

9. Defects of a Crystalline Lattice and Diffusion in Solids

9.1 Classification of Defects

In real crystals there are defects, i.e. the violations of periodicity. These structural defects strongly affect the crystal properties: electric conductivity, stability, plasticity, photoelectric conductivity, luminescence, color and others.

The defects are subdivided in accordance with their geometry. Four classes of defects are known: the **point** or **atomic**, **linear**, **surface**, and **volume defects**.

Atoms of impurity, vacancies in crystal nodes, atoms displaced from normal position and like are called the point defects.

The shift of a great number of atoms from their normal position is called the linear defect.

The boundary of grains, mosaics, and twinning, an interface between the solid and liquid phase, the external surface of a crystal are called the surface defects.

When there are volume defects, the second phase is produced. In produced heterogeneous system, the second phase does not affect much structural properties of the mother phase, but the properties of the substance as a whole can be appreciatively changed.

Very often an atom displaced to the surface of a crystal and produced vacancy is called the **Schottky defect**. In crystals formed by the different sorts of atoms there can be several types of the Schottky defects with differ surrounding of the vacant node. Usually in binary compounds the defect concentrations of both components are the same. Thus, the Schottky defect is a pair of volume charges of opposite sign, which are not necessarily located near each other. The defects are observed in crystals with tight packing where formation of inter-node atoms is performed with great difficulty. The generation of the Schottky defects increases the crystal volume. These defects dominate in alkaline-haloid crystals.

An atom displaced from the node to the crystal surface is called the **inter-node atom**. If an atom is displaced from a node (the vacancy is formed) to the inter-atomic place inside the crystal the pair defect is generated too. That defect is called the **Frenkel defect**. Those defects have been thoroughly investigated. The Frenkel defects are easily generated in crystals when the distance between atoms is great.

The generation of defects is shown in Fig9.1. The vacancies and inter-node atoms can move through a crystal.

The point defects can be in thermodynamic equilibrium at room temperature. The linear and surface defects are metastable. Thus it is possible to produce a crystal without linear and surface defects (not taking into account the external surface) but the point defects are present always.

Defects affect the structure. They interact with each other and form associations. For example, the vacancies can build pairs or even bigger complexes. The inner dislocations unite with the edge dislocations building steps along the dislocation line. The impurity atoms and vacancies form the impurity 'atmosphere' around dislocations. Impurities strongly affect the electric, magnetic, optic, thermal, and mechanic properties. Even more, the equilibrium concentration of intrinsic defects depends on that one of impurities.

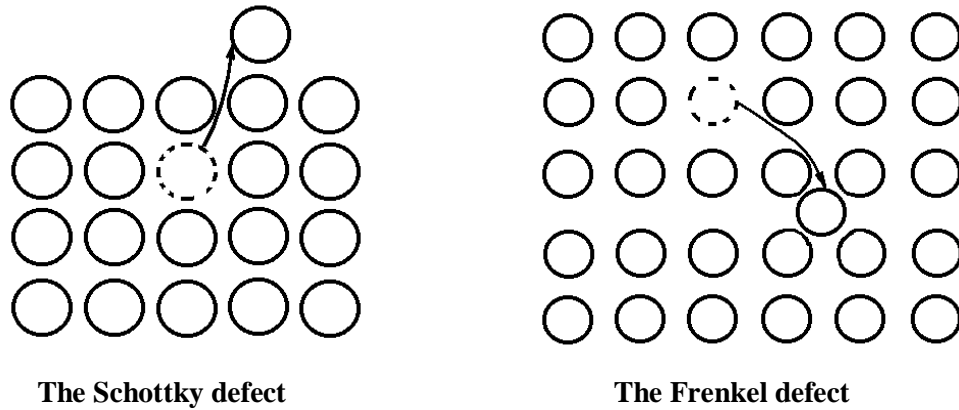


Fig.9.1. Thermal defects in crystals

9.2 Point Defects in the Equilibrium State

Assume that generation of point defects is an equilibrium process. In an equilibrium state, the free energy of a system is minimal.

