INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
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SMR.550 - 38

SPRING COLLEGE IN MATERIALS SCIENCE ON
"NUCLEATION, GROWTH AND SEGREGATION IN MATERIALS
SCIENCE AND ENGINEERING"
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RADIATION INDUCED ORDERING

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These are preliminary lecture notes, intended only for distribution to participants.

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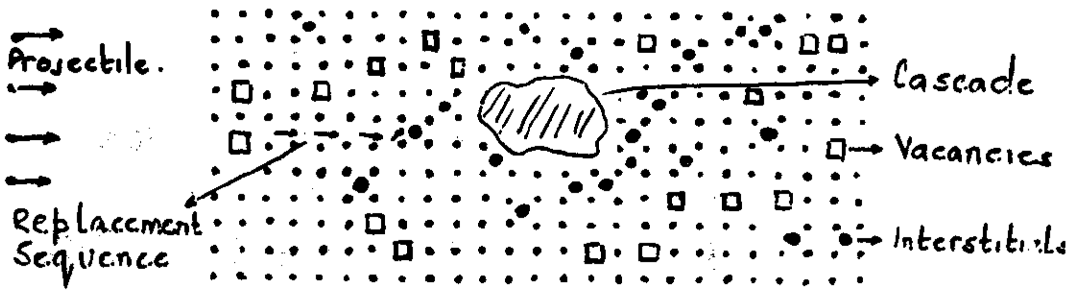
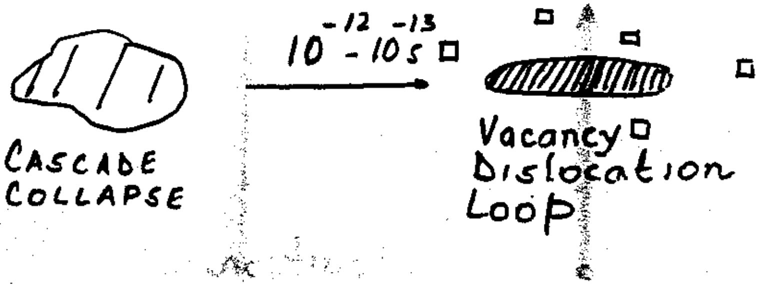
RADIATION INDUCED ORDERING

1 A. • Pair Production / Cascade damage
2 • Displacements Per Atom (DPA)
3 • Differences between electron/ion and neutron irradiation
4 • Sink strength / Recombination Rate
5 • Replacement sequences
6 • Bias
7 B • VOID / VACANCY LOOP / INTERSTITIAL LOOP PRODUCTION
8 • RATE THEORY – RADIATION DAMAGE
9 • LINEAR STABILITY ANALYSIS
10 • CRITICAL POINT / SOFT MODE / BIFURCATION
11 • DEFECT INTERACTIONS.
12 • FLUCTUATIONS.
13 C. • Void Lattices
14 • Bubble Lattices
15 • Defect Walls
16 • Spinodal Decomposition
17 • Phase Stability of alloys during irradiation.

THE IRRADIATION PROCESS.

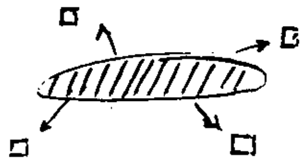


Concentration of vacancies/interstitials	v / i
Production Rate	K (DPA)
Recombination Rate	$\alpha v i$



Cascade efficiency	ϵ
Production Rate for Cascade	ϵK.
Vacancy Production Rate	$K(1-\epsilon)$

VACANCY LOOP DYNAMICS.

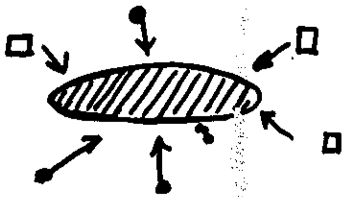


Vacancy Thermal emission Rate

$$\left(\frac{dQ_L}{dt}\right)_{Thermal} = - D_v C_v^{eq} p_L$$

$$p_L = \exp\left[\left(\gamma_{SF} + F_{el}(r_L)\right) b^2 / k_B T\right]$$

$$F_{el}(r_L) = \left(\mu b^2 / 4\pi(1-\nu)\right) \ln\left[(r_L+b)/b\right] / (r_L +$$



Interstitial & Vacancy absorpti

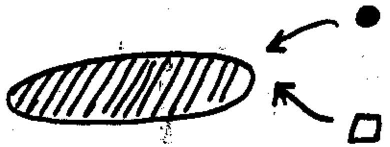
$$\left(\frac{dQ_L}{dt}\right)_{Absorption} = \rho_L \left(D_v v - Z_i D_i i\right)$$

Bias

$$\rho_L = 2\pi N_L r_L$$

Density → sink term.

