ROYAL INSTITUTE
OF TECHNOLOGY

Kinetic Monte-Carlo simulations

Alloy ordering
Defect clustering
Defect annihilation
Isochronal annealing

Pär Olsson
polsson@kth.se
0737-650538
Nuclear Engineering
KTH – AlbaNova, Stockholm, Sweden

Kinetic Monte-Carlo

Extremely short summary:

Residence time algorithm used to advance time in the simulation:

Lattice diffusion: $D = D_0 \exp(-\frac{E_a}{kT})$

Jump frequency: $\Gamma = \nu \exp(-\frac{E_a}{kT})$

activation energy

attempt frequency

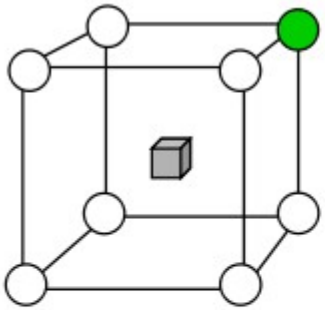
Time step: Probability distribution for time of first escape P(t). Average time <t> from this!

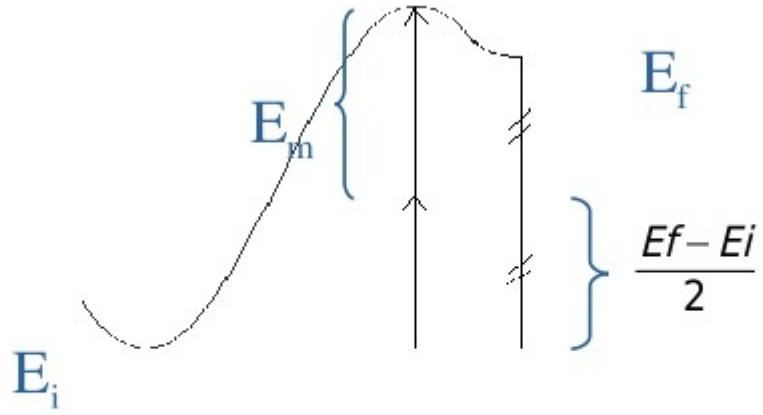
$$\int_0^{t'} P(t)dt = 1 - P_{\text{stay}}(t')$$

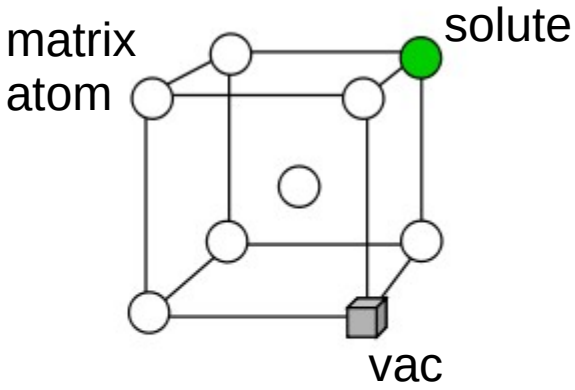
* From exercise set 3: Derive an expression for <t> !

Kinetic Monte-Carlo

Heuristic model for activation energy:







$$E_a = E_m + \frac{E_f - E_i}{2}$$

* E_f (final) and E_i (initial) given by cohesive model for the alloy in question
  (here two-band model of Olsson05 PRB for FeCr or ab initio pair interaction Model for Fe and FeMn of Ngayam-Happy12 JNM)

* Species and defect dependent E_m set in KMC input files

LAKIMOCA (LAttice KInetic MOnte-CArlo)

Code developed by C. Domain, EDF R&D, France

Description of the simulation in an input file “input”

- interaction potential (cohesive model)
- crystal
- simulation parameters
  * attempt frequency
  * number of loops
  * number of kmc steps per loop
  * boundary conditions
  * etc
- simulation (kmc or mmc algorithm)
- material parameters
  * solute concentration (Cu = Cr or Mn in the syntax)
  * solute specific migration barriers

To run:

lakimoca inputfile name > name.out

LAKIMOCA (LAttice KInetic MOnte-CArlo)

ROYAL INSTITUTE
OF TECHNOLOGY

Code and directories in the same machine as the MD lab.

ssh inside
cd KMC
cd Your_name

Look around!