The process performs at constant pressure and the Gibbs potential is to be used:

$$G = H - TS \quad (9.1)$$

The quantity H is enthalpy. S is entropy. It is known that [5]:

$$S = k_B \ln P \quad (9.2)$$

The quantity k_B is the Boltzmann constant, P is a thermodynamic probability. Thermodynamic probability is a number of possibilities by which the system can be build. That kind of entropy is called (in the theory of defects) the **configuration entropy** because it describes the redistribution of lattice atoms.

Assume that atoms (N) of a crystal occupy all the nodes. While heating, a small (in comparison with N) number of atoms (n) displace on to the external side of the crystal. Thus n new nodes and vacancies are formed. The number of unlike combinations to distribute the atoms into $(N + n)$ nodes:

$$P = \frac{(N + n)!}{N!n!} \quad (9.3)$$

In accordance with the Stirling formula:

$$\ln N! \approx N \ln N - N \quad (9.4)$$

It follows from (9.4):

$$\ln P = (N + n) \ln(N + n) - N \ln N - n \ln n \quad (9.5)$$

Assume that the number of vacancies n ($n < N$) is the only variable and the quantity E_{Sh} is the enthalpy increment when one vacation is produced, then for all vacancies: $H = nE_{Sh}$. The Gibbs potential:

$$G = nE_{Sh} - k_B T [N \ln(N + n) + n \ln(N + n) - N \ln N - n \ln n] \quad (9.6)$$

The equilibrium condition:

$$\left(\frac{\partial G}{\partial n}\right)_{T=const.} = 0 \quad (9.7)$$

Differentiating (9.6):

$$E_{Sh} - k_B T \ln \frac{N+n}{n} = 0. \quad (9.8)$$

Having in mind that $n \ll N$:

$$n = N \exp\left(-\frac{E_{Sh}}{k_B T}\right). \quad (9.9)$$

For copper the activation energy $E_{Sh} \sim 1,6 \cdot 10^{-19}$ jole. At temperature of 1000 K:

$$\frac{n}{N} = \exp\left(-\frac{E_{Sh}}{k_B T}\right) \approx 10^{-5}.$$

In binary compounds when cation and anion vacancies are formed in pairs, a crystal is electrically neutral:

$$P = \frac{(N+n)!}{N!n!} \cdot \frac{(N+n)!}{N!n!} \quad (9.10)$$

It corresponds the Schottky model. Following the mentioned procedure:

$$E_S - 2k_B T \ln \frac{N+n}{n} = 0, \quad (9.11)$$

E_S is the pair vacancy enthalpy. Hence:

$$n = N \exp\left(-\frac{E_S}{2k_B T}\right). \quad (9.12)$$

Let us use the Frenkel model. Assume that there are N nodes. A certain quantity of atoms (n) leave their nodes and occupy the (N') places between the nodes. The number of possibilities for n vacancies to be distributed into N nodes:

$$P = \frac{N!}{(N-n)!n!}. \quad (9.13)$$

The number of possibilities for n vacancies to be distributed into N' inter-nodes:

$$P = \frac{N'!}{(N'-n)!n!}. \quad (9.14)$$

The configuration entropy increment:

$$S = k_B \left[\ln \frac{N!}{(N-n)!n!} + \ln \frac{N'!}{(N'-n)!n!} \right] \quad (9.15)$$

Applying the Stirling formula:

$$S = k_B [N \ln N - (N-n) \ln(N-n) - n \ln n] + k_B [N' \ln N' - (N'-n) \ln(N'-n) - n \ln n] \quad (9.16)$$

If the enthalpy of a Frenkel defect is E_Φ , $H = n E_\Phi$. Following the standard procedure we get:

$$E_\Phi - k_B T \ln \left(\frac{N-n}{n} \cdot \frac{N'-n}{n} \right) = 0, \quad (9.17)$$

Having in mind that $n \ll N$ and $n \ll N'$ the number of Frenkel pairs:

$$n = \sqrt{NN'} \exp\left(-\frac{E_\Phi}{2k_B T}\right). \quad (9.18)$$

Discussing the both types of defects, we have not taken into account the oscillation frequency change caused by vacancies and inter-node atoms, which distort the crystalline structure. To take that circumstance into account, a **thermal entropy** S_T is of use. That quantity characterizes the number of ways to distribute the energy between the frequencies.

