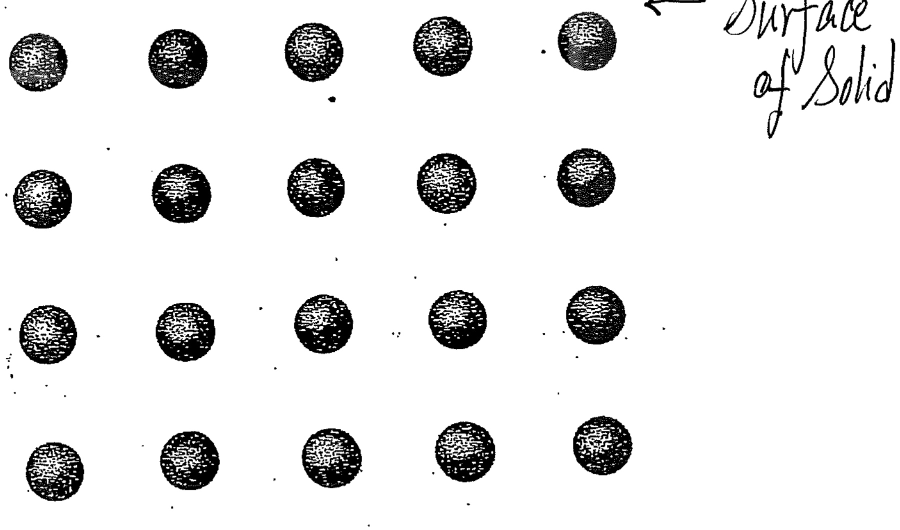
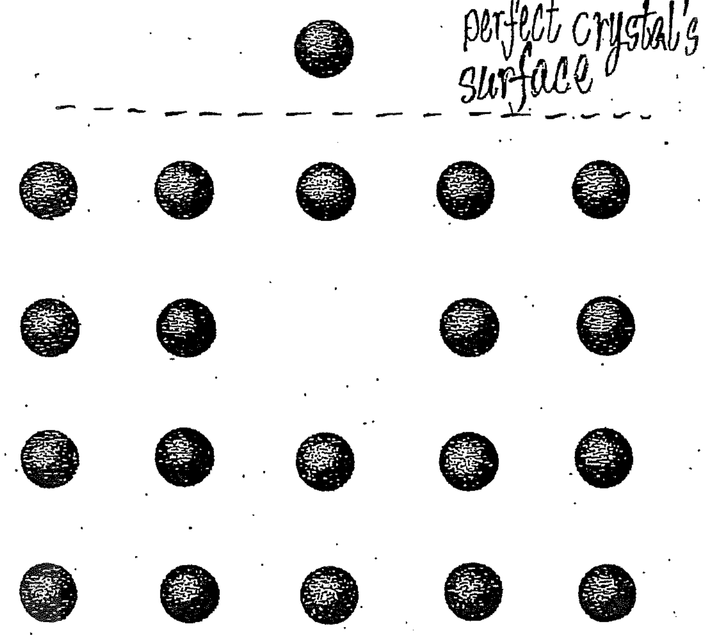
Number of Defects thermally generated in a solid

T = 0, Atoms sit still





T ≠ 0, many things could happen!
Atoms vibrate, some atoms moved out of its site to intersitial sites, some migrate to the surface, ...

Schottky (1935) defects

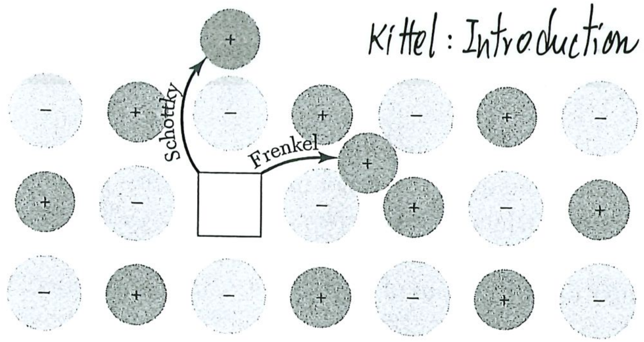
- Atoms moved, left vacancies
- "point defects"

Other types of defects

Schottky defects

Frenkel defects

Kittel: Introduction to Solid State Physics



Schottky and Frenkel defects in an ionic crystal. The arrows indicate the displacement of the ions. In a Schottky defect the ion ends up on the surface of the crystal; in a Frenkel defect the ion is removed to an interstitial position.

