantities u and v are small in comparison with x . Thus, Δu and Δv are small in comparison with Δx , and $\theta \approx \Delta v / \Delta x = e_{21}$. The component e_{12} is a rotation of the linear element that is parallel to y-axis about y-axis clockwise. The component e_{13} is the rotation of the linear element about y-axis in the opposite direction. The components e_{23} and e_{32} determine the rotation of x-axis about the y-axis clockwise and respectably the rotation of x-axis about the y-axis in the opposite direction. Let us find the total

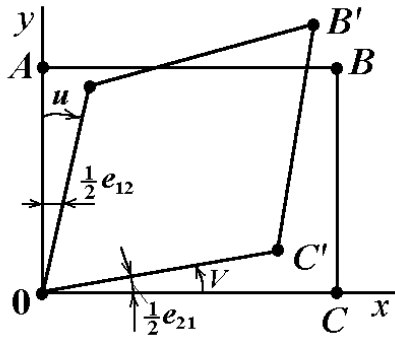


Fig.3.8 The shearing deformation

shearing in the plane xy (Fig.3.8). A square $OABC$ under action of the tangent strains is transformed into the rhomb $OA'B'C'$. The side OA is turned clockwise through the angle $\frac{1}{2}e_{12}$, the side C is

turned in the opposite direction through angle $\frac{1}{2}e_{21}$.

That shearing is called pure. A glance at Fig.3.8 and 3.5 shows the difference between the pure and simple shearing. Let u be the displacement in x -

direction of a point located in the side OA , v is the displacement in y -direction of point located in the side OC . The displacement v is proportional to x -

coordinate. Thus, $\frac{1}{2}e_{21} = \partial v / \partial x$ and $\frac{1}{2}e_{12} = \partial u / \partial y$. The resultant shearing in the xy -plane can be written as follows:

$$\frac{1}{2}(e_{12} + e_{21}) = \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}. \quad (3.11)$$

Analogously,

$$\frac{1}{2}(e_{23} + e_{32}) = \frac{\partial v}{\partial z} + \frac{\partial w}{\partial y}; \quad \frac{1}{2}(e_{13} + e_{31}) = \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x}. \quad (3.12)$$

The deformation tensor determines the strained state of a solid. It is convenient to subdivide the tensor into symmetrical and anti-symmetrical components. Anti-symmetrical component $\frac{1}{2}(e_{12} - e_{21})$ describes the rotation of the body. Symmetrical component $\frac{1}{2}(e_{12} + e_{21})$ describes the deformation of the body. The deformation tensor is the symmetrical tensor or the second rang, six components (from nine) are independent. The components symmetrical relative the main diagonal are identical.

$$T_{def} = \begin{vmatrix} e_{11} & \frac{1}{2}(e_{12} + e_{21}) & \frac{1}{2}(e_{13} + e_{31}) \\ \frac{1}{2}(e_{21} + e_{12}) & e_{22} & \frac{1}{2}(e_{23} + e_{32}) \\ \frac{1}{2}(e_{31} + e_{13}) & \frac{1}{2}(e_{32} + e_{23}) & e_{33} \end{vmatrix} = \begin{vmatrix} e_{11} & e_{12} & e_{13} \\ e_{21} & e_{22} & e_{23} \\ e_{31} & e_{32} & e_{33} \end{vmatrix}. \quad (3.13)$$

The diagonal components ε_{ii} characterize the lengthening or contraction, the other components ε_{ij} characterize the shearing. The shearing angle in a certain plane is equal to the corresponding element ε_{ij} .

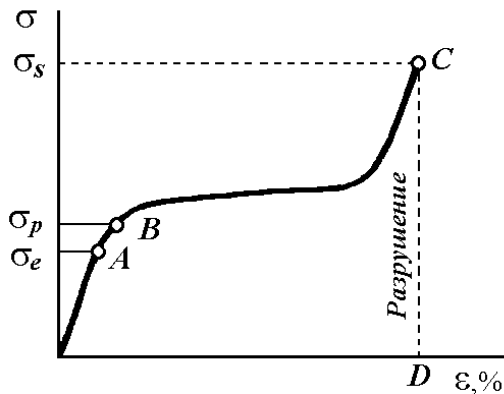


Рис.3.9. Deformation as function of strain

3.2 The Hooke Law.

The dependence of deformation on mechanic strain is called the *deformation diagram*. The diagram describes the mechanical properties of a solid. The deformation diagram for lengthening of a cylinder is shown in Fig.3.9. When the deformations are small the function

$\sigma = f(\varepsilon)$ is linear. When the strain is taken off rather quickly and the initial form of a body restores, the deformation is reversible. Such region is called the region of elastic deformation ($\varepsilon \ll 1\%$), and the strain corresponding to the point A is called the *elastic limit*. The region $B-B'$ is called the region of *plastic deformation*, and the strain corresponding to the point B is called the *flow limit*. The flow limit is the minimal strain when deformation slightly depends on the strain. The point 3 of the function $\sigma = f(\varepsilon)$ corresponds to the *tolerance limit*.

The Hooke law (1678) is the linear dependence of the deformation on the strain for isotropic bodies. For the lengthening:

$$\varepsilon = S\sigma \quad (3.14)$$

$\varepsilon = \frac{\Delta l}{l}$ is a longitudinal deformation, l is the initial length, Δl is the length decrement, S is the elasticity. The Hooke law can be written in the form:

$$\sigma = E\varepsilon. \quad (3.15)$$

$E = 1/S$ – the constant of rigidity or Yong modulus.

For shearing under action of tangent strains τ , the Hooke low takes the form:

$$\tau = F/S = G\Delta l/h = Gtg\alpha, \quad (3.16)$$

G – shearing modulus, α - shearing angle, S – cross-section, F – applied force.

For volume contraction,

$$P = \kappa \frac{\Delta V}{V} = \kappa\Omega, \quad (3.17)$$

P – hydrostatic pressure, κ - the volume contraction coefficient, Ω - volume deformation.

Transversal deformation accompanying the contraction is characterized by the Poisson coefficient ν , which represents the ratio of transversal increment to longitudinal increment of the linear size of body. It follows (see Fig.3.10).

$$\nu = \frac{(r_1 - r_0)/r_0}{(l_1 - l_0)/l_0} = -\frac{dr/r_0}{dl/l_0}; \quad \varepsilon_y = \varepsilon_z - \nu\varepsilon_x.$$

$$(3.16)$$

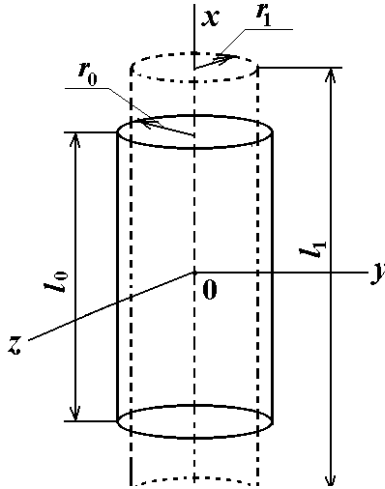


Fig.3.10 A single axis lengthening of a cylinder sample. The longitudinal size of the body increases.

The Hooke law in a generalized form is the relation between the strain tensor ($\sigma_{11}, \sigma_{22}, \sigma_{33}, \sigma_{12}, \sigma_{23}, \sigma_{31}$)

and deformation tensor ($\varepsilon_{11}, \varepsilon_{22}, \varepsilon_{33}, \varepsilon_{12}, \varepsilon_{23}, \varepsilon_{31}$). For an isotropic body, we get:

$$\begin{aligned} \varepsilon_{11} = \varepsilon_x &= \frac{1}{E} [\sigma_{11} - \nu(\sigma_{22} + \sigma_{33})] = \frac{1}{E} [\sigma_x - \nu(\sigma_y + \sigma_z)] \\ \varepsilon_{22} = \varepsilon_y &= \frac{1}{E} [\sigma_{22} - \nu(\sigma_{11} + \sigma_{33})] = \frac{1}{E} [\sigma_y - \nu(\sigma_x + \sigma_z)] \\ \varepsilon_{33} = \varepsilon_z &= \frac{1}{E} [\sigma_{33} - \nu(\sigma_{11} + \sigma_{22})] = \frac{1}{E} [\sigma_z - \nu(\sigma_x + \sigma_y)] \end{aligned} \quad (3.17)$$

For the searing deformation:

$$\begin{aligned}\varepsilon_{12} = \varepsilon_{xy} &= \frac{\sigma_{12}}{G} = \frac{\tau_{xy}}{G}; & \varepsilon_{23} = \varepsilon_{yz} &= \frac{\sigma_{23}}{G} = \frac{\tau_{yz}}{G}; \\ \varepsilon_{31} = \varepsilon_{zx} &= \frac{\sigma_{31}}{G} = \frac{\tau_{zx}}{G}.\end{aligned}\quad (3.18)$$

The elastic constants E,G and ν are related by:

$$G = E/[2(1+\nu)] \quad (3.19)$$

$$\varepsilon_{ij} = S_{ijkl}\sigma_{kl} \quad (3.20)$$

$$\sigma_{ij} = C_{ijkl}\varepsilon_{kl}, \quad (3.21)$$

S_{ijkl} and C_{ijkl} are the elastic constants and the rigidity constants. There are 81 components S_{ijkl} and 81 components C_{ijkl} .

If two tensors of the second rank are related by equations of the type (3.20) and (3.21), the quantities S_{ijkl} and C_{ijkl} form the tensor of the fourth rank. The tensor C_{ijkl} is called the elasticity tensor. The tensor formed by S_{ijkl} is called the tensor of elastic susceptibility. The deformation and strain tensors are symmetric tensors of the second rank ($\varepsilon_{ij} = \varepsilon_{ji}$; $\sigma_{ij} = \sigma_{ji}$). Thus, the number of independent components S_{ijkl} and C_{ijkl} is 36.

$$\begin{aligned}S_{ijkl} &= S_{jikl}; & C_{ijkl} &= C_{jikl} \\ S_{ijkl} &= S_{jilk}; & C_{ijkl} &= C_{jilk}\end{aligned}\quad (3.22)$$

The components S_{ijkl} and C_{ijkl} are symmetrical relative the transposition of the index pairs:

$$S_{ijkl} = S_{klji}; \quad C_{ijkl} = C_{klji}, \quad (3.23)$$

Thus, the number 21 restricts the quantity of independent components of elastic module tensor. That is the number of tensor components, which is not symmetrical in any way. The matrix symbols are widely used to designate the elastic modules and deformations. It leads to the less number of indexes. The method of transformation of components S_{ijkl} and C_{ijkl} is discussed in [6].

In matrix notation, the Hooke law is:

$$\begin{aligned}\varepsilon_i &= S_{ij}\sigma_j \quad (i, j = 1, 2, \dots, 6) \\ \sigma_i &= C_{ij}\varepsilon_j \quad (i, j = 1, 2, \dots, 6)\end{aligned}\quad (3.24)$$

The coefficients of elastic rigidity C_{ij} and of elastic susceptibility S_{ij} are listed as follows:

$$C_{ij} = \begin{vmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \end{vmatrix}. \quad S_{ij} = \begin{vmatrix} S_{11} & S_{12} & S_{13} & S_{14} & S_{15} & S_{16} \\ S_{21} & S_{22} & S_{23} & S_{24} & S_{25} & S_{26} \\ S_{31} & S_{32} & S_{33} & S_{34} & S_{35} & S_{36} \\ S_{41} & S_{42} & S_{43} & S_{44} & S_{45} & S_{46} \\ S_{51} & S_{52} & S_{53} & S_{54} & S_{55} & S_{56} \\ S_{61} & S_{62} & S_{63} & S_{64} & S_{65} & S_{66} \end{vmatrix}$$

The number of elastic constants depends on crystalline symmetry. For a three-cornered symmetry, this number is 21. For a cubic symmetry, the number is 3. In cubic crystals, the directions x , y , and z are equivalent. Thus,

$$C_{11} = C_{22} = C_{33}; \quad C_{12} = C_{23} = C_{31}; \quad C_{44} = C_{55} = C_{66}. \quad (3.25)$$

The other components are zero. In a cubic crystal, there are three independent components C_{11} , C_{12} , and C_{44} :

$$C_{ij} = \begin{vmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{vmatrix}. \quad (3.26)$$

Under condition that the forces between particles are central, the particles are spherical and located at the symmetry centers; in initial state there is no strain. The elasticity coefficients:

$$\begin{aligned} C_{23} = C_{44}, \quad C_{56} = C_{14}, \quad C_{64} = C_{25}, \\ C_{31} = C_{55}, \quad C_{12} = C_{66}, \quad C_{45} = C_{36}. \end{aligned} \quad (3.27)$$

Those relations are known as the *Koshi condition*. For cubic symmetry, we get $C_{12} = C_{44}$. In many ionic crystals, those conditions hold very well, particularly when the fraction of covalent or metallic bond is small. For metals and substances of covalent bonds, the Koshi condition holds badly.