If you haven’t yet, please install *jmol* or *Ovito* for visualization

Simulation of thermal ageing

Thermal ageing in most metallic alloys is due to *vacancy diffusion*.

ROYAL INSTITUTE
OF TECHNOLOGY

In order to simulate this process, insert one vacancy in a *large enough* simulation cell and let it jump around *a sufficient* number of times.

* What is large enough? Discuss!

* What is a sufficient number of times? Discuss!

Follow some quantity of interest, like the SRO.
(also, look at the evolution of the distribution using a graphical tool, e.g. jmol or xmakemol and step through the frames of the kmc.xyz or kmc_2.xyz file)

Time in KMC

ROYAL INSTITUTE
OF TECHNOLOGY

The time, as given by the code, is the KMC time due to the residence time algorithm.

Why is that not the real time?

Hint: What is the vacancy concentration?

Time in KMC

How can we get the real time?

* What is the vacancy concentration in the simulation? (choose one simulation)

* What is the real vacancy concentration? (choose the corresponding real conditions)

Time in KMC

ROYAL INSTITUTE
OF TECHNOLOGY

How can we get the real time?

Time is scaled by the supersaturation factor: $$f_{scale} = \frac{c_{vac}^{simulation}}{c_{vac}^{real}}$$

* What is the vacancy concentration in the simulation? (choose one simulation)

* What is the real vacancy concentration? (choose the corresponding real conditions)

Concentration of defects at thermal equilibrium

Concentration given by the Boltzmann factor $\exp\left(-E^f / kT\right)$

ROYAL INSTITUTE OF TECHNOLOGY

estimates

Temp.	C(vac)	C(int)
300 K	10^{-29}	10^{-61}
600 K	10^{-15}	10^{-31}
900 K	10^{-10}	10^{-21}

In Fe – thermal ageing: diffusion by vacancy mechanism

It is the case in most metals
Not necessarily true for semi-conductors:
in Si for example $E^f(\text{int}) < E^f(\text{vac})$

a) Short range ordering

The short range order (SRO) is a quantity that can be measured using diffuse neutron scattering or X-rays. It is determined using the Warren-Cowley parameters:

$$\alpha(R) = 1 - P_{AB}(R)/x$$

where $P_{AB}(R)$ is the probability of finding an atom A at distance R from atom B and x is the concentration of A.

It can be measured from the diffuse scattering cross-section:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = x(1-x)(b_\mathrm{A} - b_\mathrm{B})^2 \sum_R \alpha(R) f(K) \exp(iK \cdot R)$$

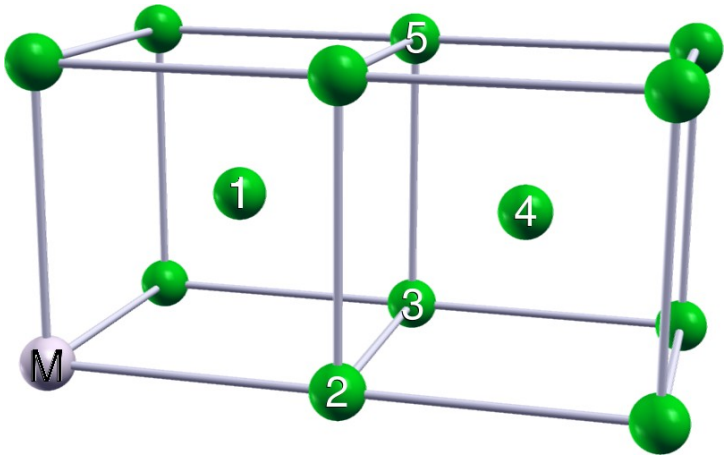
where b_A and b_B are the scattering lengths of A and B atoms, and $f(K) = \exp(-C|K|^2)$ is the attenuation factor.