$n(T)$ = # $\underbrace{\text{Schottky defects}}_{\text{easy to treat}}$ at temperature T in a solid of N atoms

Think like a physicist

kT must be competing with $\underbrace{\text{some energy}}$ of the problem

ε = energy needed to create one defect [it is about $\underbrace{1\,eV}_{\text{quite high in solid state physics}}$]

$$\boxed{\begin{array}{l}\underline{\text{Common Sense}}\\ kT_{room} \approx \frac{1}{40}\,eV \simeq 0.025\,eV\end{array}}$$

Apply Microcanonical Ensemble Approach

E = available energy to create defects = $n\varepsilon$ creating n defects out of N atoms

[we assume $n \ll N$, as justified by the result, but both n and N are $\gg 1$]

<u>Counting Problem</u>: Number of Microstates = # ways to move n atoms among N atoms to surface and leave vacanies

$$W(E(n),N) = {}_N C_n = \frac{N!}{n!\,(N-n)!} = \frac{N!}{\left(\frac{E}{\varepsilon}\right)!\left(N-\frac{E}{\varepsilon}\right)!} \qquad (B1)$$

<u>Use Boltzmann's Formula</u>

$$S(E,N) = k \ln W(E,N) = k \ln N! - k \ln\left(\frac{E}{\varepsilon}\right)! - k \ln\left(N-\frac{E}{\varepsilon}\right)!$$

Stirling Approx. and cancelling terms (Ex.)

$$= k\left[N\ln N - \left(\frac{E}{\varepsilon}\right)\ln\left(\frac{E}{\varepsilon}\right) - \left(N-\frac{E}{\varepsilon}\right)\ln\left(N-\frac{E}{\varepsilon}\right)\right] \qquad (B2)$$

Derivative of S gives $\frac{1}{T}$

$$\frac{1}{T} = \frac{\partial S}{\partial E} = -\frac{k}{\varepsilon}\ln\left(\frac{E}{\varepsilon}\right) - \cancel{\frac{k}{\varepsilon}} + \frac{k}{\varepsilon}\ln\left(N-\frac{E}{\varepsilon}\right) + \cancel{\frac{k}{\varepsilon}} = \frac{k}{\varepsilon}\ln\left[\frac{N-n}{n}\right] \quad (B3)$$

Extract result and physics:

$$n(T) = N \cdot \frac{1}{e^{\varepsilon/kT}+1}$$

$\varepsilon \sim 1\,eV$

$kT_{room} \sim \frac{1}{40}\,eV$ $\Big\rangle$ $e^{\frac{\varepsilon}{kT}} \sim e^{40} >> 1$

