Lec 14: Crystal Plastic Deformation 1. : Point defects

Bibliography:

Assigned Reading:

[*Brady*, 1995]

General Diffusion References:

[*Ganguly*, 2002; *Lasaga*, 1998; *Shewmon*, 1963]

Intro: Deformation Mechanism Maps

As depth increases, pressure and temperature increase as well. Rate-dependent (creep, crytal-plastic, viscous) processes favored. Pressure dependent (brittle, frictional, dilatant) processes de-emphasized.
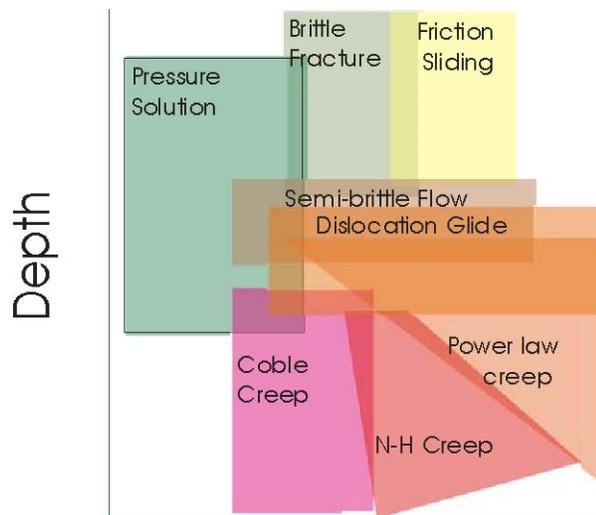
The lower four mechanisms involve the production, motion, and consumption of crystal defects. One important aspect of rock mechanics/mineral physics is to develop quantitative descriptions of the mechanical behavior of rocks under the appropriate natural conditions.

What constitutive laws can be developed to predict the strength of rocks?

Defects:

Deformation at higher temperatures and slower strain rates occurs by the generation, motion and elimination of defects. The defects may be points, linear, or planar

1. Point defects
   a. Ionic
      i. Vacancies
      ii. Interstitials
      iii. Impurities
2. Paired defects (Schottky, Frenkel, etc.)
      i. Vacancy clusters
      ii. Electronic
         1. Localized valence band
         2. Delocalized conduction band
3. Line defects
      i. Dislocation, disclinations
      ii. Partial dislocations
      iii. Stacking faults
4. Planar Defects
      i. Twins
      ii. Exsolution lamellae
      iii. Antiphase boundaries
      iv. Subgrain boundaries
      v. Grain boundaries
      vi. Interphase boundaries

Point Defects in Minerals:

Vacancies, intersititials, impurities. Charge balance not an issue.
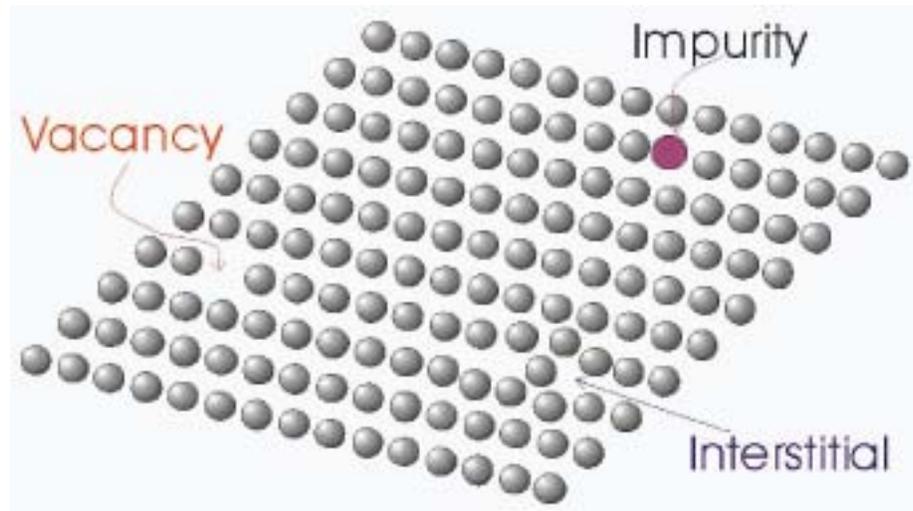
Intrinsic Point Defects:

Local elastic distortions within the lattice occur and relax the energy associated with the defect. *Vacancies* and *interstitials* may also occur as paired defects, especially if elastic interactions or electrostatic charge interactions occur. When the distortions occur over a substantial number of sites interstitials and vacancies are called crowdions or relaxions, respectively.