a) Short range ordering

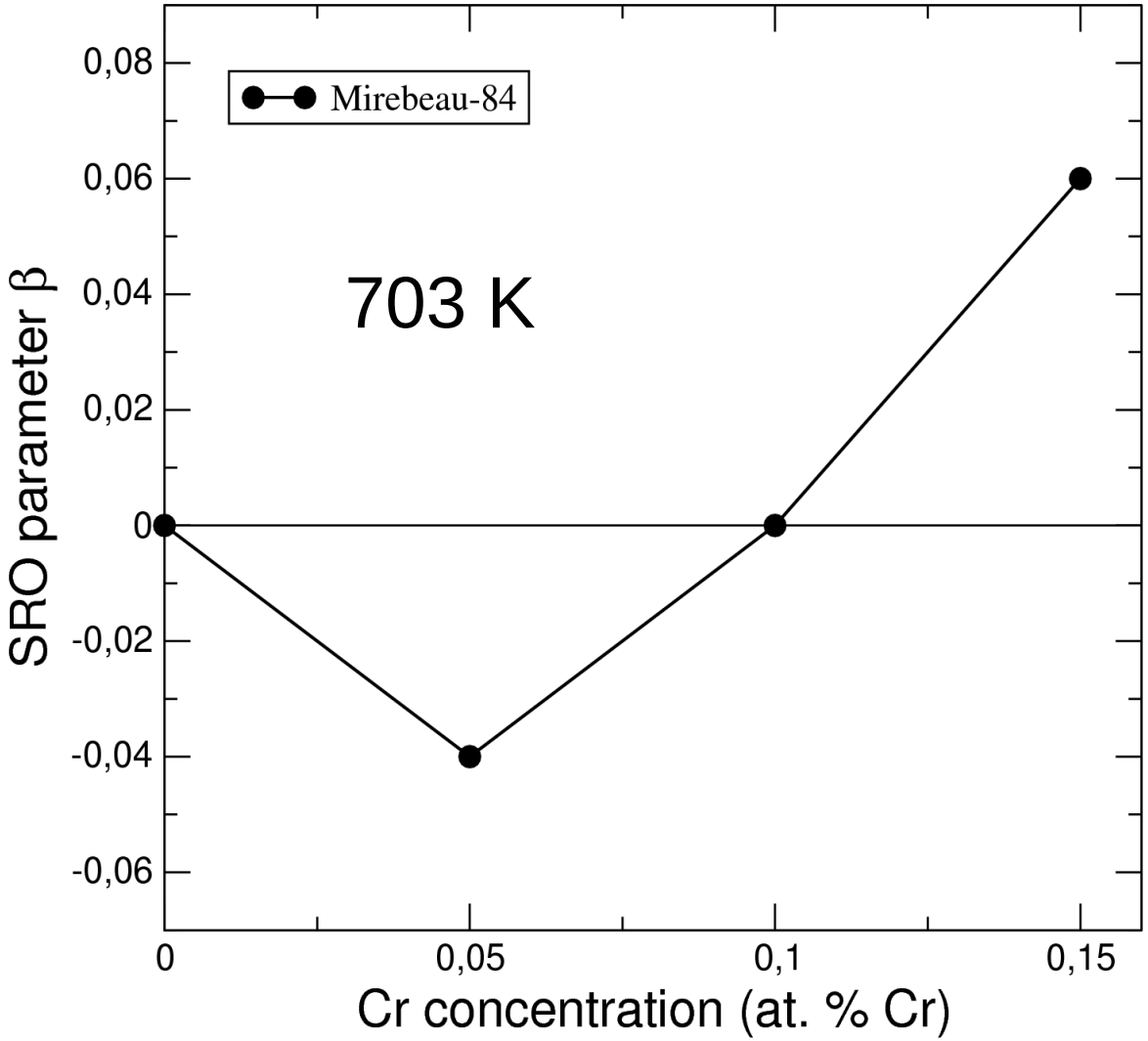
In bcc lattices, the first nearest neighbour and second nearest neighbour distances are very close and it is difficult to distinguish them in experiments. Therefore, one often uses the parameter β:

$$\beta = (8\alpha_1+6\alpha_2)/14$$

* Explain the definition of β



bcc lattice neighbours



a) Short range ordering

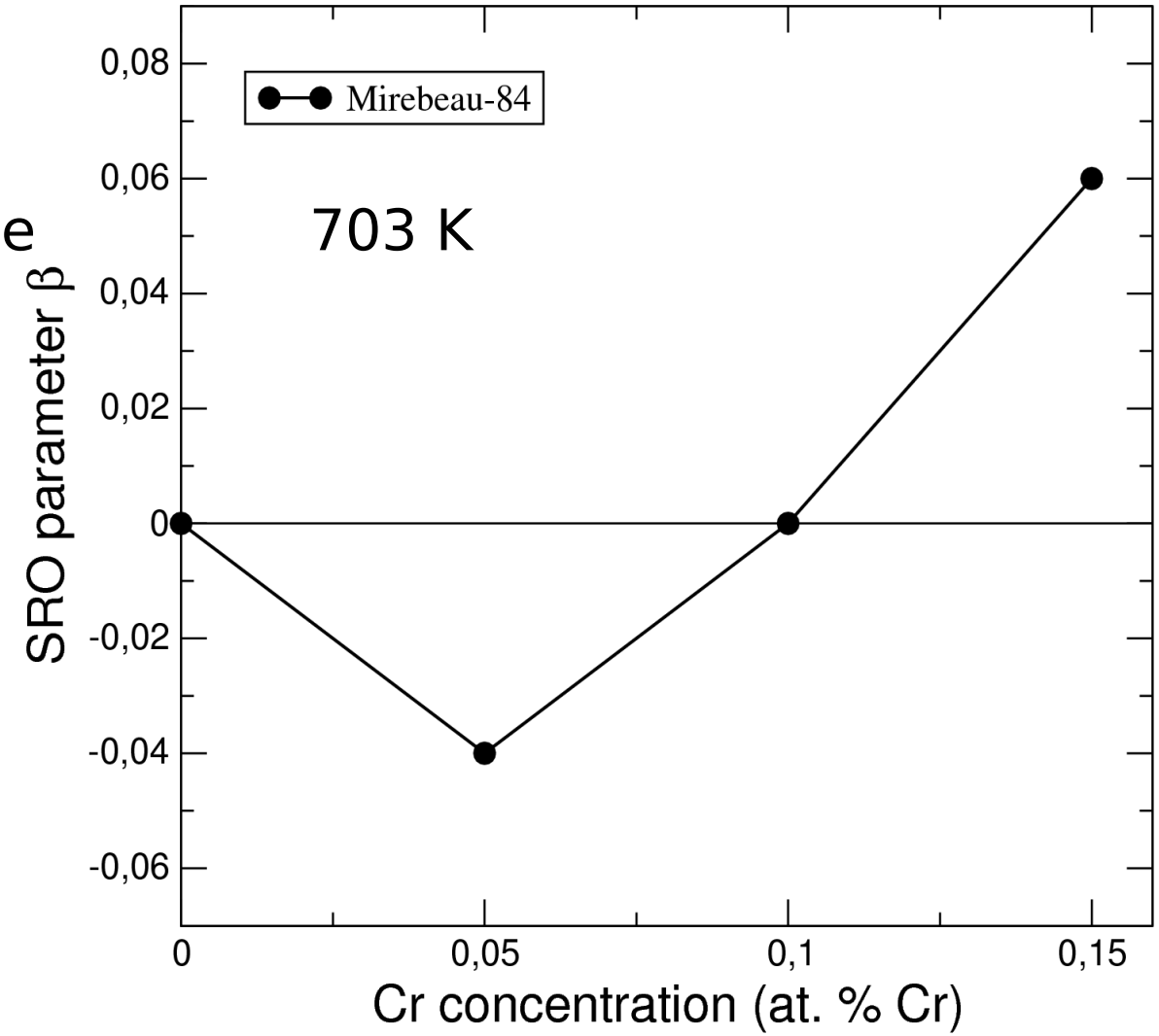
$\alpha = 0$, no order

$\alpha < 0$, a tendency for unlike pairs

$\alpha > 0$, a tendency to cluster

In the Mirebeau experiment, the SRO is seen to vary drastically with the Cr content.