3.3. Plastic Properties of Substances

The Hooke law (Fig./3.9) is true only for a narrow region ($\epsilon \ll 0,1\%$).

When the strain is more then the elastic limit (point A), the Hooke law does not hold, i.e. if the strain is removed the initial form of a sample would be changed. As a result, the permanent deformation is produced This deformation does not depend on the time interval of the strain application. The deformation is called the *plastic deformation*. The strain when the plastic deformation appears is called the *elastic limit*.

Not all crystals can be plastically deformed. For example, quartz, antimony, arsenic, corund, and certain metals are known to break off at a small plastic deformation (or even without it). This phenomenon is called the *fragile rupture (breking off)*. Certain crystals and especially pure metals are very plastic and can be strongly deformed without breaking off.

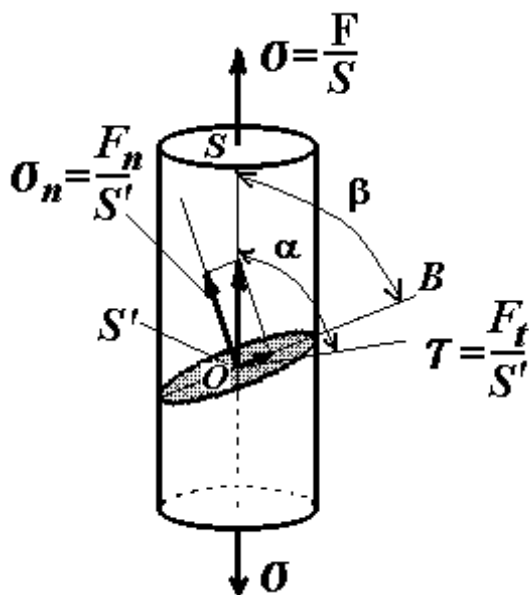


Fig.3.12 Sliding while lengthening

The tangent (shearing) strains are needed to produce the plastic deformation. There are two processes leading to plastic deformation: sliding and twinning.

Twinning is a shift of a crystalline region to a position, which corresponds to the mirror reflection of the initial regions. Such symmetrical shift is produced relative a crystallographic plane favorably oriented to the applied strain τ . The plane is called the *twinning plane* (Fig.3.11). The twinning is mainly observed in crystals with hexagonal or volume-centered cubic cell.

The plastic sliding is shown in Fig.3.11. A part of a crystal moves relatively the other in a direction (direction

of sliding) of certain crystallographic plane (plane of sliding).

While sliding, atoms are transmitted by the integer number of translations. As a result, the continuity of the crystalline lattice (and the atomic structure) is not violated.

Sliding is an anisotropy process. It means, that the shift of atomic layers is produced not in the direction of a force but in the direction, which depends on the crystalline structure. *The planes of sliding are as a rule more tightly packed.* Those planes are known to be the planes of small crystallographic Miller indices (hkl). The sliding along the tightly packed planes is due to the fact that for certain lattices (especially metals), the distance between two neighbor tightly packed atomic planes is greater than that one between the other planes.

The directions of the more tightly packed atoms are as a rule the directions of sliding. The atoms are located in tightly packed plane of sliding. The elementary shifts in those or perpendicular directions are the smallest.

When there are several possible frames of sliding, the plastic deformation would be initiated in a system, which are more favorably oriented relative active strains than the other systems.

If the orientation of a crystal relative active strains is known the tangent strain, which initiates the plastic deformation in a given direction, can be found for all sliding frames.

A cylindrical sample of cross-section S undergoes the lengthening strain F (Fig.3.12). The shift is produced in the plane S' (the surface $S/\sin \alpha$) in the direction OB. α is the angle between the plane of sliding and the cylinder axis. F_n and F_t are the normal and tangent components. The direction of tangent component coincides with the direction of a possible sliding OB. The breaking-off strain associated with the direction of sliding

$$\tau = (F/S)\sin \alpha \cos \beta = \sigma \sin \alpha \cos \beta, \quad (3.28)$$

σ - the strain of lengthening. The inspection of equation (3.28) shows that the break-off strain is maximal at angles $\alpha = \beta = 45^\circ$. At this condition, $\tau_{max} = 0,5\sigma$.

It was proved that the normal strain almost does not affect the plastic flow of crystals. The tangent strains produce the plastic deformation. The flow limit strongly depends on the orientation of crystal, but the associated shearing strain τ is constant for a given metal. The typical magnitudes are $(10^{-5} - 10^{-4})G$. The law of the constancy of critical breaking-off strain was established by E.Schmidt and B.Baas. In accordance with the law, if the sample undergoes permanently growing strain, the sliding is small till the breaking-off strains do not overtake certain limit quantity. At room temperature, for Cu (the sliding plane $\{111\}$, the direction of sliding $\langle 110 \rangle$), this quantity is $0,49 \cdot 10^6$ Pa.

In the deformation process, the sliding layers change its orientation. When the deformation is going on the other favorable frames begin to act.

The critical breaking-off strain needed for initiation of plastic sliding deformation is usually less then the critical strain of twinning. Thus, the twinning is a rather rare process. For example, the critical strain of sliding is $0,18 \cdot 10^6$ Pa, and that of twinning is $29 \cdot 10^6$ Pa. Certain substances can be deformed in both ways. It is due to the fact that the twinning generates the new orientations, which promote the sliding.

For sliding plastic deformation if even the energy needed to translate an atom is small, the presence in the sliding plane about 10^{20} atom/m² requires essential strain.

The break-off strain to shift a region of crystal relative the other region evaluated under assumption that the shearing force depends on displacement in sine way is:

$$\tau_{meop} = \frac{b G}{a 2\pi}, \quad (3.28)$$

B – period of the shift force, a – distance between the rows of atoms, G – shear modulus. More accurate calculations lead to:

$$\tau_{meop} \approx G/30, \quad (3.29)$$

The experimental magnitudes of break-off strains is essentially less than the theoretical ones and are of the order of $(10^{-5} - 10^{-4}) G$. Thus, for copper, the experimental value is $0.49 \cdot 10^6$ Pa, the theoretical magnitude is $G/30 = 75,2 \cdot 10^9 / 30 = 2,5 \cdot 10^9$ Pa.

That discrepancy is due to dislocations in real crystals. The dislocations move easily. Their motion produces sliding at very small-applied strains. When there is a dislocation, the shift begins moving not in the entire plane but only in part of it. Then under the action of tangent strains, the shift propagates upon the entire sliding plane. The dislocation moves in the direction of the Burgers vector (b). Fig.3.13 shows the development of a unit shift (per unit inter atomic distance) of the upper part of a crystal relative to the down one when there is an edge dislocation.

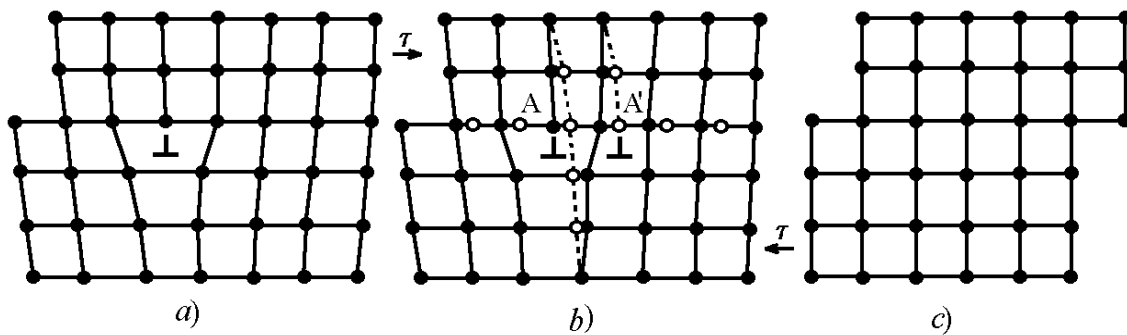


Fig.3.13 The motion of the edge dislocation leads to formation of the unit-shearing step: a) the initial state; b) the dislocation has transmitted by one inter-atomic distance; 3) the dislocation has reached the crystal interface and performed the unit shearing.

According Fig.3.13 to transmit the dislocation, rather small force is needed because for translation of dislocation through an inter-atomic distance (from the point A to the point A') a small displacement of atoms is needed (from positions designated by the dark circle to ones designated by the bright circles). In an ideal crystal, in a process of slide deformation, all the atoms are displaced simultaneously. When there is a dislocation, the deformation is produced by the great number of successive translations of atoms. Thus, its motion easily justifies the small critical break-off strains in the initial stage of a plastic deformation (even when the number of dislocations is small and when there is a strain).

In the process of plastic deformation, the new dislocations are born. Their motion leads to the macroscopic shift along the plane of sliding.

In order to deform crystal further in the region of plasticity, the strain should be permanently increased (Fig.3.9). It is due to the fact that during the irreversible deformation, the sample becomes more stable (riveting). The process continues up to destruction. The observed strengthening is associated with decreasing of dislocation mobility. The elastic interaction between dislocations affects strongly the process of strengthening: the strengthening grows when the dislocation density is increased. Thus, the dislocation density increases from $10^{10} - 10^{12} \text{ m}^{-2}$ in non-deformed substances up to $10^{15} - 10^{16} \text{ m}^{-2}$ in strongly strengthened by deformation materials. The bending of slide planes near the clusters of edge dislocations, intersecting of dislocations that produces

the steps, the interaction between dislocations and impurities decrease the mobility of dislocations.

When the great strains are applied the reaction of a solid essentially depends on its defects; destruction begins at the more weak places. Ideal crystals are many times strengthener than the real ones (Table 3.1).

Table 3.1. Mechanical parameters of ideal and real crystals

Crystal	Strengthening limit Πa	Elastic deformation, %	Plastic deformation, %
Ideal crystal	$(1,5—2) \cdot 10^{10}$	1—5	0
Real crystal (metals)	$(0,1—1) \cdot 10^7$	10^{-2}	From scores to hundreds
String crystals	$(0,5—1,4) \cdot 10^{10}$	0,5—2	1—1.5

All methods of strengthening (riveting while rolling, alloying, thermal treatment and some others) are associated with increasing of dislocation density. The strengthening can be increased up $10^{-3}G$.

When there are no defects, the crystal is the most stable. For example, the string crystals ('moustaches') (without dislocations) are produced from many substances (iron, germanium, gold, tin, cadmium, nickel, copper, and others). Diameter of string crystals is of order of 100 pm. A single screw dislocation causes the spiral growth of the string crystals in a unique direction. A single dislocation does not violate the crystal stability because while lengthening of crystal, the shift strain does not act upon the dislocation. The strengthening limit of 'moustaches' is very great. For example the copper holds $5,9 \cdot 10^9$ Pa instead of $1,8 \cdot 10^9$ Pa. The elastic deformation can be of several per cents, while for usual crystals it is not higher then hundredth fraction of per cent (see Table 3.1).

3.4 Fragile Destruction.

The plastic deformation precedes the viscosity destruction of a solid. Opposite to the viscosity destruction, the fragile destruction can be produced after small plastic deformation or even without it. The fragile destruction is observed in many non-metallic substances and metallic substances at very low temperatures.