BIAS Z or Z_i or $\Delta Z = Z-1$

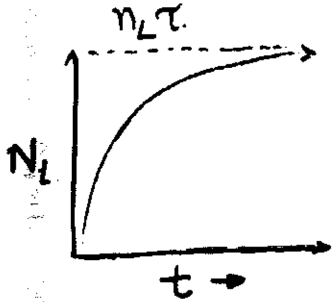


$Z \approx 1.05$

$5-10\%$

Vacancy loop life time τ

$$\frac{dN_L}{dt} = n_L - \frac{N_L}{\tau}$$



1. $N_L = n_L \tau \left(1 - e^{-t/\tau}\right)$

$\tau = -r_{L0} \Big/ \left(\frac{dr_L}{dt}\right)_{r_{L0}}$

$Q_L = \pi r_L^2 N_L / b^2$ 2. $\rho_L = 2\pi N_L r_L$

$$\frac{dQ_L}{dt} = \underbrace{\epsilon K}_{\text{Production}} + \underbrace{\rho_L \left(D_v v - Z_i D_i i\right)}_{\text{Bias}} - \underbrace{\rho_L D_v C_v^{eq} p_v}_{\text{Thermal.}}$$

VOID GROWTH MECHANISM

$$\frac{dQ_s}{dt} = \underbrace{\rho_s \left(D_v v - D_i i\right)}_{\text{Irradiation term}} - \underbrace{\rho_s D_v C_v^{eq} p_s}_{\text{Thermal.}}$$

$$p_s = \exp\left[\left(\frac{2\gamma}{r_s} - P_g\right) / k_B T\right] \qquad \rho_s = 4\pi N_s r_s \qquad Q_s = \frac{4\pi r_s^3}{3 b^3}$$

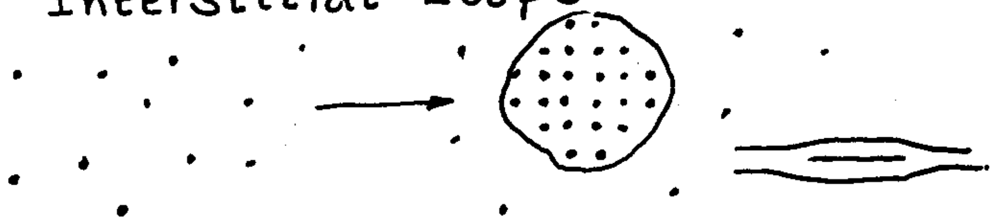
Growth of bubbles:

$i = 0 \qquad v = C_v^{eq}$

$$\frac{dQ_s}{dt} = \rho_s D_v C_v^{eq} \left[1 - p_s\right]$$

$p_s > 1$	shrinkage	$\frac{2\gamma}{r_s} > P_g$
$p_s < 1$	growth	$\frac{2\gamma}{r_s} < P_g$
$p_s = 1$	Equilibrium	$\frac{2\gamma}{r_s} = P_g$

Interstitial Loops



$$\frac{dQ_I}{dt} = \rho_I \left(-D_v v + Z D_i i\right) + \rho_I D_i C_v^{eq} P_I$$

$$P_I = \exp - \left[\left(\gamma_{SF} + F_{el}(r_L) b^2\right) / k_B T\right]$$

$$\rho_I = 2\pi N_I r_I \qquad Q_I = \pi r_I^2 N_I / b^2$$

Point Defect kinetics

$$\beta_v = D_v \left(\rho_S + \rho_L + \rho_I \right)$$

$$\beta_i = D_i \left(\rho_S + Z_i (\rho_L + \rho_I) \right)$$

VOIDS $\downarrow$ Neutral Sinks

DISLOCATIONS $\downarrow$ Biased Sinks.