When there are z closest neighbors near a vacancy, a number of oscillators ($3nz$) with frequency $\nu' < \nu$ and $(3N - 3nz)$ with frequency ν are generated. The calculation leads to:

$$S_T = 3k_B z \ln\left(\frac{\nu}{\nu'}\right) \quad (9.19)$$

In accordance with the standard procedure, the Schottky defect concentration:

$$n = N\left(\frac{\nu}{\nu'}\right)^{3z} \exp\left(-\frac{E_S}{k_B T}\right). \quad (9.20)$$

The Frenkel defect concentration:

$$n = \sqrt{NN'}\left(\frac{\nu}{\nu'}\right)^{3z} \exp\left(-\frac{E_F}{2k_B T}\right). \quad (9.21)$$

For NaCl, the quantity $(\nu/\nu')^{3z} \approx 64$.

When the vacation concentration is great, the associations of two, three, and more vacancies are built. Cavities can be formed. The energy of vacancy complexes is always less than the energy of isolated vacancies. For example the energy of a binary vacancy:

$$E_{2V} = 2E_V - E_c, \quad (9.21)$$

The quantity E_c is the bond energy. E_V is the energy needed to build up a vacancy.

In real crystals there are impurities. The complex defect-impurity can be produced. Its production depends on defect and impurity concentration. The concentration of vacancy-impurity atom complex (in equilibrium state):

$$\frac{C}{I_0 - C} = zV \exp\left(-\frac{E_c}{k_B T}\right). \quad (9.22)$$

The quantity C and I_0 is the concentration of complex and impurity (in atomic units), z – coordination number of impurity, E_c – the bond energy between the vacancy and impurity atom, V – the relative concentration of vacancies.

We can expect the vacancies are attracted to the constriction zones and intr-node atoms are attracted to lengthening zones. The theory of defect-impurity interaction is very complicated.

9.3. Diffusion

The Fick laws describe the phenomenon. Assume that component concentration of a binary alloy is not uniform. C is the impurity concentration, which depends on time and space. The diffusion flux is produced.

The first Fick law states that the diffusion flux is proportional to the concentration gradient:

$$J_1 = -D_1 \frac{\partial C}{\partial x_1}, \quad (9.23)$$

The quantity D_1 is called the **diffusion coefficient**. The sign ‘minus’ in (9.23) means that the direction of the flux is opposite the gradient. It was observed that the flux in a given direction is proportional to gradients along other directions (the generalized Fick law):

$$J_1 = -D_{11} \frac{\partial C}{\partial x_1} - D_{12} \frac{\partial C}{\partial x_2} - D_{13} \frac{\partial C}{\partial x_3}. \quad (9.24)$$

$$J_2 = -D_{21} \frac{\partial C}{\partial x_1} - D_{22} \frac{\partial C}{\partial x_2} - D_{23} \frac{\partial C}{\partial x_3}, \quad (9.25)$$

$$J_3 = -D_{31} \frac{\partial C}{\partial x_1} - D_{32} \frac{\partial C}{\partial x_2} - D_{33} \frac{\partial C}{\partial x_3}. \quad (9.26)$$

The quantity D_{ij} is a flux in (i)-direction produced by the (j)-component of gradient.

Introducing three ort \mathbf{i}_1 , \mathbf{i}_2 , and \mathbf{i}_3 , the density flux:

$$\mathbf{J} = J_1 \mathbf{i}_1 + J_2 \mathbf{i}_2 + J_3 \mathbf{i}_3. \quad (9.27)$$

The analysis shows that the quantities D_{ij} are components of a tensor of the second rank:

$$\mathbf{D} = \begin{pmatrix} D_{11} & D_{12} & D_{13} \\ D_{21} & D_{22} & D_{23} \\ D_{31} & D_{32} & D_{33} \end{pmatrix}. \quad (9.28)$$

Thus the Fick law:

$$\mathbf{J} = -\mathbf{D} \cdot \nabla C. \quad (9.29)$$

The second Fick law can be deduced from the first one. The continuity equation:

$$\frac{\partial C}{\partial t} + \nabla \cdot \mathbf{J} = 0. \quad (9.30)$$

The equation states that the mass increment in s given volume is due to the fluxes of mass entering and leaving that volume.