It is supposed that ideally the fragile destruction is produced as a result of instantaneous breaking-off inter-atomic bonds in the plane perpendicular to the acting normal strength. Evaluations show that

$$\sigma_{meop} \approx E/10. \quad (3.30)$$

More accurate calculations lead to

$$\sigma_{meop} = (\gamma_s E/a)^{1/2}. \quad (3.31)$$

γ_s , - specific surface energy; a – inter-atomic distance.

For a glass σ_{meop} ($E = 8 \cdot 10^{10}$ Pa) is about $8 \cdot 10^9$ Pa. The real strengthening limit is $8 \cdot 10^9$ Pa, i.e. two orders lower then the theoretical evaluation. Analogue results are obtained for other substances.

To explain this discrepancy, A.Griffits (1920) supposed that in solids there are micro-fissures that are the centers of strains. According to him, the fragile destruction of a solid can be interpreted as the process of transformation of elastic energy concentrated inside the body volume into the surface energy of its parts produced during the destruction. He developed a method to evaluate the technical strengthening limit of solids. .

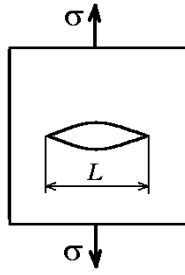


Fig.3.14 The fissure model

When a lengthening strain is applied to a plate of unique thickness, the energy stored in the unique volume:

$$\frac{1}{2} \sigma \epsilon = \frac{1 \sigma^2}{2E} . \quad (3.32)$$

When a transversal plane ellipsoid fissure of the length L is produced (see Fig.3.14), in the fissure zone (the ellipse axes are L и $L/2$, volume is $\pi L^2/2$) the elastic energy is liberated. The plate elastic energy decreases by:

$$W = \frac{1}{2} \frac{\sigma^2}{E} \frac{\pi L^2}{2} = \frac{\pi \sigma^2 L^2}{4E} . \quad (3.33)$$

The appearance of the fissure is accompanied by formation of two new surfaces, the energy needed is

$$U = 2\gamma_s L , \quad (3.34)$$

γ_s – specific surface energy. The total energy increment is:

$$T = U - W = 2\gamma_s L - \frac{\pi \sigma^2 L^2}{4E} . \quad (3.35)$$

If $\partial T / \partial L = 0$, the equilibrium is not stable. A fissure of great size quickly propagates because the elastic energy decreases faster (with increase of L) than the surface energy increases. The fissure of smaller size would not grow at all and close because the surface energy decreases faster than the elastic energy increases. The critical size of a fissure can be found using condition $\partial T / \partial L = 0$:

$$L_{kp} = 4\gamma_s E / (\pi \sigma^2) . \quad (3.36)$$

With an aid of equation (3.36), it is possible to evaluate the strain needed to destroy the body with the fissure of the size of L_{kp} .

$$\sigma = 2 \left(\frac{\gamma_s E}{\pi L} \right)^{1/2} . \quad (3.37)$$

Griffits found a condition of the unstable growth of fissure. He did not take into consideration the strained state near the fissure edge the strains are concentrated.

The sharp fissure with the vertex radius a (the distance between two atoms) leads to the local increasing of strain up to:

$$\sigma = \sigma \left(1 + 2\sqrt{L/2a} \right) . \quad (3.38)$$

Combining (3.38) and (3.31) at the condition $\sigma_{max} = \sigma_{meop}$, we get

$$\sigma = \left(\frac{\gamma_s E}{2L} \right)^{1/2} . \quad (3.39)$$

It means that if in a solid there is a fissure of length L and radius near the vertex is a , and the applied strain is σ the local strain at the vertex is σ_{meop} and the fissure propagates till the plate is destroyed or the fissure becomes blunt.

To take into account the plastic deformation, it is necessary to insert the expression (3.40) in formula (3.7).

$$\sigma = \left(\frac{(\gamma_p + \gamma_s)E}{\pi L} \right)^{1/2}. \quad (3.40)$$

The great number of experiments proved this formula.

The fissures produce the fragile destruction. The fissures are generated in the process of

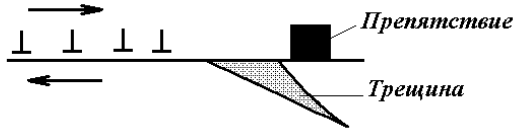


Fig.3.15 The dislocation mechanism of the fissure formation under the action of normal strains

formation of a solid and especially in the process of mechanic treatment. There are a number of mechanisms producing the fissures when the mechanic strain is applied to a solid. The dislocation

mechanism is described in [6].

Let a lengthening strain to be applied to a crystal. The strain produces the sliding of edge dislocations along certain plane

(Fig.3.15). There is a barrier that can not be overrun by dislocations (boundary of grains, intersections of slide planes, and others). If the temperature is not high, the head dislocation stops in front of barrier. The following dislocations also stop. If a barrier would stop n dislocations, the head dislocation would undergo the strain n -times greater than the external one. This strain can be too great. The wedge fissure would appear near the head dislocation. The fissure is due to unifying of nearest to barrier dislocations.

Thus, the stability of solids strongly depends on micro fissures inside of a sample. Besides, the surface quality of a sample and the external medium are of very importance. The surface-active substances that can be strongly adsorbed decrease the surface energy. The particles adsorbed by the surface enter the embryo fissures, penetrate inside of the body, and decrease its strengthening.

In order to diminish the influence of surface layer on the strengthening, this layer should be 'cured' or removed entirely by certain chemical methods. Irradiation of the surface by accelerated ions or inert gases or metals with the following thermal treatment is widely used.

3.5 Oscillation of Atoms in Crystals.

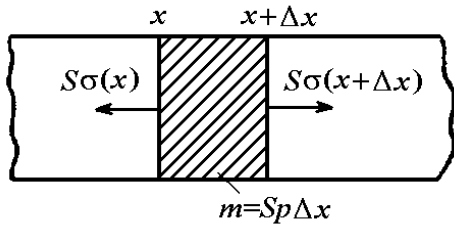
In solids, the atoms are known to oscillate about their equilibrium position. When the oscillation amplitude is small, those oscillations can be considered as the sine-type. The more is the temperature, the more is the amplitude and energy of oscillations.

In a solid, all atoms are strongly bonded. Thus, we can consider all the possible oscillations as a set of interacting elastic waves that propagate through the entire volume of a body. The volume of the body is finite, and superposition of standing waves is produced.

The oscillations of the crystalline lattice determine many physical phenomena in solids: thermal capacity, thermal conductivity, thermal expansion, electric conductivity, and others. The theory of oscillations of the lattice atoms is very complicated. Thus, at first we will study the propagation of elastic waves inside a uniform string, and through a crystal having not taken into account the discrete structure of the body. We will study the oscillations of atoms of one-dimensional lattice. Then, we will generalize the results for a three-dimensional crystalline lattice.

3.5.1 Oscillations of a Uniformed String

Let the longitudinal wave to propagate through a uniform unlimited string of the linear density ρ . The motion of each element is linear. When the wave transmits through the distance Δx (F.g.3.16), the forces acting upon the element are from the left: $S\sigma(x)$; and



from the right: $S\sigma(x + \Delta x)$. S is the string cross-section. $\sigma(x)$ и $\sigma(x + \Delta x)$ are the normal elastic strains. The resultant force acting upon element Δx is:

$$F = S\sigma(x + \Delta x) - S\sigma(x). \quad (3.41)$$

Under action of this force, the elementary element Δx is displaced. Designating the displacement of the mass-center of the element by $u(x,t)$, we get:

Fig.3.16. Concerning the problem of the motion of an elastic wave in a string

$$\rho S \Delta x \frac{\partial^2 u}{\partial t^2} = S\sigma(x + \Delta x) - S\sigma(x), \quad (3.42)$$

$\rho S \Delta x$ – the element mass. Equation (3.42) can be written as follows:

$$\rho \frac{\partial^2 u}{\partial t^2} = \frac{\sigma(x + \Delta x) - \sigma(x)}{\Delta x}. \quad (3.43)$$

When $\Delta x \rightarrow 0$:

$$\rho \frac{\partial^2 u}{\partial t^2} = \frac{\partial \sigma}{\partial x}. \quad (3.44)$$

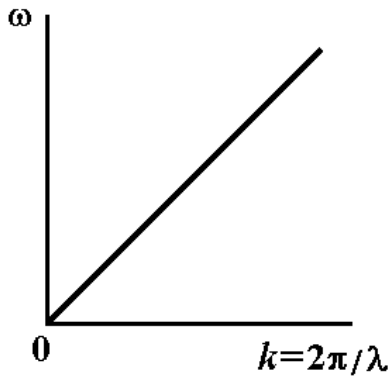


Fig.3.17 Frequency as function of the wave number for a continuous string

In accordance with the Hooke law: $\sigma = E\varepsilon$. Here, E is the Young modulus; $\varepsilon = \partial u / \partial x$ is deformation. Thus,

$$\frac{\partial \sigma}{\partial x} = E \frac{\partial \sigma}{\partial x} = E \frac{\partial^2 u}{\partial x^2}. \quad (3.45)$$

The motion equation can be written as follows:

$$\frac{\partial^2 u}{\partial t^2} = \frac{E}{\rho} \frac{\partial^2 u}{\partial x^2}. \quad (3.46)$$

The solution is plane monochromatic wave:

$$u = u_0 \exp[i(kx - \omega t)] = u_0 \sin 2\pi \left(\frac{x}{\lambda} - \nu t \right) = u_0 \sin(kx - \omega t). \quad (3.47)$$

u_0 – oscillation amplitude, ν - frequency, $\omega = 2\pi\nu$ - angular frequency; t – time; λ - wavelength; $k = 2\pi/\lambda$ - wave number. Inserting equation (3.47) in (3.46) we arrive to dispersion relation:

$$\omega = \sqrt{E/\rho} \cdot k = v_l \cdot k. \quad (3.48)$$

Thus, for an elastic wave that propagates in continuous unlimited string, the frequency depends linearly on the wave number (Fig.3.17). The wave propagation speed $v_l = \sqrt{E/\rho}$ depends only of material. For example, for iron ($E = 2,1 \cdot 10^{11}$ Pa, $\rho = 7,8 \cdot 10^3$ kg/m³) $v = 5 \cdot 10^3$ m/c.

3.5.2 Elastic Waves in Crystals

The processes of propagation of elastic waves are more complicated than those ones of electromagnetic waves. The electromagnetic waves are transversal. The elastic (sonic) waves are of two kinds: longitudinal and transversal. The first ones are the waves of lengthening and contraction; the second ones are the waves of shearing deformation. Generally, in every direction in crystal, three polarized elastic waves with different speed can propagate.

Assume that an elementary volume of crystal (density ρ) is chosen in a form of a parallelepiped with edges Δx , Δy , Δz , which are parallel to crystallographic axes x , y , z (Fig.3.18). When the wave propagates through crystal, every side of an elementary parallelepiped performs small oscillations under action of the strain σ_i . Let us discuss the propagation of the elastic wave along x -direction.

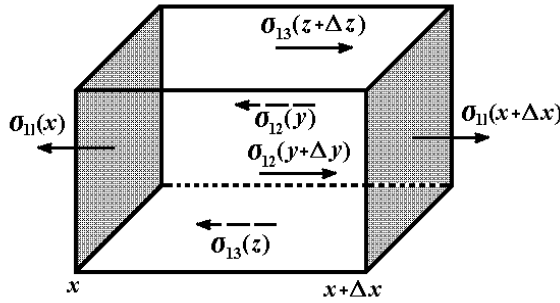


Fig.3.18. The forces act upon an elementary parallelepiped when the elastic wave propagates through a substance.