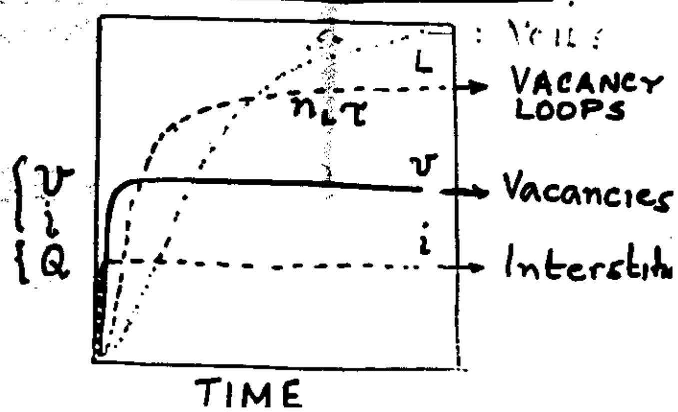
$$\frac{dv}{dt} = K_v - \beta_v v - \alpha v i$$

$$\frac{di}{dt} = \underbrace{K_i}_{\text{Production}} - \underbrace{\beta_i i}_{\text{Sink}} - \underbrace{\alpha v i}_{\text{Recombination}}$$

FAST MODES AND SLOW MODES

$$\frac{dv}{dt} \Big/ \frac{di}{dt}$$

$$\frac{dQ}{dt}$$



Steady State Solution.

$$\frac{di}{dt} = 0 \qquad \frac{dv}{dt} = 0$$

Sink Dominant Regime

$$\frac{dv}{dt} = K_v - \beta_v v = 0$$

$$\frac{di}{dt} = K_i - \beta_i i = 0$$

$$\bar{v} = \frac{K_v}{\beta_v} = \frac{K_v}{D_v \rho_{terms}} \qquad D_v \rightarrow \text{Small}$$

$$\bar{i} = \frac{K_i}{\beta_i} = \frac{K_i}{D_i \rho_{terms}} \qquad D_i \rightarrow \text{Large}$$

$$\bar{v} >> \bar{i}$$

Recombination Dominant Regime

$$\frac{dv}{dt} = K_v - \alpha v i =$$

$$\frac{di}{dt} = K_i - \alpha v i =$$

If $K_v = K_i = K$ $\underline{v = i}$

Provided $(v - i) = 0$ at time $t = 0$

$$v = i = \sqrt{\frac{K}{\alpha}}$$

What Do we Plan to do?

First we look at the problem of production and recombination of defects

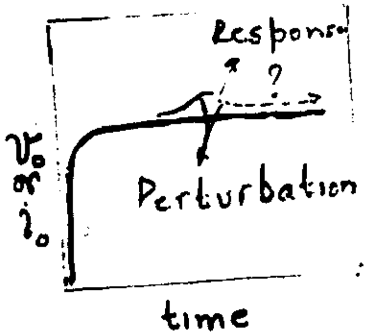
$$\frac{dv}{dt} = K - \alpha v i \qquad C_- = i - v$$
$$\frac{di}{dt} = K - \alpha v i \qquad C_+ = i + v$$

INITIAL CONDITION $t=0$

$C_- = i - v = D \qquad C_+ = i + v = E$

What is the nature of the solutions?

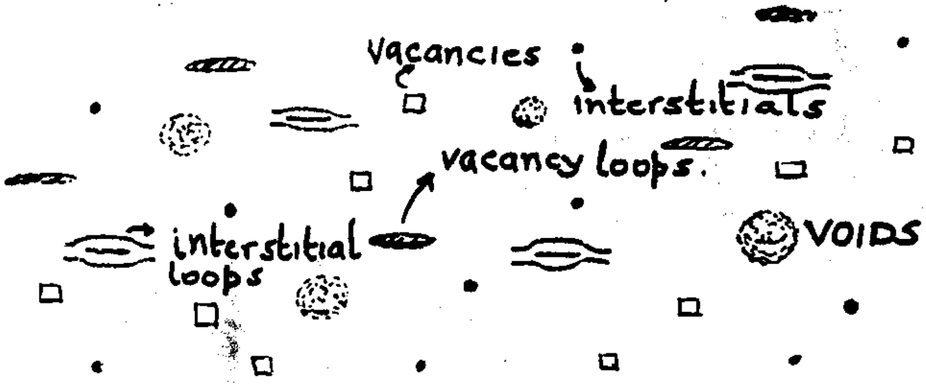
Examine the Steady state solution
→ Stability Aspects



$$v = v_0 + \delta v' \exp \underline{\omega} t$$
$$i = i_0 + \delta i' \exp \underline{\omega} t$$