Can we reproduce this behaviour in a KMC simulation?



a) Short range ordering

ROYAL INSTITUTE
OF TECHNOLOGY

A multitude of output files are created. In order to look at the short range order:
 * use the file kmc.sro

The first line explains the format:

#nstep time a(1) a(2) a(3) a(4) a(5) a(6) a(7) a(8) ... a(10)

First column = number of KMC steps
Second = KMC time
Third = SRO in first shell
Fourth, etc = SRO in second, etc shells

Run simulations between 5 and 15 at. % Cr and plot the time evolution of the β parameter.

* At what time does the simulation compare **best** to experiments? (How do you **best** compare the two?)

b) Defect clustering

An Fe matrix is injected with a number of vacancies in random positions

ROYAL INSTITUTE
OF TECHNOLOGY

The boundary conditions are periodic

* What will be the ultimate fate of the vacancies?

Run the simulation and see what happens!

Check the kmc.stat_decad file and visualize the kmc_2.xyz file in jmol

* Explain how one **could** set up a simulation to calculate the diffusion coefficient of
a) a single vacancy
b) a vacancy cluster of n defects

b) Defect clustering

ROYAL INSTITUTE
OF TECHNOLOGY

An Fe matrix with dilute Mn is injected with a number of vacancies in random positions

The boundary conditions are periodic

* What will be the ultimate fate of the vacancies?
* idem of the Mn atoms?

Run the simulation and see what happens!

Check the kmc.stat_decad file and visualize the kmc_2.xyz file in jmol

b) Defect clustering

ROYAL INSTITUTE
OF TECHNOLOGY

An Fe matrix with is injected with a number of SIAs in random positions

The boundary conditions are periodic

* What will be the ultimate fate of the SIAs?

Run the simulation and see what happens!

Check the kmc.stat_decad file and visualize the kmc_2.xyz file in jmol

*Why do the clusters move less rapidly than the monomers?

b) Defect clustering

ROYAL INSTITUTE
OF TECHNOLOGY

An Fe matrix with dilute Mn is injected with a number of SIAs in random positions

The boundary conditions are periodic

* What will be the ultimate fate of the SIAs?
* Idem of the Mn atoms?

Run the simulation and see what happens!

Check the kmc.stat_decad file and visualize the kmc_2.xyz file in jmol

Notice difference btw kmc.xyz (all defects+all solutes) and kmc_2.xyz (all defects+clustered solutes)

* How do you explain the redistribution of the Mn atoms (there are no vacancies in the simulation cell)?

c) Defect annihilation

An Fe matrix is injected with a number of vacancies and self-interstitials in random positions at a given temperature