The strain $\sigma_{11}(x)$ acts upon the side x . The parallel side $x + \Delta x$ is affected by the strain

$$\sigma_{11}(x + \Delta x) \approx \sigma_{11} + \frac{\partial \sigma_{11}}{\partial x} \Delta x$$

The resultant force in x -direction is $\left(\frac{\partial \sigma_{11}}{\partial x} \Delta x \right) \Delta y \Delta z$. Changing the

strains σ_{12} and σ_{13} inside the parallelepiped produces the other forces in x -direction. Thus, the resultant force is

$$F(x) = \left(\frac{\partial \sigma_{11}}{\partial x} + \frac{\partial \sigma_{12}}{\partial y} + \frac{\partial \sigma_{13}}{\partial z} \right) \Delta x \Delta y \Delta z \quad (3.49).$$

If to designate the components of the displacement vector of the center of mass by u , v , and ω , the motion equation would be written as follows:

$$\rho \frac{\partial^2 u}{\partial t^2} = \frac{\partial \sigma_{11}}{\partial x} + \frac{\partial \sigma_{12}}{\partial y} + \frac{\partial \sigma_{13}}{\partial z} \quad (3.50).$$

If displacements u , v , and ω are designated by symbols x_i ($i = 1, 2, 3$), we get:

$$\rho \frac{\partial^2 x_i}{\partial t^2} = \sum_j \frac{\partial \sigma_{ij}}{\partial x_j} \quad (j = 1, 2, 3). \quad (3.51).$$

σ_{ij} are the components of strain tensor.

For a cubic crystal, taking into account the restrictions upon the elastic constants C_{ij} [see matrix (3.26)] and equation (3.9) and (3.10), we get:

$$\begin{aligned}\sigma_{11} &= C_{11} \frac{\partial u}{\partial x} + C_{12} \left(\frac{\partial v}{\partial y} + \frac{\partial \omega}{\partial z} \right); \\ \sigma_{12} &= C_{44} \left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \right); \quad \sigma_{13} = C_{13} \left(\frac{\partial u}{\partial z} + \frac{\partial \omega}{\partial x} \right);\end{aligned}\tag{3.52}$$

Introducing this equation in (3.50), we arrive to the motion equation:

$$\rho \frac{\partial^2 u}{\partial t^2} = C_{11} \frac{\partial^2 u}{\partial x^2} + C_{44} \left(\frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right) + (C_{12} + C_{44}) \left(\frac{\partial^2 v}{\partial x \partial y} + \frac{\partial^2 \omega}{\partial x \partial z} \right)\tag{3.53}$$

The equations for displacements v and ω are easily got from (3.53) by cyclic transposition:

$$\rho \frac{\partial^2 v}{\partial t^2} = C_{11} \frac{\partial^2 v}{\partial y^2} + C_{44} \left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial z^2} \right) + (C_{12} + C_{44}) \left(\frac{\partial^2 u}{\partial x \partial y} + \frac{\partial^2 \omega}{\partial x \partial z} \right)\tag{3.54}$$

$$\rho \frac{\partial^2 \omega}{\partial t^2} = C_{11} \frac{\partial^2 \omega}{\partial z^2} + C_{44} \left(\frac{\partial^2 \omega}{\partial x^2} + \frac{\partial^2 \omega}{\partial y^2} \right) + (C_{12} + C_{44}) \left(\frac{\partial^2 u}{\partial x \partial z} + \frac{\partial^2 v}{\partial y \partial z} \right)\tag{3.55}$$

Let us find the solution for plane waves, which propagate in direction [100]. The solution can be chosen in the form of plane wave:

$$u = u_0 \exp[i(kx - \omega t)].\tag{3.56}$$

u_0 is the oscillation amplitude; $|\mathbf{k}| = 2\pi/\lambda$ is the wave vector.

The wave vector \mathbf{k} and displacement u are oriented along the cube edges i.e. in x -direction. Thus, vector \mathbf{k} is normal to the wave front.

Inserting equation (3.56) in (3.53) we get:

$$v_l = \omega/k = \sqrt{C_{11}/\rho}.\tag{3.57}$$

v_l – velocity of propagation of the elastic longitudinal (sonic) wave in direction [100].

The other solution is a transversal wave (shearing wave), that propagates in x -direction, but displacement v is in y -direction.

$$v = v_0 \exp[i(kx - \omega t)].\tag{3.58}$$

Inserting equation (3.58) in (3.54) we get:

$$v_t = \omega/k = \sqrt{C_{44}/\rho}.\tag{3.59}$$

v_t – velocity of propagation of the elastic transversal wave in direction [100].

The third solution is also the shearing wave in x -direction, but ω is in z -direction.

$$\omega = \omega_0 \exp[i(kx - \omega t)].\tag{3.60}$$

Inserting equation (3.60) in (3.55) we get:

$$v_t = \sqrt{C_{44}/\rho}.\tag{3.61}$$

Thus, three elastic waves propagate in direction [100]: one longitudinal and two transversal waves. It should be noted that two independent transversal waves propagate with the same speed. *When the direction of a wave vector is arbitrary there are three polarized waves. Their velocities are different and do not depend on frequency.* According to equations (3.57), (5.59), and (5.61) the greater the rigidity and the less the density of a crystal the greater the velocity of propagation of elastic (sonic) waves. It follows also that the cyclic frequency ω is proportional to the wave number k , i.e. *the dispersion relations are of the same form as those ones of the elastic string*

3.5.3. Oscillation of One-Atomic Linear Chain

The simplest model of a solid is the linear chain of atoms (Fig.3.19) consisting of N identical atoms of mass M arranged at the distance a . The atoms can move along the straight line. Thus, the degree of freedom of the entire system is N . The model can be interpreted by the Bravais linear primitive cell with the translation $T = na$ (n is an integer).

Assume that at $t = 0$ atom of number $n = 0$ is displaced from the equilibrium position at a distance u_0 . The atoms of the chain are bonded. Thus, the excitation in the form of contraction wave propagates along the chain, and all atoms are displaced from their equilibrium positions.

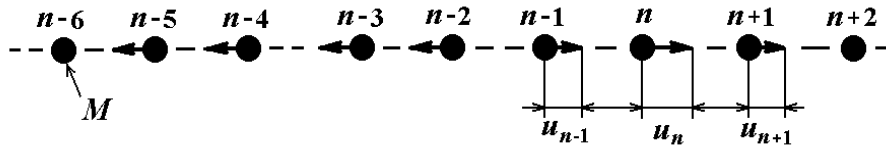


Fig.3.19 The linear chain of identical atoms

Let $u_n(x, t)$ be the displacement of a n -atom relative its coordinate $x_n = na$. If the displacement is small in comparison with the distance a , the forces between atoms can be considered quasi-elastic. In accordance with Hooke's law those forces are proportional to displacements. We can assume that atoms of chain are bound by springs with an elasticity constant C , and the displacement u_n describes the oscillations of atom near its equilibrium position.

Let us assume that the forces are short-handed. Thus, n - atom interacts only with its closest neighbor atoms of $(n-1)$, and $(n+1)$ number. The force acting upon the atom

$$F_n = \beta(u_{n+1} - u_n) - \beta(u_n - u_{n-1}) = \beta(u_{n+1} + u_{n-1} - 2u_n), \quad (3.62).$$

β - force constant, which is related with the elastic constant by $C = \beta a$. The motion equation is:

$$M \frac{\partial^2 u_n}{\partial t^2} = \beta(u_{n+1} + u_{n-1} - 2u_n) \quad (3.63)$$

We can find the normal oscillation modes i.e. types of motion when all atoms oscillate with the identical frequency ω in accordance to; $\exp(-i\omega t)$. The solution of equation (3.63) is chosen as (running wave):

$$u_n = u_0 \exp[i(kna - \omega t)] = u_0 \exp[i(kx_n - \omega t)]. \quad (3.64)$$

u_0 is the displacement of an atom of number $n = 0$ at the time moment $t = 0$; $k = 2\pi/\lambda$ - wave number; ω - the mode cyclic frequency.

It follows from equation (3.64) that the type of normal mode is determined by the displacement of the atom of number $n = 0$. Inserting the solution (3.64) into equation (3.63) we get:

$$-M \omega^2 = \beta[\exp(ika) + \exp(-ika) - 2] = -4\beta \sin^2(ka/2). \quad (3.65)$$

Thus, the definite quantity ω^2 corresponds to each wave number. ω^2 is the even function of the wave number k . Using equation (3.65) we get the dispersion relation for the waves that propagate through the linear chain of identical atoms:

$$\omega = \pm(4\beta/M)^{1/2} \sin(ka/2) \quad (3.66)$$

The negative sign corresponds to the region of negative wave numbers k .

It follows from (3.66) that the oscillation frequency of n -atom does not depend on n , i.e.

all atoms oscillate with the same frequency. The function (3.66) is shown in Fig. 3.20.

According to (3.66) at $|k| = 2\pi/\lambda = \pi/a$ (short waves) $\lambda = 2a$, and the cyclic frequency is maximal.

$$\omega = \omega_{\max} = (4\beta/M)^{1/2} \quad (3.67)$$

Let us evaluate the quantity

$\omega_{\max} \approx v_{3\beta} k$, $v_{3\beta} = \sqrt{C/\rho}$ is the velocity of sonic waves. $v_{3\beta} \approx 5 \cdot 10^3$ м/с. Assume that for solids, $a = 10^{-10}$ m. Thus, $k = \pi/a \approx 10^{10}$ m⁻¹

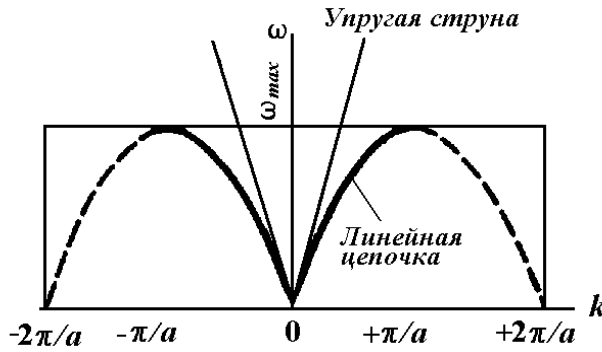


Fig.3.20. The linear chain dispersion

$\omega_{\max} = 5 \cdot 10^{13}$ s⁻¹, which (by the order) corresponds to the thermal oscillation frequency of atoms in solids. When k is small i.e. the wavelength is greater than the distance between atoms of a chain, the dependence of ω on k is linear as in the case of continuous string with the linear density $\rho = M/a$:

$$\omega = \left(\frac{4\beta}{M}\right)^{1/2} \sin \frac{ka}{2} \approx \left(\frac{4\beta}{M}\right)^{1/2} \frac{ka}{2} \left(\frac{C}{\rho}\right)^{1/2} k = v_{3\beta} k. \quad (3.68)$$

Thus, in discrete chain there is no proportionality between frequency and the wave number. We remind our readers that in continuous string there is such proportionality. It is due to the wave dispersion. The short waves, which correspond the high oscillation frequency of particles propagate not so fast as the long waves (it is due to inertia of particles). The function $\omega = \omega(k)$ is not linear as that of the elastic string (see Fig.3.20). Behavior of the chain of identical atoms relative to the propagation of sonic waves is like that one of the elastic string when $\lambda \gg 2a$.

The propagation velocity depends on wavelength (in a uniform string there is not such dependence):

$$v = \frac{\omega(\lambda)}{2\pi} = \lambda \left(\frac{\beta}{M}\right)^{1/2} \sin \frac{\pi a}{\lambda}. \quad (3.69)$$

This dependence is characteristic for discrete structures. The relation (3.64) describes the waves that propagate along the chain with *phase velocity*

$$v_{\phi} = \frac{\omega}{k} = v_{3\beta} \left| \frac{\sin(ka/2)}{ka/2} \right| \quad (3.70)$$

group velocity

$$v_{zp} = \frac{\partial \omega}{\partial k} = v_{3e} \left| \cos \frac{ka}{2} \right| \quad (3.71)$$

When k is small (F.g.3.21) the phase and group velocities are identical with the sonic speed:

$$v_{\phi} = v_{zp} = v_{3e} \quad (3.72)$$

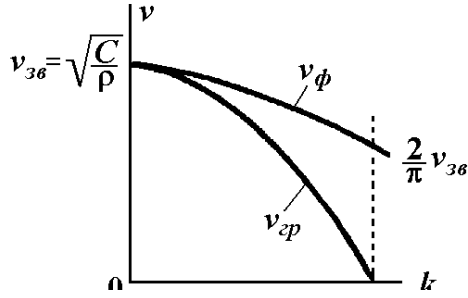


Fig.3.21. Dependence of phase and group velocity on the wave number

A glance at equation (3.71) and Fig.3.21 shows that the magnitude of the group velocity (the velocity of the energy transmittance) of the shortest waves ($k = \pi/a$) is zero. Thus, the standing waves of the type

$$u_n = u_0 \exp[i(kna - \omega t)] = u_0 \exp(-i\omega t) \cos n\pi \quad (3.73)$$

are produced. Those waves are the result of superposition of two running waves of the same amplitude and frequency but propagating in the opposite directions.