$$\boxed{n(T) \approx N e^{-\varepsilon/kT}} \quad (B4)$$

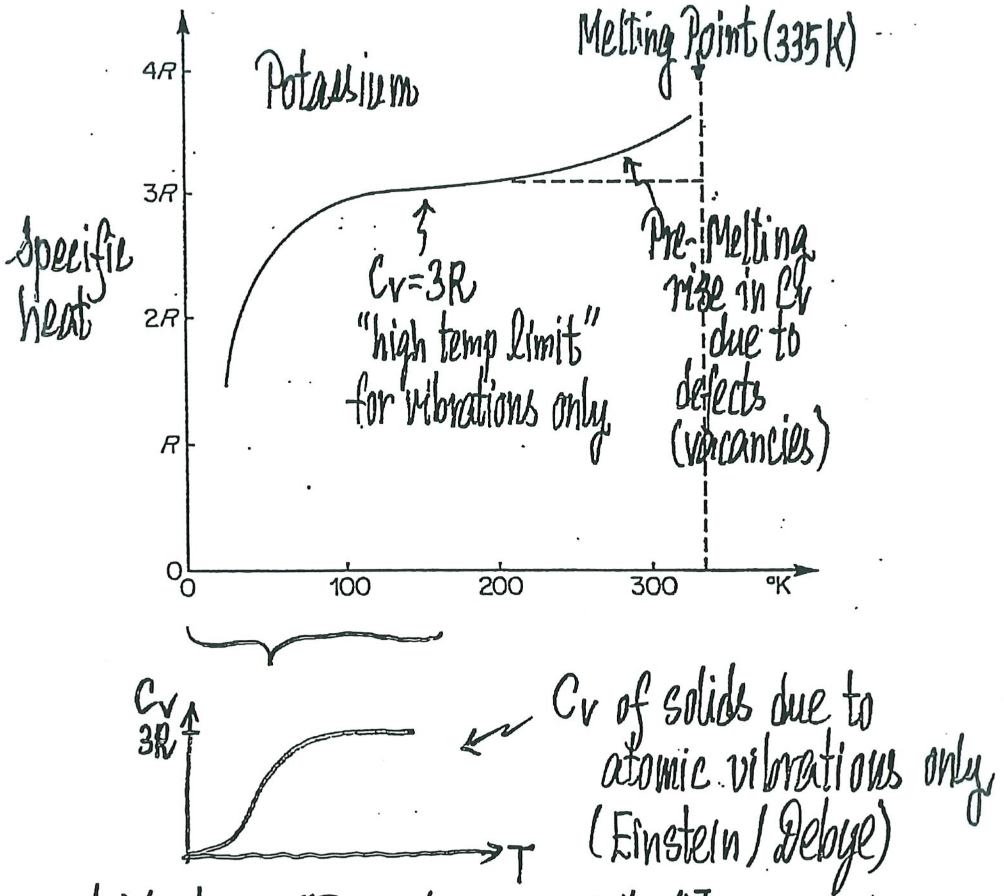
(hence $n \ll N$ at room temp)

gives (n/N) the defect concentration in a crystal which is in thermal equilibrium at temperature T

[$N \sim 10^{23}$ (cm^3 of solid), $n(T_{room}) \approx 10^5$; $n/N \sim 10^{-17}$]

$e^{-\varepsilon/kT}$ appears very often (Boltzmann factor), appears when there is an energy barrier ε to overcome

Observable Effect: Pre-melting behavior



[See Flowers and Mendoza, "Properties of Matter"]

T=0 crystal

T≠0 (low temp.) [before defects creation]
atoms vibrate [c.f. $C_V(T)$ of Einstein model]

T≠0 (higher)

$\underbrace{\text{Vibrations}} + \underbrace{\text{Vacanies}}_{}$ important in understanding melting

even for T ~ melting point,
amplitude ~10% lattice spacing

Remarks

- The Schottky defects problem is typical of "Two-level" systems

  Each atom has a choice of two levels of different energies

"upper"	ε	——	migrate to surface and create a vacancy
"lower"	0	——	sitting in equil. site

← energy spectrum for each atom (it is **bounded**+)

- Counting Problem means: n of N atoms are in upper level

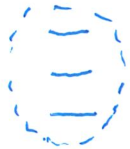
  How many ways are there?

List out: (#1 up, #2 low, #3 low, #4 up, ..., #N low) ← this is one microstate (with n "ups")

There are ${}_N C_n$ lists ← number of accessible microstates given $E = n\varepsilon$

+ Recall the oscillator problem has an unbounded spectrum for each oscillator

- Like other subjects in physics "2-level" systems are not so different from "3-level" systems

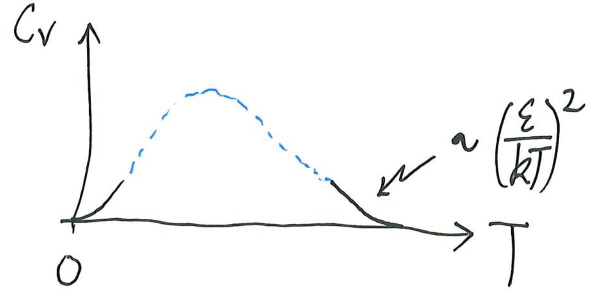
 ← both are bounded →  for each particle

But "2-level" systems behave differently from "unbounded" spectrum systems

e.g. Work out $C_V(T)$ of "2-level" systems

$$E = n\varepsilon = N\varepsilon\, e^{-\varepsilon/kT}$$

$$C_V = \frac{\partial E}{\partial T} = Nk\left(\frac{\varepsilon}{kT}\right)^2 e^{-\varepsilon/kT}$$



qualitatively different from $C_V(T)$ of oscillators