The boundary conditions are periodic

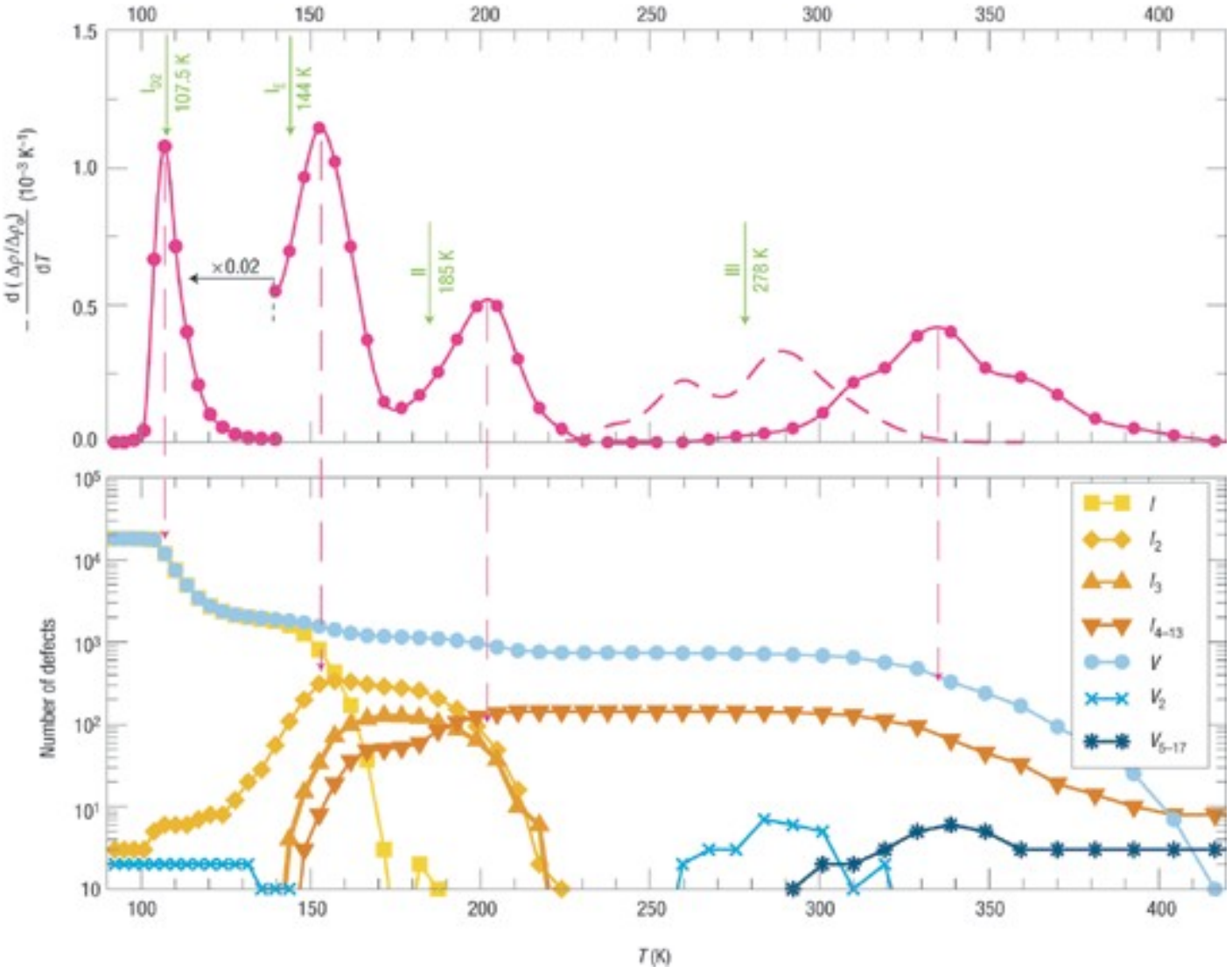
* What will be the ultimate fate of the defects?