Having discussed the differential equation (3.63) we said nothing about the boundary conditions. Those conditions restrict the interval of the wave number and its magnitude in this interval. When the length of a chain is limited the forces, which act upon the middle atoms, differ from that ones which act on the atoms at its ends. Thus, the state of equilibrium at the edges of the chain is violated. This difficulty can be excluded if suppose that atoms form a big ring in such way that the last atom ($n = N$) is again at a distance a from the first one ($n = 1$). If N is great the properties of the ring slightly differ from those of a linear chain. Then, the periodic border condition of Born-Karman can be chosen:

$$u_{n+N} = u_n, \quad (3.74)$$

The integers n and $n+N$ characterize the same atom. Inserting the solution (3.64) into condition (3.74) we arrive to:

$$u_{n+N} = u_n \exp i(kNa), \quad \text{если} \quad \exp(ikNa) = 1, \quad (3.75)$$

It follows that solution (3.64) is in accordance with the boundary condition (3.74) if

$$kNa = 2\pi n, \quad \text{где целое число} \quad (n = 0, \pm 1, \pm 2, \pm 3, \dots). \quad (3.76)$$

Thus $k = 2\pi n/aN$ is a quantum quantity. The interval of the wave number can be chosen as follows:

$$-\pi/a \leq k \leq +\pi/a \quad (3.77)$$

This interval coincides with the Brillouin zone of the electron wave vector.

Obviously, the allowed quantity of wave numbers within the interval (3.77) (taking into account (3.74) and (3.76)) is N , i.e. the number of atoms or elementary cells in a chain. Every proper quantity k corresponds to its proper function (see 3.64). The number of those functions can not be more than N .

The general solution of the motion equation can be build up as the superposition of waves (3.64) of the wave number k , frequency ω_k and amplitude A_k :

$$u_n = \sum_k A_k \exp[i(kna - \omega_k t)], \quad (3.78)$$

Summation is performed by all magnitudes of k , which satisfied the condition (3.76).

The motion of any oscillating system can be written as the motion of independent oscillators with the *normal coordinate* q_k . Those coordinates are independent and follows the harmonic law:

$$q_k = A_k \sqrt{N} \exp(-i\omega_k t). \quad (3.79)$$

Inserting (3.79) into (3.78) leads to:

$$u_n = \frac{1}{\sqrt{N}} \sum_k q_k \exp(ikna). \quad (3.80)$$

By differentiation of (3.79) with respect to t we would come to the conclusion that coordinate q_k satisfies the equation

$$\ddot{q}_k + \omega_k^2 q_k = 0 \quad (k = 1, 2, 3, \dots, N). \quad (3.81)$$

This equation describes the motion of linear harmonic oscillator. The oscillator total energy is given by the classical expression:

$$E_k = \frac{M}{2} \dot{q}_k^2 + \frac{M}{2} \omega_k^2 q_k^2. \quad (3.82)$$

M – mass of an oscillator. Thus, the total energy of atomic chain is:

$$E = T + U = U_0 + \sum_k E_k, \quad (3.83)$$

T – kinetic energy; U_0 – potential energy in the state of equilibrium; U – potential energy.

The Hamilton function of a classical linear oscillator is:

$$H = \frac{p_x^2}{2M} + \frac{M\omega_k^2}{2} x^2. \quad (3.84)$$

Here, p_x – momentum, M – mass, x – deviation from the equilibrium position, ω_k – proper frequency. A quantum linear oscillator is a system, which can be described by the Hamilton operator (see equation (3.82)):

$$\hat{H} = \frac{\hat{p}_x^2}{2M} + \frac{M\omega_k^2}{2} \hat{x}^2, \quad (3.85)$$

Here, $\hat{p}_x = i\hbar \frac{d}{dx}$ – momentum operator; \hat{x} – coordinate operator.

The Schrödinger stationary equation is:

$$\hat{H}\psi = -\frac{\hbar^2}{2M} \frac{d^2\psi}{dx^2} + \frac{M\omega_k^2}{2} x^2 \psi = E_k \psi. \quad (3.86)$$

\hbar – Plank's constant; ψ – wave function; E_k – total energy of oscillator. The proper energies of equation (3.86) are:

$$E_k = \hbar\omega_k \left(n + \frac{1}{2}\right), \quad n = 0, 1, 2, 3, \dots, \quad (3.87)$$

The integer n is called the principal quantum number. The energy is discrete. The total energy of the atomic chain:

$$E = U_0 + \sum_k E_k = U_0 + \sum_k \hbar\omega_k \left(n + \frac{1}{2}\right). \quad (3.88)$$

Factor $\frac{1}{2}$ in bracket corresponds to zero energy (at the temperature of 0 degrees). Even at that temperature, the atoms oscillate. It is due to the fact that precise localization of atoms would produce too great uncertainty in their momentum (in accordance with the Geizenberg uncertainty principle ($\Delta p_x \Delta x \geq \hbar$)).

3.5.4. Oscillation of a Two-Atomic Linear Chain

The chain is shown in Fig.3.22. Parameter of a linear elementary Bravais cell is $2a$. The basis consists of two atoms of different mass: M_1 and M_2 . N atoms are arranged along a straight line. The number of degrees of freedom is two. The springs can be considered as the forces acting between the atoms.

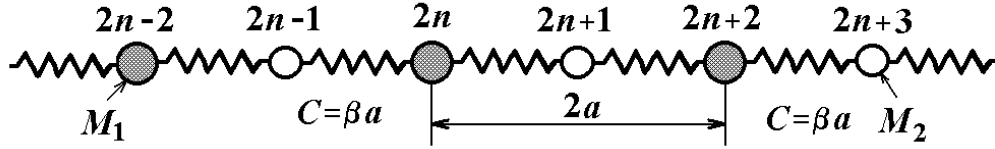


Fig.3.22 Two-atomic linear chain In an elementary cell (parameter $2a$) there are two atoms of mass M_1 and M_2 . C is the spring rigidity.

Let $2na$ be the even equilibrium positions of atoms with the mass M_1 , and $(2n + 1)a$ be the uneven equilibrium positions of atoms with the mass M_2 (n is an integer). Let u_{2n} be the displacement of M_1 atom from its equilibrium position in direction of x -axis. Let u_{2n+1} be the analogue quantity of M_2 atom. Assume that the displacements are small in comparison with inter atomic distances a . Assume that the interaction forces are quasi-elastic.

Taking into account only the forces produced by the closest neighbors the forces acting upon the M_1 and M_2 are:

$$F_{2n} = \beta(u_{2n+1} - u_{2n}) - \beta(u_{2n} - u_{2n-1}) = \beta(u_{2n+1} + u_{2n-1} - 2u_{2n})$$

$$F_{2n+1} = \beta(u_{2n+2} - u_{2n+1}) - \beta(u_{2n+1} - u_{2n}) = \beta(u_{2n+2} + u_{2n} - 2u_{2n+1}),$$

The quantity β and the elasticity constant are connected by relation: $C = \beta a$.

The Newton equation for displacement u_{2n} and u_{2n+1} can be written as follows:

$$M \frac{\partial^2 u_{2n}}{\partial t^2} = \beta(u_{2n+1} + u_{2n-1} - 2u_{2n})$$

$$M \frac{\partial^2 u_{2n+1}}{\partial t^2} = \beta(u_{2n+2} + u_{2n} - 2u_{2n+1})$$
(3.89).

The longitudinal excitation propagates through the chain. The atoms of different mass oscillate with different amplitudes.

The solution of equation (3.89) can be chosen as harmonic waves:

$$u_{2n} = u_1 \exp[i(2nka - \omega t)]$$

$$u_{2n+1} = u_2 \exp[i(2n+1)ka - \omega t]$$
(3.90)

Inserting solutions (3.89) into equation (3.89) and canceling out the common factor $\exp[i(2nka - \omega t)]$ we arrive to the system of equations relative u_1 and u_2 :

$$\begin{aligned} (2\beta - M_1\omega^2)u_1 - 2\beta \cos ka \cdot u_2 &= 0 \\ -2\beta \cos ka \cdot u_1 + (2\beta - M_2\omega^2)u_2 &= 0 \end{aligned}$$
(3.91)

The system of uniform equations can be solved if its determinant is zero:

$$\begin{vmatrix} (2\beta - M_1\omega^2) & (-2\beta \cos ka) \\ (-2\beta \cos ka) & (2\beta - M_2\omega^2) \end{vmatrix} = 0.$$
(3.92)

It follows that the frequency ω and the wave number k satisfy the equation:

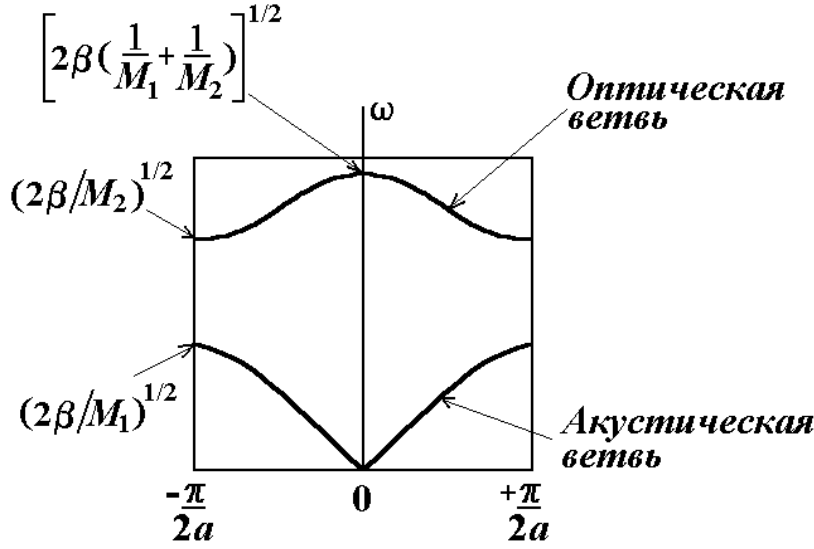


Fig.3.23. The dispersion curves for a longitudinal wave, that propagates along the linear two-atomic chain. The down curve represents the acoustic branch, the upper curve represents the optical branch of the optical spectrum.

$$\omega^4 - 2\beta \left(\frac{M_1 + M_2}{M_1 M_2} \right) \omega^2 + \frac{4\beta^2}{M_1 M_2} \sin^2 ka = 0. \quad (3.93)$$

It leads to:

$$\omega^2 = \beta \left(\frac{M_1 + M_2}{M_1 M_2} \right) \pm \sqrt{\left(\frac{M_1 + M_2}{M_1 M_2} \right)^2 - \frac{4}{M_1 M_2} \sin^2 ka}. \quad (3.94)$$

The negative k is forbidden. It follows from equation (3.94) that to a single wave number k , two frequencies ω correspond (hence, two modes). Using the border condition of Born-Karmann

($u_{2n+2N} = u_{2n}$ or $u_{(2n+1)+2N} = u_{2n+1}$) we find the allowed wave numbers. The condition ($u_{2n+2N} = u_1 \exp[i(2n+2N)ka - \omega t] = u_1 \exp i(2nka - \omega t) \exp i2Nka$) holds if $\exp(i2Nka) = 1$ or $2Nka = 2\pi m$ (m is an integer). Hence:

$$k = \frac{2\pi m}{2a N}. \quad (3.95)$$

The factor k is present only in the expressions of the type of $\exp(i2nka)$. Nothing would change if to add a quantity multiply $2\pi/(2a)$. Thus, the range of k can be restricted as:

$$-\pi/(2a) \leq k \leq +\pi/(2a) \quad (3.96)$$

It follows from equation (3.95) and (3.96) that the allowed number of k in the interval (3.96) is inside the range $-N/2 \leq m \leq +N/2$ and equals N (the number of elementary cells in the chain). Two modes correspond to a single wave number. Thus, the number of the normal modes inside the interval (3.96) equals the number of degrees of freedom i.e. $2N$. Interval (3.96) is a Brillouin zone of two-atomic chain.