Such defects are called intrinsic point defects, because they do not require the introduction of impurities or aliovalent ions and are intrinsically related to the structure of the compound. A certain small number of these intrinsic point defects are always present at any temperature above absolute zero.

Number of Intrinisic Point Defects

The number of point defects at thermal equilibrium represents a balance between the cost of enthalpy to produce the defect and the gain in entropy from mixing the defect into the crystal and disordering it.

Consider the formation of a vacancy in a monatomic crystal. Suppose there are N sites from which to pluck an atom:

The total Gibbs free energy for the formation of n vacancies is

$$\Delta G = n_v \Delta H_{fv} - T\Delta S_{fv\ total}$$

where ΔH_{fv} is the enthalpy of formation for a single defect and $\Delta S_{fv\ total}$ is the total configurational entropy of the n vacancies-(all of them).

From statistical mechanics, the total configurational entropy is

$$S = k\ln W$$

where W is proportional to the number of ways that a given thermodynamic state can be realized. This description of configurational entropy is largely a statement of probability. For a combination where the items are indistinguishable,

$$W = \frac{N!}{(N-n_v)!\,n_v!}$$

If N is big, then Stirling's theorem holds

$$\ln(N!) = N\ln N - N$$

Then expressing the entropy as the difference of the logs and using Stirling's theorem gives

$$\Delta S_{vtotal} = k\{N\cdot\ln N - (N-n_v)\cdot\ln(N-n_v) - n_v\cdot\ln n_v\}$$

The change in Gibbs free energy to add n_v vacancies is

$$\Delta G = n_v\Delta H_{fv} - T\left[k\{N\ln N - (N-n_v)\ln(N-n_v) - n_v\ln n_v\}\right]$$

and at equilibrium:

$$\frac{d\Delta G}{dn_v} = \Delta H_{fv} - kT\frac{d}{dn_v}\left[\{n_v\ln(N-n_v) - n_v\cdot\ln n_v\}\right]$$

$$= \Delta H_{fv} - kT\left[\{\ln(N-n_v) - \ln n_v\}\right] = 0$$

And so, $$\Delta H_{fv} = kT\left\{\ln\frac{n_v}{N-n_v}\right\}$$

For $n_v \ll N$ $$\boxed{\frac{n_v}{N} = \exp-\left(\frac{\Delta H}{kT}\right)}$$

ΔG
ΔH
TΔS

Defect concentration

−ΔH/k

ln (n$_v$)