Introducing (9.29) into (9.30) we arrive to the second Fick law:

$$\frac{\partial C}{\partial t} = \nabla \cdot \mathbf{D} \cdot \nabla C. \quad (9.31)$$

In scalar terms, equation (9.31) is written as follows:

$$\begin{aligned} \frac{\partial C}{\partial t} = & D_{11} \frac{\partial^2 C}{\partial x_1^2} + D_{12} \frac{\partial^2 C}{\partial x_1 \partial x_2} + D_{13} \frac{\partial^2 C}{\partial x_1 \partial x_3} + D_{21} \frac{\partial^2 C}{\partial x_2 \partial x_1} + D_{22} \frac{\partial^2 C}{\partial x_2^2} + D_{23} \frac{\partial^2 C}{\partial x_2 \partial x_3} + \\ & + D_{31} \frac{\partial^2 C}{\partial x_3 \partial x_1} + D_{32} \frac{\partial^2 C}{\partial x_3 \partial x_2} + D_{33} \frac{\partial^2 C}{\partial x_3^2} \end{aligned} \quad (9.32)$$

We can choose a coordinate system in which the tensor is diagonal:

$$\mathbf{D} = \begin{pmatrix} D_1 & 0 & 0 \\ 0 & D_2 & 0 \\ 0 & 0 & D_3 \end{pmatrix}. \quad (9.33)$$

The quantity D_1 , D_2 , and D_3 are called the **principal diffusion coefficients**. The axes of the coordinate system are called the **principal axes of the diffusion tensor**.

In isotropic cubic structures $D_1 = D_2 = D_3$. The diffusion laws are:

$$\mathbf{J} = -D \cdot \nabla C, \quad (9.34)$$

$$\frac{\partial C}{\partial t} = D \nabla^2 C. \quad (9.35)$$

The temperature dependence of diffusion coefficient very often is:

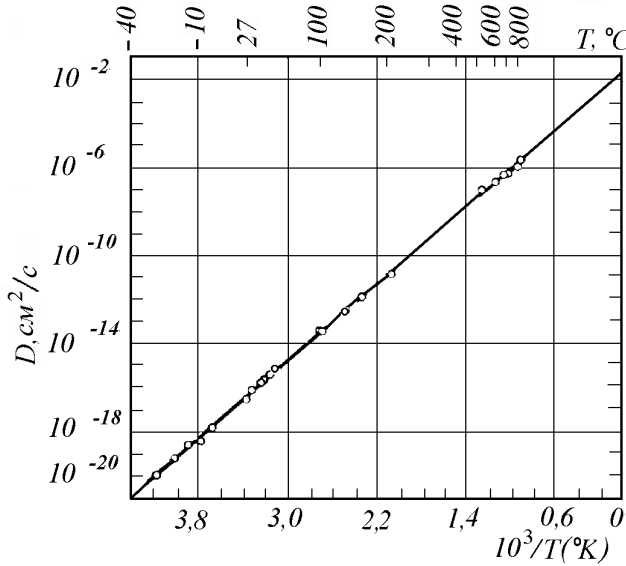


Fig.9.2. The temperature dependence of diffusion coefficient of carbon in α - iron

$$D = D_0 \exp(-E/k_B T). \quad (9.36)$$

The quantity E is the activation energy. The experimental data of diffusion of carbon in α -iron ($E=0.87$ eV, $D_0=0.020$ cm²/c) are shown in Fig.9.2. .

To diffuse, an atom has to pass the potential barrier produced by its closest neighbors. Let us discuss diffusion of impurity atoms through inter-nodes. The result could be applied while discussing the diffusion of holes. If the barrier height is E , the probability of penetration through the barrier is proportional to $\exp(-E/k_B T)$.