Spatial Dependence $\delta v' = \bar{\delta} v'' e^{i \underline{k} \cdot \underline{r}}$

RADIATION INDUCED ORDERING - ?



$$\frac{dv}{dt} = K(1-\epsilon) - \beta_v v - \alpha v i + TE$$
$$\frac{di}{dt} = K - \beta_i i - \alpha v i$$

$$\beta_v = \rho_S + \rho_L + \rho_I$$
$$\beta_i = \rho_s + Z(\rho_L + \rho_I)$$

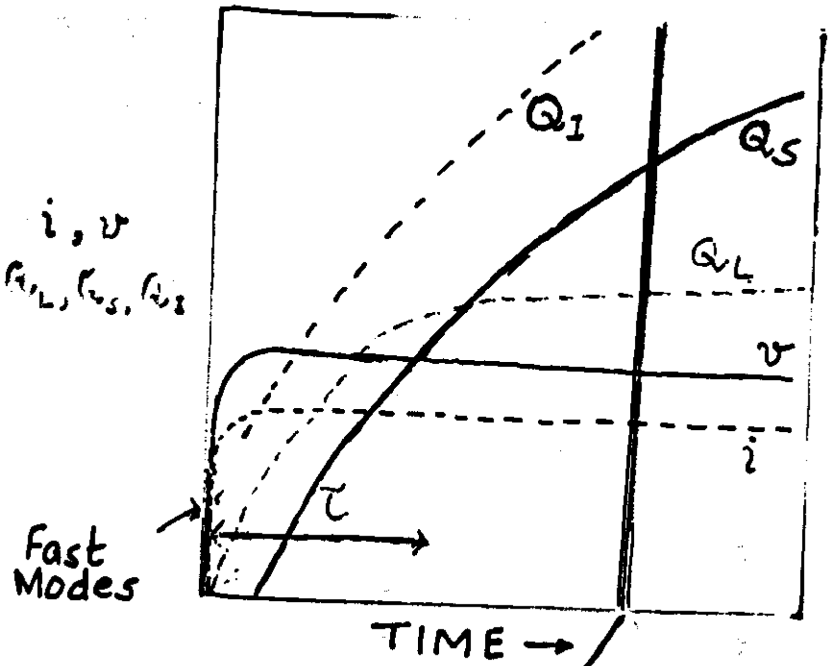
$$\frac{dQ_L}{dt} = \epsilon K + \rho_L(D_v v - Z D_i i) + TE$$
$$\frac{dQ_S}{dt} = \rho_S (D_v v - D_i i) + TE$$
$$\frac{dQ_I}{dt} = \rho_I (-D_v v + Z D_i i) + TE$$

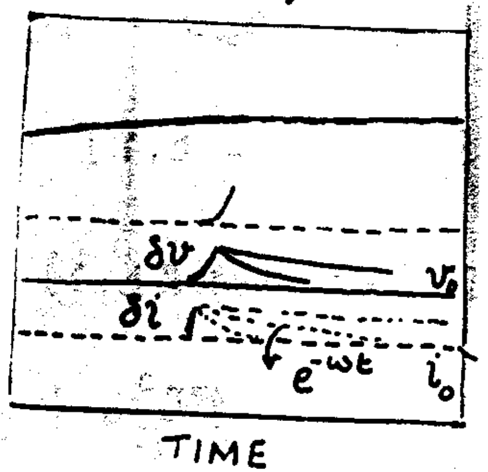
$Q_{L,I} = \pi r_{L,I}^2 N_{L,I}/b^2 \quad \Big| \quad Q_S = \frac{4\pi}{3} r_S^3 \frac{N_S}{b^3} \quad \Big| \quad \frac{dN_L}{dt} = n_L - \frac{N_L}{\tau}.$