1/T
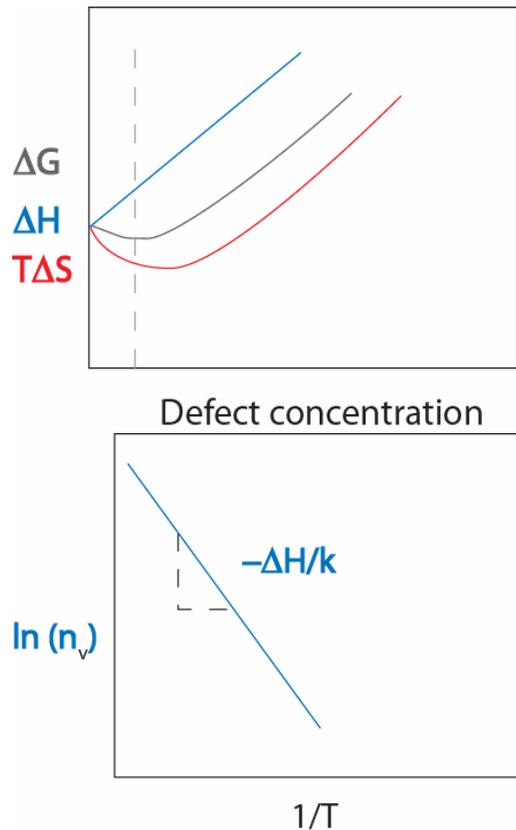
Conclusions:
1. *A minimum in free energy occurs because the entropy term has a minimum.*
2. *For very small defect concentrations the driving force to insert a new defect is VERY LARGE.*
3. *The graph above assumes that the formation energies don't depend on temperature.*
4. *An Arrhenius plot can be used to visualize the vacancy concentration.*
5. *Crystal structure is important in determining formation energies. For example, close packed lattices don't easily accommodate interstitials.*
6. *For crystals with the same structure, may scale the concentration with the melting temperature, by assuming that ΔH is proportional to the melting temperature*
   $\Delta H \prec qT_m$
   $n_v = N \exp - (q/\tau)$ *where* $\tau = T_m / T$

Point Defects in Polyatomic Solids

In crystals containing more than one ion, vacancies and interstitials might occur on either anion or cation sites. In addition to elastic coupling, there will be electrostatic interactions between the defects on the cation and anion sub lattices.

For example, for a simple halide compound where only vacancies are formed, the number of cation vacancies must equal the number of anion vacancies.

Alternately, if only cation defects tend to be formed, then the number of cation vacancies must equal the number of cation interstitials.There are four possibilities for the paired defects:

Frenkel	Positive interstitials=positive vacancies	Small cations in large anion framework
Antifrenkel	Negative interstitials=Negative vacancies	Anion Interstitials unlikely in Minerals
Schottky	Negative vacancies = Positive Vacanices	Relaxions
Antischottky	Negative interstitials=Positive interstitials	Anion Interstitials Unlikely

Schottky defects are "different ions on Same sites". Frenkel defects are "same ions on diFFerent sites".

The defect concentrations are constrained to obey charge neutrality, that is, the sum of the effective charges of all the defects must sum to 0, and the number of sites in the crystal must remain constant.

The energy of formation and hence, the concentration of defects on each sub lattice depends on the details of the crystallography. For example: Close-packed sub-lattices do not accommodate interstitials. In general, the anions are quite large and thus one could expect anion interstitials to have a much higher energy of formation than anion vacancies, cation vacancies, or cation interstitials.

A particular example of this limitation might be the oxygen sublattice in minerals. Interstitials might be more likely for very loosely packed structures like quartz (?)
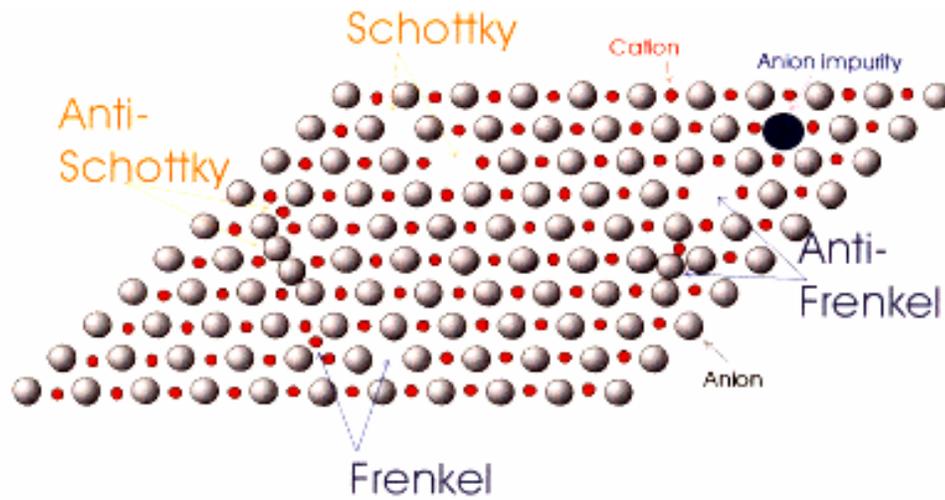
Aside: Kroger Vink Notation [Kröger, 1974]:

$$Ion_{Site}^{Eff.charge} \begin{cases} \bullet & \textit{Postive Eff} \\ \times & \textit{Neutral Eff} \\ ' & \textit{Negative Eff} \end{cases}$$
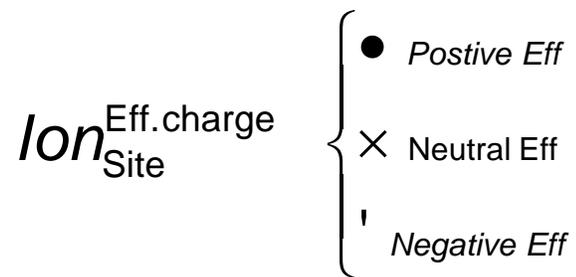
Example:

In olivine, $(Fe, Mg)_2 SiO_4$

$$V_{Mg}^{"}$$ vacancy on Mg site with effective charge of -2

$$Mg_i^{\bullet\bullet}$$ magnesium ion on interstitial site

$$(H_4)_{Si}^{\times}$$ hydrogarnet defect (four hydrogen ions occupying a silicon site

Because of neutrality conditions, defects on one sub lattice may be coupled to the concentration of defects on another sub-lattice.

Charge balance requires $2[Fe_{Si}'] = [V_O^{\bullet\bullet}]$
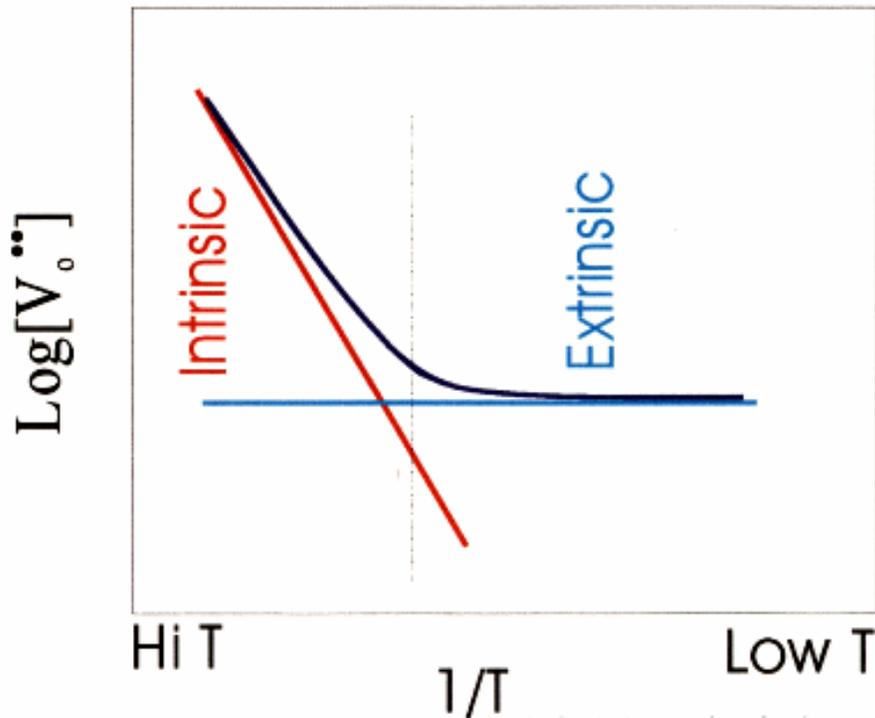
Both intrinsic and extrinsic defects may interact with electrons

Trapped electrons can result in farbenzentrum (color centers).

$\Delta G_{formation}$ also affected by interactions with electrons and holes.

Total defect content = extrinsic + intrinsic

High T, intrinsic dominates; Low T, extrinsic dominates

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