The probability per second

$$P \approx \nu \exp(-E/k_B T). \quad (9.37)$$

The quantity v (about 10^{14}) is a number of strokes onto barrier per second (frequency).

Let us imagine two parallel planes filled with impurity atoms located in inter-node positions. The distance between the planes designate by 'a'. The number of atoms in one plane is S . The number of atoms in the other plane $S + a \frac{dS}{dx}$. The atomic flux per second $\approx -pa \frac{dS}{dx}$. If N is the impurity concentration, then $S = aN$ atoms/cm². The diffusion flux density:

$$J_N \approx -pa^2 \frac{dN}{dx}. \quad (9.38)$$

Comparing (9.38) and (9.34) and having in mind (9.37) we get

$$D = va^2 \exp(-E/k_B T). \quad (9.39)$$

Thus: $D_0 = va^2$.

Using the equation $k_B T \mu = qD$ we find the ion mobility and conductivity:

$$\mu = (qva^2 / k_B T) \exp(-E/k_B T), \quad (9.40)$$

$$\sigma = Nq\mu = (Nq^2 va^2 / k_B T) \exp(-E/k_B T). \quad (9.41)$$

N is the impurity ion concentration (the charge q).

When the two valence metallic ions dominate the number of vacancies, the relative quantity of vacancies does not depend on temperature. The derivative of the dependence of $\ln \sigma$ on $1/k_B T$ determines the activation energy (E_+) needed for positive ion vacancies to overcome the potential barrier. At room temperature about one vacancy overcomes the barrier per second. At 100 °K, that quantity diminishes to 10^{-25} .

When the heat generation of defects dominates the relative number of vacancies:

$$f \approx \exp(-E_f / k_B T). \quad (9.42)$$

E_f is the activation energy of the vacancy pair. The derivative [in accordance with (9.40) and (9.42)] is $E_+ + E_f / 2$.

The direct measurement of the diffusion coefficient can be made by the radioactive indicator method. To do it, it is necessary to find the variation of the initial time-space radioactive ion distribution. The found quantities can be compared with those ones from ion conductivity measurements. The data of the two types of measurements do not coincide. May be it is due to some diffusion mechanism, which is not associated with the electric charge transportation. The diffusion of vacancies of the opposite sign and two valence ion-vacancy complexes may be the cause.

While investigating the vacancy diffusion, the diffusion coefficients measured by two mentioned methods must differ a little.

The diffusion coefficient of radioactive atoms is smaller then that one of vacancies. Let us imagine that a radioactive atom passed the barrier (forward) and occupied the vacancy. The vacancy is 'behind' the atom. There is a probability that atom can 'jump' back and populate the vacant node.

Diffusion of basic atoms of a substance is called the **self-diffusion**. The activation energy needed to initiate that process in copper according to calculation of Handingtone is 2.4 – 2.7eV (along vacancies) and 5.1 – 6.4eV (along inter-nodes). The experimental data are 1.7 – 2.1eV.

Thus the migration energy of metals is about 1eV, and the effective frequency is about 10^{13} c^{-1} . At temperature 1000K the number of jumps is about 10^8 per second. That quantity rapidly decreases with temperature.

9.4 The diffusion coefficient

Таблица 9.1.

Metal	$D_0,$ cm^2/c	$E,$ cal/mol	$D_0,$ cm^2/c	$E,$ cal/mol
Aluminum	0,035	28750	Niobium	1,1
Chrome	0.20	73700	Palladium	0,21
Cobalt	0,83	67700	Platinum	0,33
Copper	0,62	49560	Potassium	0,31
Germanium	7,8	68500	Silicon	1,800
Gold	0,091	41700	Silver	0,44
α -Iron	2,0	57300	Sodium	0,145
Lead	1,37	26060	Tantalum	0,124
Lithium	0,39	13490	β -Thallium	0,7
Molybdenum	0,1	92200	A-Thorium	1.2
Nickel	1,9	68000	Tungsten	42,8