$\rho_{L,I} = 2\pi N_{L,I} r_{L,I} \quad \Big| \quad \rho_S = 4\pi N_S r_S$

$$\frac{di}{dt} - \frac{dv}{dt} = \frac{dQ_L}{dt} + \frac{dQ_S}{dt} - \frac{dQ_I}{dt} = 0$$

$$(i - v) = Q_L + Q_S - Q_I = \text{Const}$$





$$\frac{di}{dt} = K - \beta_i i$$

$$\frac{dv}{dt} = K - \beta_v v$$

Sink Dominant

$$i = i_0 + \delta i' e^{\omega t}$$

$$v = v_0 + \delta v' e^{\omega t}$$

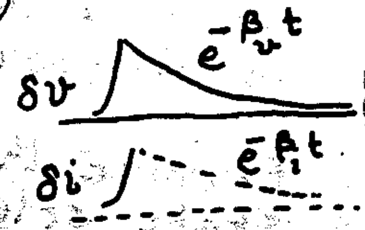
$K - \beta_i i_0 = 0$
$K - \beta_v v_0 = 0$
Steady State

$$\omega e^{\omega t} \delta i' = -\beta_i \delta i' e^{\omega t}$$

$$\omega e^{\omega t} \delta v' = -\beta_v \delta v' e^{\omega t}$$

$$\begin{pmatrix} \beta_i + \omega & 0 \\ 0 & \beta_v + \omega \end{pmatrix} \begin{pmatrix} \delta i' \\ \delta v' \end{pmatrix} = 0$$

$$\omega = \left\{ \begin{matrix} \omega_1 = -\beta_i \\ \omega_2 = -\beta_v \end{matrix} \right\}$$

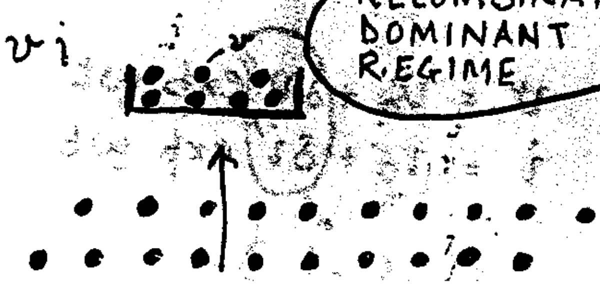


$$\frac{di}{dt} = K - \alpha v i$$

$$\frac{dv}{dt} = K - \alpha v i$$

$C_- = i - v = -3 = D \quad t=0$
$C_+ = i + v = 7e^6$

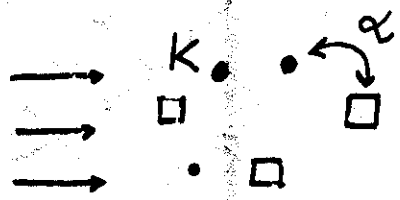
RECOMBINATION DOMINANT REGIME



INHOMOGENEOUS EFFECTS, REACTIVE-DIFFUSIVE BEHAVIOUR, DEFECT REACTIONS

Point Defect Concentrations during irradiation. A simple model.

$$\frac{di}{dt} = K - \alpha i v, \qquad \frac{dv}{dt} = K - \alpha i v$$



$= 1$ Initial conditions $t = 0$ $C_- = i - v = D$, $C_+ = i + v = E$

$$\frac{dC_-}{dt} = 0 \qquad \frac{dC_+}{dt} = -\left(\frac{\alpha}{2}\right)C_+^2 + (\alpha D^2 + 4K)/2 \quad \text{Riccati Equation}$$

$$C_+ = \left(D^2 + \frac{4K}{\alpha}\right)^{1/2} \frac{E + \left(D^2 + \frac{4K}{\alpha}\right)^{1/2} \tanh \frac{1}{2}\alpha\left(D^2 + \frac{4K}{\alpha}\right)^{1/2} t}{E \tanh \frac{1}{2}\alpha\left(D^2 + \frac{4K}{\alpha}\right)^{1/2} t + \left(D^2 + \frac{4K}{\alpha}\right)^{1/2}}$$

the asymptotic Limit $t \to \infty$

$$(i_0, v_0) = \left(\frac{D}{2} + \frac{1}{2}\sqrt{\left(D^2 + \frac{4K}{\alpha}\right)},\ -\frac{D}{2} + \frac{1}{2}\sqrt{\left(D^2 + \frac{4K}{\alpha}\right)}\right)$$

$$\simeq \left(\sqrt{\frac{K}{\alpha}},\ \sqrt{\frac{K}{\alpha}}\right), \quad D = 0, \quad di/dt = dv/dt = 0$$

examine these solutions near the critical point (i_0, v_0)

$$i = i_0 + \delta i' \exp \omega t$$

$$v = v_0 + \delta v' \exp \omega t$$

Linearization of the equations.