Run the simulation and see what happens!
Change the temperature and rerun

* Plot the final distribution as a function of temperature

Check the kmc.stat_decad file and visualize the kmc_2.xyz file in jmol

d) Isochronal annealing



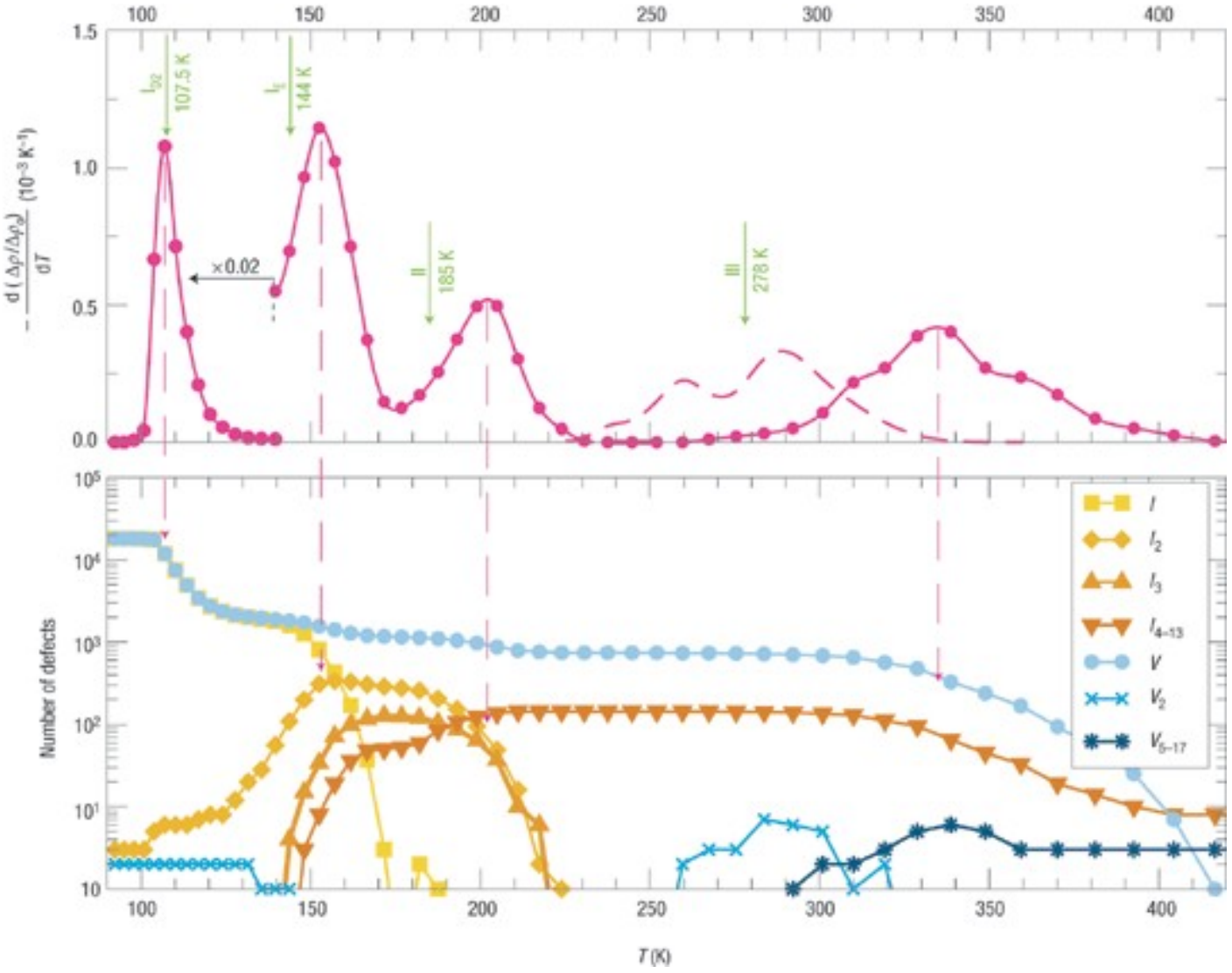
A standard experimental technique to estimate the migration barriers of different types of defects is isochronal annealing (or resistivity recovery) experiments.

A sample is irradiated by electrons at very low T (4K)

The sample is then slowly heated up (const K/s) and the resistivity is measured after each heating step

Here: a KMC simulation (Nature materials 2005) of resistivity recovery in Fe

d) Isochronal annealing



Bottom graph: Number of defects in the simulation cell (I,I2,I3, V, V2, etc)

The variation is due to recombination

An approximate model of resistivity is that each defect contributes equally to a resistivity increase

When they recombine, ρ decreases

Top graph: $-d\rho/dT$
i.e. the peaks correspond to the maximal rate of recombination → the activation temperature of a given defect type → activation energy

d) Isochronal annealing

ROYAL INSTITUTE
OF TECHNOLOGY

Simulate the resistivity recovery in
a) pure Fe
b) dilute FeMn

Check the file kmc.iso which contains the number of vacancies, SIAs and the temperature.

* Identify the recovery peaks

* What mechanisms do you propose for the first three?

* At what temperatures do they appear?

* What is the effect of alloying with Mn?

Report/Presentation

ROYAL INSTITUTE
OF TECHNOLOGY

- Discuss and answer all the questions in red

- Make it readable/presentable and describe properly what you are doing (with figures, or animations when appropriate)