There are the following formulas:

$$D_I = \frac{1}{6} v_I r_I^2 e^{-\left(E_I^m + PV_I^m\right)/kT}, \quad (9.43)$$

$$D_V = \frac{1}{6} v_V r_V^2 e^{-\left(E_V^m + PV_V^m\right)/kT}, \quad (9.44)$$

$$D_S = \frac{1}{6} v_V f r_V^2 e^{-\left(E_V^m + PV_V^m\right)/kT} C_V, \quad (9.45)$$

Atomic concentration of vacancies:

$$C_V = e^{-\left(E_V^f + PV_V^f\right)/kT}. \quad (9.46)$$

Thus, the equation (9.43) – (9.54) can be written as follows:

$$D = D_0 e^{-\left(E + PV^*\right)/kT}, \quad (9.47)$$

The inter-node diffusion:

$$\begin{aligned} D_0 &= \frac{1}{6} v_I r_I^2, \\ E &= E_I^m, \\ V^* &= V_I^m. \end{aligned} \quad (9.48)$$

Vacancy diffusion:

$$\begin{aligned}
 D_0 &= \frac{1}{6} v_v r_L^2, \\
 E &= E_v^m, \\
 V^* &= V_v^m.
 \end{aligned}
 \tag{9.49}$$

Self-diffusion:

$$\begin{aligned}
 D_0 &= \frac{1}{6} v_I f r_I^2, \\
 E &= E_v^m + E_v^f, \\
 V^* &= V_v^m + V_v^f.
 \end{aligned}
 \tag{9.50}$$

The quantity D_I , D_v , and D_s are the coefficients of diffusion through inter-nodes, vacancies and intrinsic atoms; v is the frequency; r_I , r_L the distance between inter-nodes and the distance between atoms; V_I , V_v are the migration volumes of an inter-node atom and vacancy; P is the pressure. The formula (9.50) are of success.

9.5. Surface Defects

An **inter-grain boundary** is a region between two neighbor grains of different space orientation. Five parameters are needed to characterize the orientation of grains. Three of them give position of the second grain relative the first crystal; two parameters describe the orientation of the boundary plane.

Imagine two simple cubic crystals with a common axis [001].

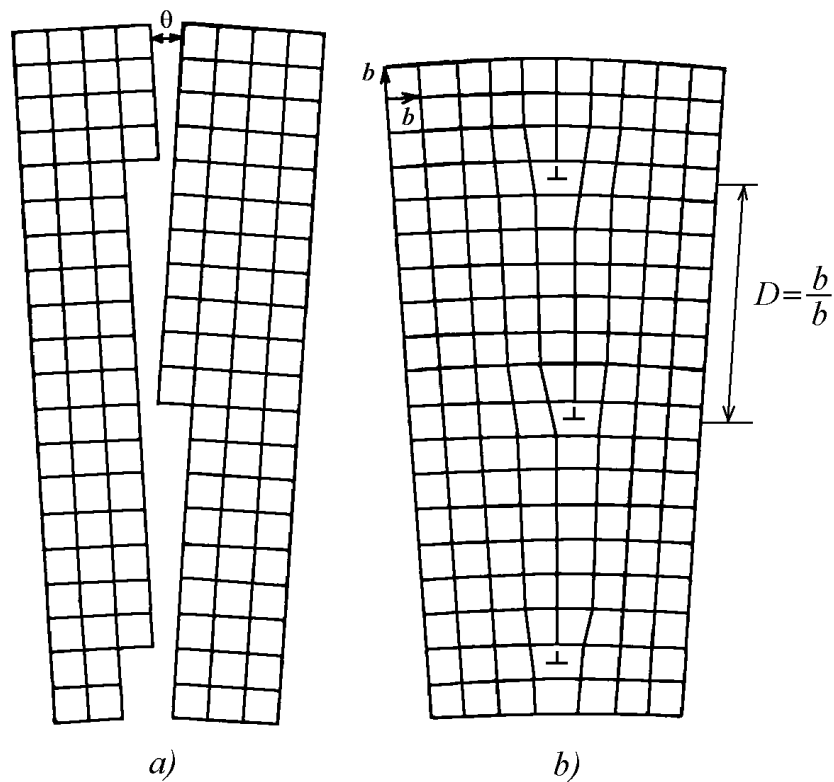


Fig.9.3. The dislocation structure of the boundary between crystals

The grains are shifted at angle θ relative each other (Fig.9.3). The boundary surface is the plane of symmetry. The boundary is called the **simple** or **inclined boundary**. When two disoriented grains are brought together a binary crystal is build. In boundary region there are two defects: displacement of atoms from their usual positions (Fig.9.3a) and the elastic deformation (Fig.9.3b).