$$\frac{di}{dt} = K - \alpha i v \qquad i = i_0 + \delta i$$

$$\frac{dv}{dt} = K - \alpha i v \qquad v = v_0 + \delta v$$

$$\frac{d\,\delta v}{dt} = -\alpha i_0 \delta v - \alpha v_0 \delta i \qquad i_0 = \frac{D}{2} + \frac{1}{2}\sqrt{\left(D^2 + \frac{4K}{\alpha}\right)}$$

$$\frac{d\,\delta i}{dt} = -\alpha i_0 \delta v - \alpha v_0 \delta i \qquad v_0 = -\frac{D}{2} + \frac{1}{2}\sqrt{D^2 + \frac{4K}{\alpha}}$$

$$\frac{d}{dt}\begin{pmatrix} \delta v \\ \delta i \end{pmatrix} = \begin{pmatrix} -\alpha i_0 & -\alpha v_0 \\ -\alpha i_0 & -\alpha v_0 \end{pmatrix}\begin{pmatrix} \delta v \\ \delta i \end{pmatrix}$$

$$\delta i = \delta i' e^{\omega t} \qquad \delta v = \delta v' e^{\omega t}$$

$$\begin{pmatrix} \alpha i_0 + \omega & \alpha v_0 \\ \alpha i_0 & \alpha v_0 + \omega \end{pmatrix}\begin{pmatrix} \delta i' \\ \delta v' \end{pmatrix} = 0$$

Solutions exist only if

$$\det \begin{vmatrix} \alpha i_0 + \omega & \alpha v_0 \\ \alpha i_0 & \alpha v_0 + \omega \end{vmatrix} = 0$$

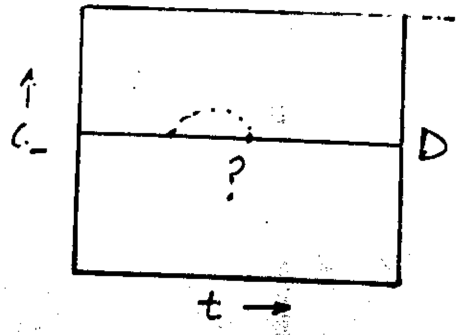
$$\det\begin{vmatrix} \omega+\alpha\left(-\frac{D}{2}+\frac{1}{2}\sqrt{D^2+\frac{4K}{\alpha}}\right) & \alpha\left(\frac{D}{2}+\frac{1}{2}\sqrt{D^2+\frac{4K}{\alpha}}\right) \\ \alpha\left(-\frac{D}{2}+\frac{1}{2}\sqrt{D^2+\frac{4K}{\alpha}}\right) & \omega+\alpha\left(\frac{D}{2}+\frac{1}{2}\sqrt{D^2+\frac{4K}{\alpha}}\right) \end{vmatrix}$$

$$\omega_- = 0 \qquad \omega_+ = -\alpha\sqrt{D^2+\frac{4K}{\alpha}}$$

$$i - v = c_- = D$$

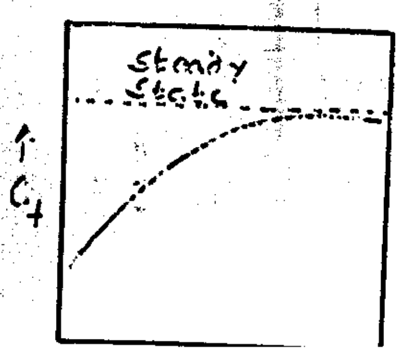
$$i + v = c_+ = \left(D^2+\frac{4K}{\alpha}\right)^{1/2}\left[1 - \left\{\frac{2\left(E-\sqrt{D^2+4K/\alpha}\right)}{E+\sqrt{D^2+4K/\alpha}}\right\}\exp(\omega_+ t)\right.$$

PHASE DIAGRAMS / SOFT MODE / AND THE PHYSICAL INTERPRETATION OF THE EQUATIONS.