There are two solutions: $k > 0$ (the wave running to the right) and $k < 0$ (the wave running to the left).

Thus, there are two dependencies of ω on k , which are called *two branches of the dispersion law*. The branches in Brillouin zone are shown in Fig.3.23 ($M_1 > M_2$).

The down curve is called the *acoustic branch*; the upper curve is called the *optic curve*. For all wave numbers, the frequency of optic oscillations is greater than the frequency of acoustic oscillations. In order to understand the origin of definitions let us discuss the situation when k is small and $k = \pm\pi/(2a)$. When $ka < 1$, $\sin^2 ka \approx k^2 a^2$. It is known that the roots of a square equation ($x^2 + px + q = 0$) follow the relations: $x_1 + x_2 = -p$, $x_1 x_2 = q$. The frequency of the optic branch varieties weakly near $k = 0$. Under those assumptions, we find that the roots of equation (3.93) are:

$$\omega_1 = \sqrt{2\beta \left(\frac{1}{M_1} + \frac{1}{M_2} \right)} \quad (\text{optical branch}) \quad (3.97)$$

$$\omega_2 = \left(a \sqrt{\frac{2\beta}{M_1 + M_2}} \right) \cdot k \quad (\text{acoustic branch}) \quad (3.98)$$

Comparing the equation (3.98) and (3.68) we arrive to the conclusion that the function $\omega = \omega(k)$ describes the branch of longitudinal acoustic oscillations. When k is small the frequency is proportional to the wave number (as for a mono-atomic chain). The sonic speed of long waves is:

$$v_{3\theta} = a \sqrt{2\beta / (M_1 + M_2)} \quad (3.99)$$

If k is small the phase and group velocities are identical: $v_\phi = v_{2p} = v_{3\theta}$. If $M_1 = M_2$ $v_{3\theta} = a \sqrt{\beta / M} = \sqrt{C / \rho}$, which is the sonic velocity in the mono-atomic chain of the density $\rho = M/a$.

When $k = \pm\pi/(2a)$, i.e. at the border of Brillouin zone $\omega_2 = \sqrt{2\beta / M_1}$; the curve is not steep, the group velocity becomes zero. Thus, the behavior of the down fraction of the curve is like that one of the mono-atomic chain.

The second branch begins at $k = 0$ and the maximal frequency $\omega_1 = \sqrt{2\beta \left(\frac{1}{M_1} + \frac{1}{M_2} \right)}$.

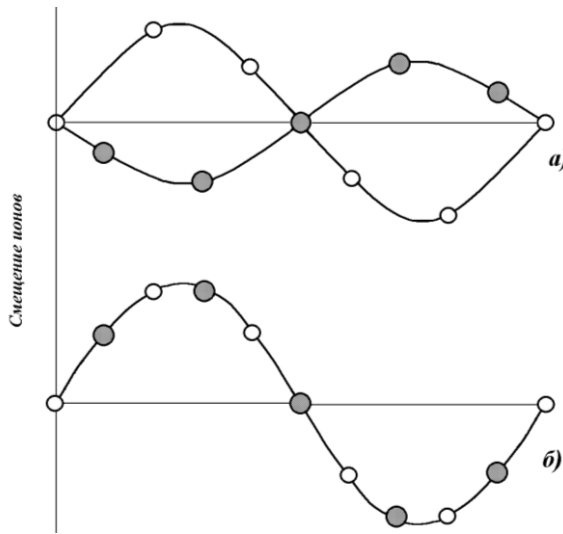
When k increases the curve slopes down. When the wave number $k = \pm\pi/(2a)$ $\omega_1 = \sqrt{2\beta / M_2}$.

The visible light can produce the optical oscillation branch (i.e. the set of optical modes). When $k \rightarrow 0$, the phase velocity of optic oscillations $v_\phi = \omega_1 / k \rightarrow \infty$, the group velocity is $v_{2p} = d\omega / dk = 0$.

Two branches (see Fig. 3.23) are divided by the band of forbidden frequencies i.e. the motion equations (3.89) have no solution in the region $\sqrt{2\beta / M_1} < \omega < \sqrt{2\beta / M_2}$.

Let us compare the ratio of amplitudes of neighbor oscillations in both branches. When $ka < 1$) taking into account relation (3.90) and inserting (3.98) into (3.91) ($k = 0$), we get:

$$\left(\frac{u_{2n}}{u_{2n+1}} \right)_{ak} = \left(\frac{u_1}{u_2} \right)_{ak} = 1 \quad (3.99)$$



Thus, the oscillation of neighbor atoms of the chain is of the same phase and amplitude i.e. the cells are displaced as a whole. Those oscillations are typical for sonic waves (Fig.3.24a).

If we insert the solution (3.97) into equation (3.91), then for an optic branch $k = 0$, we get:

$$\frac{u_1}{u_2} = -\frac{M_2}{M_1} \quad (3.100)$$

I.e. the atoms of a cell oscillate in opposite directions (in opposite phases) provided the center of mass does not move (see Fig.3.24b and formula 3.100).

Fig.3.24. Displacement of atoms when a transversal wave propagates along the two-atomic linear chain: линейной цепочки: а) acoustic mode; б) optic mode.

Thus, in the two-atomic chain there are two types of oscillation branches:

acoustic and optic. In acoustic modes, both atoms move in the same phase. In optic modes, the neighbor atoms move in opposite phase.

Under assumption that the wavelength of optic oscillations is great and the charges of atoms alternatively change, the anti-phase oscillations produce the displacement of ions, and the electric dipole moment of a cell would be changed. As a result, the wave of electric polarization propagates through a crystal. In ionic crystals, the optic oscillations are produced at infrared frequencies.

3.5.4. Oscillation of Atoms of a Three-Dimensional Cell

Assume that the three-dimensional lattice consists of identical atoms (mass M) and in a volume V there are N primitive elementary Bravais cells. Every atom has three degrees of freedom. The entire crystal has $3N$ degrees of freedom. In harmonic approximation, the displacement of each atom follows the motion equation, which is an analogue to the motion equation of the chain of identical atoms under condition that the displacement is substituted by the vector of displacement \mathbf{u}_j . As a result, we have the system of $3N$ equations. Its solution is:

$$\mathbf{u}_j = A_k \boldsymbol{\varepsilon}_v(\mathbf{k}) \exp \left[i(\mathbf{k} \mathbf{R}_j^0 - \omega t) \right], \quad (3.101)$$

\mathbf{k} - a wave vector; A_k - oscillation amplitude; $\boldsymbol{\varepsilon}_v(\mathbf{k})$ - unit polarization vector of normal mode that characterize the direction of ion motion; \mathbf{R}_j^0 - radius-vector of an atom of equilibrium configuration.

Introducing solution (3.101) in the system of motion equations, we get the set of uniform equations relative amplitudes A_k . That system has an antiviral solution if its determinant is zero. The determinant is a polynomial of the third power relative ω^2 and generally has three positive roots.

Thus, for every wave vector there are three oscillation modes, which determine three branches of dispersion relation (Fig.3.25).

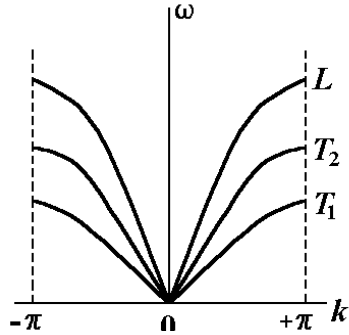


Fig.3.25. The dispersion curves for a primitive three-dimensional Bravais cell.

$$\omega = \omega_{\mathbf{k}v} \quad (v=1.2.3). \quad (3.102)$$

L mode corresponds to a longitudinal wave, T_1 and T_2 modes correspond to transversal waves. In a longitudinal wave, in isotropic medium, the polarization vector $\boldsymbol{\varepsilon}_v(\mathbf{k})$ is parallel to a wave vector \mathbf{k} . In transversal wave, the polarization vector is perpendicular to the wave vector.

In order to find the interval and number of allowed wave vectors, the cyclic condition of Bohr-Karman is used. The assumption is made that the crystal has the form of a rectangular parallelepiped with edges $N_1\mathbf{a}_1$, $N_2\mathbf{a}_2$, $N_3\mathbf{a}_3$. $\mathbf{a}_1 = \mathbf{a}$, $\mathbf{a}_2 = \mathbf{b}$, $\mathbf{a}_3 = \mathbf{c}$ are the vectors of

straight cell, N_1 , N_2 , and N_3 are the great numbers. In accordance with cyclic conditions, we have:

$$u_j(\mathbf{R}_j^0 + N\mathbf{a}_j) = u_j(\mathbf{R}_j^0), \quad (3.103)$$

The allowed magnitudes of vectors satisfy the condition:

$$\exp[i(N_j\mathbf{k}\mathbf{a}_j)] = 1 \quad (3.104)$$

Hence

$$\mathbf{k}\mathbf{a}_j = 2\pi n_j / N_j \quad (n_j - \text{целое число}) \quad (3.104)$$

$$\mathbf{k} = 2\pi \left(\frac{n_1}{N_1} \mathbf{a}^* + \frac{n_2}{N_2} \mathbf{b}^* + \frac{n_3}{N_3} \mathbf{c}^* \right), \quad (3.105)$$

\mathbf{a}^* , \mathbf{b}^* , \mathbf{c}^* - vectors of reciprocal lattice.

A single Brillouin zone (the Viger-Zeitz cell) can limit the magnitude of \mathbf{k} :

$$-\pi/\mathbf{a} \leq \mathbf{k} \leq +\pi/\mathbf{a}, \quad (3.106)$$

Obviously that the quantity of allowed wave vectors, which follow the condition (3.104) inside the interval (3.106) equals the number N of elementary cells in a crystal. All vectors \mathbf{k} are distributed in k space with the density $V/(2\pi)^3$.

When in a three-dimension lattice with basis and in an elementary cell there are p atoms, the number of degrees of freedom is $3pN$. Thus, the solution of $3pN$ equations gives $3p$ oscillation branches. Dispersion relations can be written as follows:

$$\omega = \omega_{\mathbf{k},v}^s \quad (v=1.2.3; \quad s=1,2,3,\dots,p). \quad (3.107)$$

Three down branches (Fig.3.26) at small wave numbers tend linearly to zero. They are called acoustic branches. The other $(3p - 3)$ are called the optic branches. Among them there are longitudinal and transversal oscillation branches. Velocity of longitudinal waves is greater than that one of the transversal waves because the frequencies of longitudinal waves are greater than the frequencies of transversal waves.

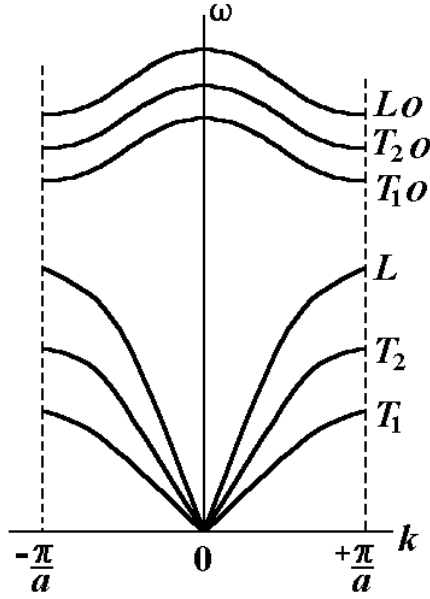


Fig.3.26. The dispersion curves for a three-dimensional cell with basis: T_1 and T_2 represent the transversal modes; L represents the longitudinal mode.