The boundary atoms can not provide the smooth conjugation of disoriented atomic structures. Thus, certain atomic planes do not pass through entire crystal, but end at the grain boundary and form the **linear dislocations**. The distance D between dislocations is given by:

$$\frac{b}{D} = 2 \sin \frac{\theta}{2} \approx \theta \quad (9.51)$$

The dislocation theory proves that: the row of dislocations is the only way to unite grains; dislocations are linear and parallel to the common axis. Their Burgers vectors are of [100] type

The energy of elastic deformation per an unit square of the boundary surface:

$$E = E_0 \theta (A - \ln \theta), \quad (9.52)$$

The quantity A is a constant, the quantity E_0 depends on the dislocation type. For the simple inclined boundary:

$$E = \frac{Gb}{4\pi(1-\gamma)}; \quad A = \frac{4\pi(1-\gamma)B}{Gb^2}, \quad (9.53)$$

G is a shear module, γ is the Poisson ratio, B is a constant characterizing the energy of the dislocation nucleus.

Dependence of inclined boundary energy on the angle between the grains is shown in Fig.9.4.

The dislocation boundary strain field is the superposition of separate dislocation strain fields. The borders attract the impurity atoms and point defects, thus they are places of accumulation of impurities and defects. The surface concentration of impurity atoms at the boundary is about 10^{14} cm^{-2} . Thus we can speak about the preferable segregation of impurities along the inter-grain border. Those borders are the places of sharp changing of all properties of crystals.

Twinning. When the condition for sliding does not hold the plastic deformation performs by twinning. Twinning is a special shearing when two parts of a crystals

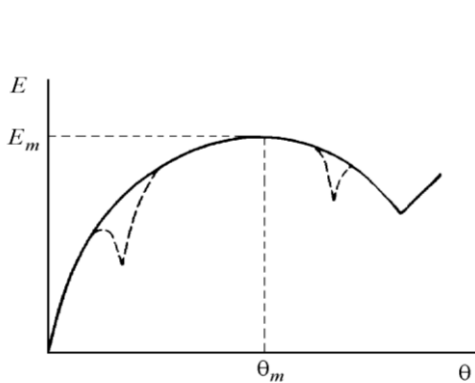


Fig.9.4 The bound energy as function of the shift angle

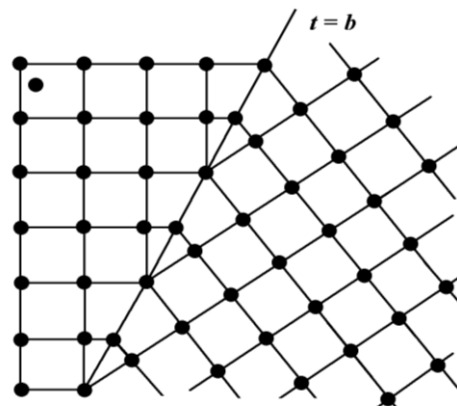


Fig.9.5. Twinning

become the mirror reflection of each other relative the border (the **twinning plane**). If a crystallographic plane is a plane of twinning, it is called the **coherent twinning border** (Fig.9.5).

The free surface energy of the coherent twinning border is very small in comparison with that quantity of others boundaries. While growing, the crystalline conglomerates are often formed. The conglomerates build of two or more crystals are called the twins. In twins, one crystalline aggregate is either turned relative the other at the angle of 180° or is a mirror reflection of the other.

In a diamond structure, the plane $\{111\}$ is the only coherent twinning border. In germanium, the twins are very thin plates formed spontaneously while uncontrolled crystallization from an overcooled liquid. It is used in the process of fast growing of dendrites.