Thus for the lattice with basis, the motion of atoms can be interpreted as superposition of $3pN$ normal oscillations or modes. Every normal oscillation represents a harmonic oscillator. The normal coordinates follow the equation:

$$\ddot{q}_{\mathbf{k},s} + \omega^2(\mathbf{k}s)q_{\mathbf{k},s} = 0. \quad (3.108)$$

The total oscillation energy of a crystal is the sum of energies of $3pN$ independent harmonic oscillators.

The energy of a quantum oscillator with a frequency $\omega(\mathbf{k},s)$ is:

$$E_{\mathbf{k},s} = \hbar\omega(\mathbf{k}s)\left[n(\mathbf{k}s) + \frac{1}{2}\right] \quad n(\mathbf{k}s) = 1,2,3, \quad s = 1,2,3,\dots p. \quad (3.109)$$

The total energy is:

$$E = \sum_{\mathbf{k}} \sum_s E_{\mathbf{k},s} = \sum_{\mathbf{k}} \sum_s \left[n(\mathbf{k}s) + \frac{1}{2}\right] \hbar\omega(\mathbf{k}s) + U_0. \quad (3.110)$$

U_0 is the potential energy of the equilibrium state.

Thus, the oscillations of strongly bonded crystalline atoms are represented by the set of independent waves with a wave vector \mathbf{k} and frequency $\omega(\mathbf{k},s)$. An oscillator with the frequency $\omega(\mathbf{k},s)$ corresponds to every wave.

Thus, summarizing all which is said above we came to the conclusion that the sonic wave with the wave vector \mathbf{k} and polarization s can be considered as the set of $n(\mathbf{k},s)$ quanta of energy $\hbar\omega(\mathbf{k},s)$ plus the energy of a basic state $\frac{1}{2}\hbar\omega(\mathbf{k},s)$. Those quanta of the sonic wave are called the **phonons**. The quantity $\hbar\omega(\mathbf{k},s)$ is the minimal excitation energy above the basic level $\frac{1}{2}\hbar\omega(\mathbf{k},s)$. A photon can be considered as the elementary excitation. The complex excitation is the sum of the simple ones. The collective motion of atoms in crystal represents the sonic wave. The corresponding excitations are sonic quanta or phonons..

An oscillation mode of classic frequency $\omega(\mathbf{k},s)$ can be excited by photons of energy $\hbar\omega(\mathbf{k},s)$. The quantity $n(\mathbf{k},s)$ (see formula (3.109)) is the number of photons with p and energy $\hbar\omega(\mathbf{k},s)$. While discussing the heat problems, it is needed to know the average number of quanta $\langle n(\mathbf{k},s) \rangle$ of the energy $\hbar\omega(\mathbf{k},s)$ at a given temperature. To find quantity $n(\mathbf{k},s)$, let us use the Plank formula for the average energy of a quantum oscillator:

$$\langle E \rangle = \frac{\hbar\omega(\mathbf{k},s)}{\exp[\hbar\omega(\mathbf{k},s)/(k_B T)] - 1} + \frac{\hbar\omega(\mathbf{k},s)}{2} \quad (3.111)$$

The factor $\frac{1}{2}\hbar\omega(\mathbf{k},s)$ can be dismissed because it does not depend on the temperature.

It follows from the formula (3.111).

$$\langle n(\mathbf{k},s) \rangle = \frac{\langle E \rangle}{\hbar\omega(\mathbf{k},s)} = \frac{1}{\exp[\hbar\omega(\mathbf{k},s)/(k_B T)] - 1} \quad (3.111)$$

This expression also describes the Boze-Einstein distribution of photons. Thus, the average number of photons per a phase cell of volume $(2\pi\hbar)^3$ with energy $\hbar\omega(\mathbf{k},s)$ is given by the expression (3.111).

In solids, two types of phonons are possible: acoustic and optic phonons. The oscillation frequency of optic phonons is higher than that one of the acoustic phonons. The energy of optic phonons is greater than the energy of acoustic phonons. Thus, at very low temperatures only the acoustic phonons can be excited.

Conception of photons gives an opportunity to consider a solid as a set of photons inside a box. The photons move from one wall to the other. They collide. As a result of those collision, the photons can be born and die. The photon gas is not a conventional gas. The number of photons in a solid is no constant. The higher is the temperature, the more is the number of photons. When the temperature tends to zero, their number tends to zero too.

Thus the oscillation of a lattice is a wave-particle duality phenomenon. The corpuscular aspect leads to the conception of **phonon**. The energy of phonon is $h\nu = \hbar\omega$, its momentum is $\hbar k$. Thermal conduction, electron scattering, and others phenomena in solids are associated with the processes of generation and annihilation of photons.

In the frequency interval when photon energy $\hbar\omega$ is comparable with the thermal energy $k_B T$ or greater than that, the classical and quantum statistics lead to essentially different results.

The corpuscular properties are of importance when the frequency is greater than $\nu_{nop} = (\omega_{nop}/2\pi) = (k_B T/h)$. At room temperature $\nu_{nop} \approx 6 \cdot 10^{12}$ Hz or $\omega_{nop} \approx 4 \cdot 10^{13}$ rad/s. The threshold wavelength $\lambda_{nop} = (2\pi\nu/\omega_{nop})$. The wave velocity is of order of 5000 m/c. Thus, at room temperature, the corpuscular properties demonstrate itself when $\lambda \leq 10^{-9}$ m. i.e. the wavelength is comparable with the inter atomic distance [$(1 - 4) 10^{-10}$ m]. At very low temperature, the quantum effects are essential even when the wavelength is much greater than the size of atoms.

3.6. Statistics of Phonons and the Heat Capacity of a Lattice

While investigating the dependence of crystalline energy on the temperature, it is very convenient to use the photon concept. If U is the total oscillation energy of a crystal, then the volume heat capacity is $C_v = (\partial U / \partial T)_v$. In actual experiments, the pressure capacity C_p is being measured. The energy needed for heat expansion is small, the quantity $(C_p - C_v)$ is small too, and we can assume that $C_v = C_p$.

3.6.1 The Classic Model for Calculation of the Lattice Energy

Assume that an atom (mass m) of a crystalline lattice harmonically oscillates with an amplitude x_m and cyclic frequency ω . The elastic constant is μ . If x is deviation from an equilibrium position, then its velocity is $v = \dot{x}$, and acceleration is $\ddot{x} = (-\mu x / m) = -\omega^2 x$. The total energy:

$$E = (mv^2/2) + (\mu x^2/2) = (m/2)[v^2 + \omega^2 x^2] \quad (3.108)$$

In accordance with the Boltzmann distribution:

$$\langle E \rangle = \frac{\int_0^{v_m} \int_0^{x_m} E \exp(-E/k_B T) dv \cdot dx}{\int_0^{v_m} \int_0^{x_m} \exp(-E/k_B T) dv \cdot dx} \quad (3.109)$$

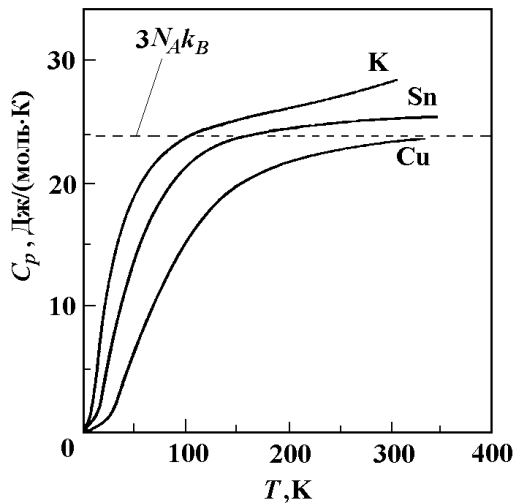


Fig.3.27 The specific heat as function of temperature

Introducing (3.108) into (3.109) we get:

$$\langle E \rangle = k_B T \quad (3.110)$$

The total energy of a lattice of N atoms with three degrees of freedom is:

$$U = 3Nk_B T. \quad (3.111)$$

The volume molar heat capacity can be written as:

$$C_v = (\partial U / \partial T)_v = 3N_A k_B = 3R = 24,94 \text{ Дж}/(\text{МОЛЬ} \cdot \text{К}) \quad (3.112)$$

$R = 8,31 \text{ Jole} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ is a universal gas constant.

Equation (3.112) is known as the Dulong-Petit law. The curves shown in Fig.3.27 are typical for many solids. As it follows from the figure, the law holds well at room and higher temperature. The law is of no use at very low temperature. Thus, at low temperature, the quantum theory should be used. Einstein was the first who took into account this discrepancy in 1907.

3.6.2 The Einstein Model

Einstein developed the ideas of the Plank (1900) quantum theory of black radiation). In accordance with that theory, the energy of an oscillator of frequency $\nu = (\omega/2\pi)$ is:

$$E_n = n\hbar\omega, \quad n = 0, 1, 2, 3, \dots \quad (3.113)$$

Probability of n-state:

$$g_n = \exp(-E_n/k_B T). \quad (3.114)$$

The average energy in the state of heat equilibrium:

$$\begin{aligned} \langle E \rangle &= \frac{\sum_{n=0}^{\infty} E_n \exp(-E_n/k_B T)}{\sum_{n=0}^{\infty} \exp(-E_n/k_B T)} = \\ &= \frac{\hbar\omega (e^{-\hbar\omega/k_B T} + 2e^{-2\hbar\omega/k_B T} + \dots)}{1 + e^{-\hbar\omega/k_B T} + e^{-2\hbar\omega/k_B T} + \dots} \end{aligned} \quad (3.115)$$

Introduce a variable $x = -\hbar\omega/(k_B T)$. The simple transformations lead to:

$$\langle E \rangle = \hbar\omega \frac{d}{dx} \ln(1 + e^x + e^{2x^2} + \dots) = \hbar\omega \frac{d}{dx} \ln \frac{1}{1 - e^x} = \frac{\hbar\omega}{e^x - 1} \quad (3.116)$$

Thus,:

$$\langle E \rangle = \frac{\hbar\omega}{e^{-\hbar\omega/k_B T} - 1} \quad (3.117)$$

The allowed energy of a quantum oscillator [7] are: $E_n = (n + 1/2)\hbar\omega$. The additional energy of each mode $1/2(\hbar\omega)$ is the energy of zero oscillations. That energy does not depend on the temperature and does not affect the heat capacity. The energy $\langle E \rangle$ tends to the classic limit $k_B T$ at the temperature higher then $(\hbar\omega/(k_B))$, but decreases essentially faster than $k_B T$ at low temperature.

The total oscillation energy of a solid with N atoms and $3N$ oscillation modes of the identical frequencies is:

$$U = \frac{3N\hbar\omega}{e^{-\hbar\omega/k_B T} - 1} \quad (3.118)$$

The volume heat capacity:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 3Nk_B F_E(\omega, T), \quad (3.119)$$

F_E - the Einstein function:

$$F_E(\omega, T) = \frac{(\hbar\omega/k_B T)^2 \exp(\hbar\omega/k_B T)}{[\exp(\hbar\omega/k_B T) - 1]^2} \quad (3.120)$$

1). The high temperature: $k_B T \gg \hbar\omega$.

$$[\exp(\hbar\omega/k_B T) - 1]^2 = \left(1 + \frac{\hbar\omega}{k_B T} + \dots - 1 \right)^2 \approx \left(\frac{\hbar\omega}{k_B T} \right)^2 \exp(\hbar\omega/k_B T) \rightarrow 1,$$

The function tends to 1 at high temperature. It leads to a classical result i.e. to the Dulong and Petit law [see (3.112)].

1). Lows temperature $k_B T \ll \hbar\omega$.

At temperature below $T_E = (\hbar\omega/k_B)$ (the Einstein characteristic temperature) the function F_E diminishes exponentially and the heat capacity equation has the form:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 3Nk_B \left(\frac{\hbar\omega}{k_B T} \right)^2 e^{-\hbar\omega/(k_B T)}, \quad (3.121)$$

The Einstein model explains the sharp decrease of heat capacity at low temperature if the frequency is chosen properly.

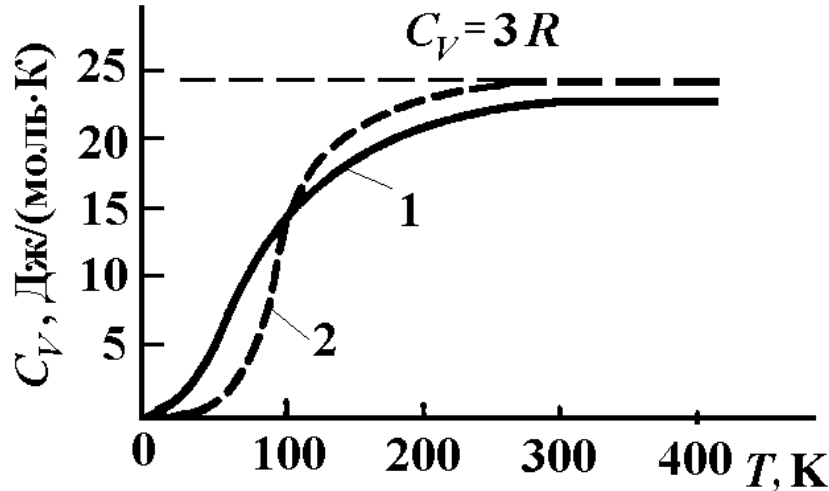


Fig.3.28 The heat capacity as function of temperature: 1-exoerimental data, 2-Einstein model.

The characteristic temperature can be find from relation $TE = k_B T_E$. If $\omega_E = 2 \cdot 10^{13} \text{ c}^{-1}$ $T_E = 150 \text{ K}$. T_E depends on the properties of a substance. вещества. Indeed, the oscillator frequency can be represented as $\omega = \omega_{\max} = (\beta/M)^{1/2}$. Thus, the greater the force constant β , the higher frequency ω_E and the Einstein temperature. At $T \ll T_E$ the quantum assumptions are needed. In Einstein model it is supposed that the quantum oscillators are independent and their frequencies are identical. It leads to the fact that the heat capacity decreases more rapidly than in reality (Fig.3.28). Experiments show that at low temperature, the heat capacity is proportional to T^3 .

Debye introduced the other model. The results of that model coincide with the experimental ones very well in the region of low temperatures.

3.6.3 The Debye Model.

Debye supposed that in a crystal there are $3N$ different oscillation modes. The energy of each mode is given by equation (3.117). The total heat energy of a crystal is:

$$U = \int \frac{\hbar\omega}{e^{-\hbar\omega/k_B T} - 1} dN, \quad (3.122)$$

dN – the number of normal oscillations in the interval from k up to dk and integration is performed through entire Brillouin zone. To determine dN in k space, consider a spherical layer (Fig.3.29). Its volume is:

$$dV_{cl.} \approx 4\pi k^2 dk. \quad (3.123)$$

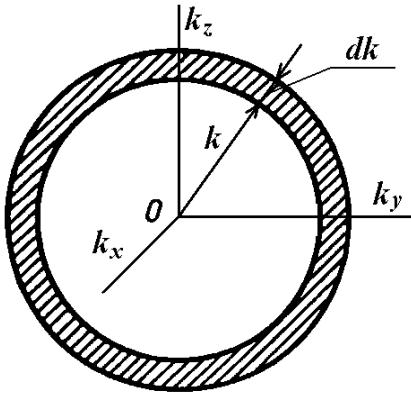


Fig.3.29 Spherical layer in k-space

Let us subdivide that layer by the elementary cells. Each cell corresponds to an allowed wave number k . The volume density of the cells is $V/(4\pi)^3$, ($V = N_1\mathbf{a} + N_2\mathbf{b} + N_3\mathbf{c}$ – the crystal volume).

It follows that in k space, each allowed wave number corresponds to a cell with the volume:

$$dV = dk_x \cdot dk_y \cdot dk_z = \frac{2\pi}{N_1 a} + \frac{2\pi}{N_2 b} + \frac{2\pi}{N_3 c} = \frac{(2\pi)^3}{V}. \quad (3.124)$$

In an acoustic branch, the number of the cells per unit volume is:

$$dN = \frac{dV_{cl.}}{dV} = \frac{4\pi V k^2 dk}{8(\pi)^3} = \frac{V k^2 dk}{2\pi^2}. \quad (3.125)$$

Assume that the sonic speed does not depend on wavelength and the polarization orientation. Thus, for all three acoustic branches, the linear dispersion law is true:

$$\omega(\mathbf{k}, s) = v_s^{3g} k \quad (s = 1, 2, 3), \quad (3.126)$$

v_s^{3g} - sonic speed. Then:

$$k^2 dk = \frac{1}{(v_s^{3g})^3} \omega^2 d\omega \quad (3.127)$$

Hence, the number of normal oscillators in the interval $d\omega$:

$$dN = \frac{V}{2\pi^2} \frac{1}{(v_s^{3g})^3} \omega^2 d\omega \quad (3.128)$$

The number of normal modes corresponding to a unit frequency interval and unit volume is determined as follows:

$$\frac{dN}{V d\omega} = \frac{1}{2\pi^2 (v_s^{3g})^3} \omega^2 = \rho(\omega) \quad (3.129)$$

In a solid, three types of acoustic waves can be present: a longitudinal with the speed v_l , and two transversal with the speed v_t . The density of the resultant mode is the sum of the separate mode densities. Thus, the spectral distribution function in interval $d\omega$ is described by an equation:

$$g(\omega) = \frac{\omega^2}{2\pi^2 v_l^3} + \frac{2\omega^2}{2\pi^2 v_t^3} = \frac{3\omega^2}{2\pi^2 v_s^3} \quad (3.130)$$

The quantity v_s is the sonic speed (averaged by crystallographic axes and oscillation modes):

$$\frac{1}{v_s^3} = \frac{1}{3} \left[\frac{1}{v_l^3} + \frac{2}{v_t^3} \right]. \quad (3.131)$$

Thus, the total heat energy of a crystal can be written as:

$$\int_0^{\omega_D = v_s k_D} Vg(\omega) \frac{\hbar\omega}{e^{-\hbar\omega/k_B T} - 1} d\omega, \quad (3.132)$$

In Eq. (3.122), the integration through the first Brillouin zone is substituted by integration through the sphere with the radius k_D chosen in such way that the sphere would include just N allowed wave vectors k . Hence,

$$\frac{4\pi}{3} k_D^3 = N \frac{(2\pi)^3}{V}. \quad (3.133)$$

And:

$$k_D = \left(6\pi^2 N/V \right)^{1/3}. \quad (3.134)$$

If $N/V = 10^{23} \text{ cm}^{-3}$, then $k_D = 2 \cdot 10^8 \text{ cm}^{-1}$. That quantity is of the same order as, the size of a Brillouin zone. The minimal wavelength $\lambda = 2\pi/k_D = 3 \cdot 10^{-8} \text{ cm}$ is of the same order as the period (a) of a crystalline lattice. The waves can not propagate through the lattice if $\lambda < 2a$, and the maximal or the Debye oscillation frequency is:

$$\omega_D = v_s k_D \approx 7 \cdot 10^{13} \text{ c}^{-1}. \quad (3.135)$$

The spectral distribution function is:

$$g(\omega) = \frac{3\omega^2}{2\pi^2 v_s^3} = A\omega^2 \quad (3.136)$$

By integration, we get:

$$\int_0^{\omega_{\max}} g(\omega) d\omega = 3N. \quad (3.137)$$

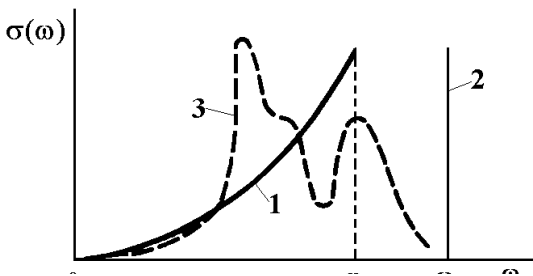


Fig.3.30 Density of states $g(\omega)$: 1 – Debye;; 2 – Einstein; 3 –experimental data

The Einstein and Debye approximations are shown in Fig.3.30.

For a given distribution function (3.136), Formula (3.122) can be written as follows:

$$U = \frac{3V\hbar}{2\pi^2 v_s^3} \int_0^{\omega_D} \frac{\omega^3 d\omega}{e^{-\hbar\omega/k_B T} - 1}, \quad (3.138)$$

Let us introduce designations:

$$x = \hbar\omega/(k_B T); \quad \Theta_D = \hbar\omega_D/k_B. \quad (3.139)$$

We can rewrite the equation (3.136) as:

$$U = \frac{3V\hbar}{2\pi^2 v_s^3} \left(\frac{k_B T}{\hbar} \right)^4 \int_0^{\Theta_D/T} \frac{x^3 dx}{e^x - 1}, \quad (3.140)$$

$$U = \frac{9Nk_B T}{(\Theta_D/T)^3} \int_0^{\Theta_D/T} \frac{x^3 dx}{e^x - 1} = 3Nk_B T D\left(\frac{\Theta_D}{T}\right). \quad (3.141)$$

The relation (3.141) is called the *Debye interpolation formula*, and $D(\Theta_D/T)$ is the *Debye function*. According to equation (3.141), the energy and heat capacity depends on a parameter Θ_D , which is called the characteristic temperature or the Debye temperature. It should be noted that the quantity $\Theta_D k_B = \hbar\omega_D$ represents the quantum of minimal energy, which can excite the lattice oscillations. Using equation (3.139) we get $\Theta_D \sim 100\text{K}$. The characteristic temperature depends on the properties of a solid. For the great number of solids, it is about 100—400 K, although it is anomaly high for beryllium ($\Theta_D = 1440\text{K}$) and diamond ($\Theta_D = 2230\text{K}$). It can be explained by the great rigidity of inter atomic bonds.

Let us discuss two approximations of Debye function.

High temperature: $\hbar\omega \ll k_B T$ или $x \ll 1$.

Decompose the denominator of equation (3.141) in series: $e^x - 1 \approx 1 + x = 1/x$. We can write:

$$U = 9Nk_B \Theta_D \left(\frac{T}{\Theta_D}\right)^4 \int_0^{\Theta_D/T} x^2 dx = 3Nk_B T = 3RT, \quad (3.142)$$

Hence, the heat capacity:

$$C_V = 3R \quad (3.143)$$

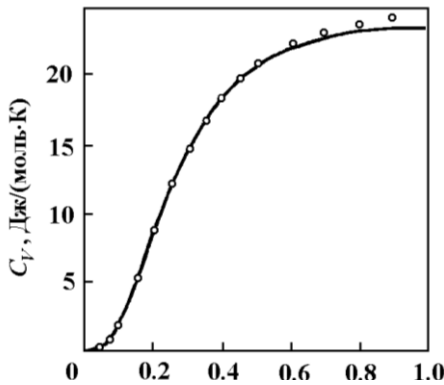


Fig.3.31 The temperature dependence of molar heat capacity of three-dimensional Debye model. The experimental data for yttrium are shown. The temperature scales is in the terms of the Debye temperature. $\Theta_D = 200\text{K}$.

I.e. the heat capacity does not depend on temperature and follows the Dulong and Petit law.

Low temperature: $\hbar\omega \ll k_B T$ or $x \ll 1$.

The upper integration limit of integral (3.141) can be submitted by ∞ .

$$\int_0^{\infty} \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15} \quad (3.144)$$

Thus, the energy of acoustic oscillations is:

$$U = \frac{3\pi^4 Nk_B \Theta_D}{15} \left(\frac{T}{\Theta_D}\right)^4. \quad (3.145)$$

According formula (3.144) at low temperature the potential energy U is proportional to T^4 .

Hence, at low temperature the heat capacity is proportional to (T^3) :

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{12\pi^4 Nk_B}{5\Theta_D^3} T^3 = \gamma_D T^3. \quad (3.146)$$

Experiments confirm that dependence (Fig.3.31).

At more high temperature ($T < \Theta_D$) there is no such agreement.

The modern numerical calculation by computers leads to results that well coincide with the experimental ones in entire range of temperature.