$c_- = i - v$
$= \text{Constant}$

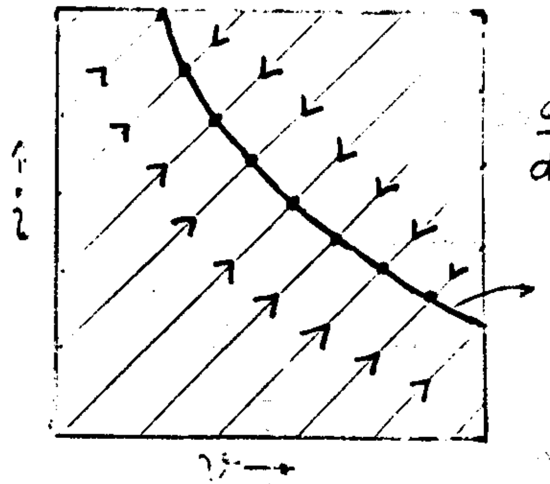
$\omega_- = 0$ (Soft Mode)!



$c_+ = i + v$
$\sim e^{(\omega_+ t)} + \left(D^2+\frac{4K}{\alpha}\right)^{1/2}$

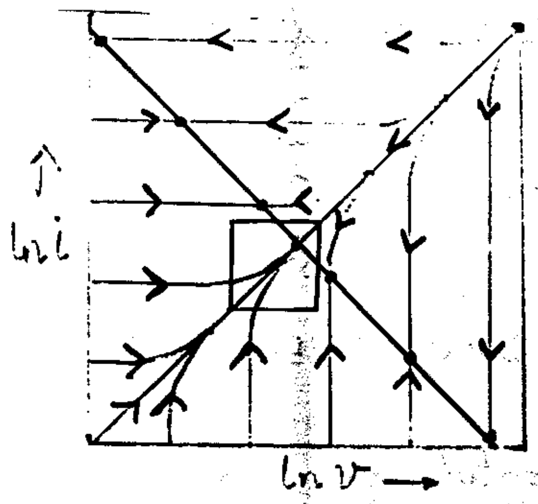
PHASE DIAGRAM

GENERATION AND RECOMBINATION



$$\frac{di}{dv} = +1$$

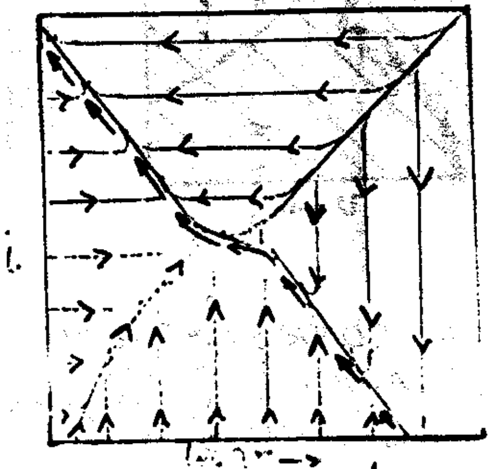
Steady state



Phase diagram
ln scale

PHASE DIAGRAMS - CONTD.

Unequal Production rates and recombination.



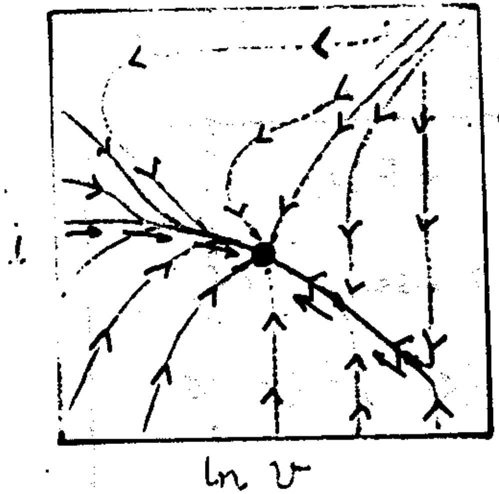
$$\frac{di}{dt} = K_I - \alpha i v$$

$$\frac{dv}{dt} = K_v - \alpha i v$$

$$\frac{dc_-}{dt} = \dot{i} - \dot{v} = K_i - K_v$$

$$C_- = (K_i - K_v)t + C$$

Unequal Production rates - recombination and loss to sinks.



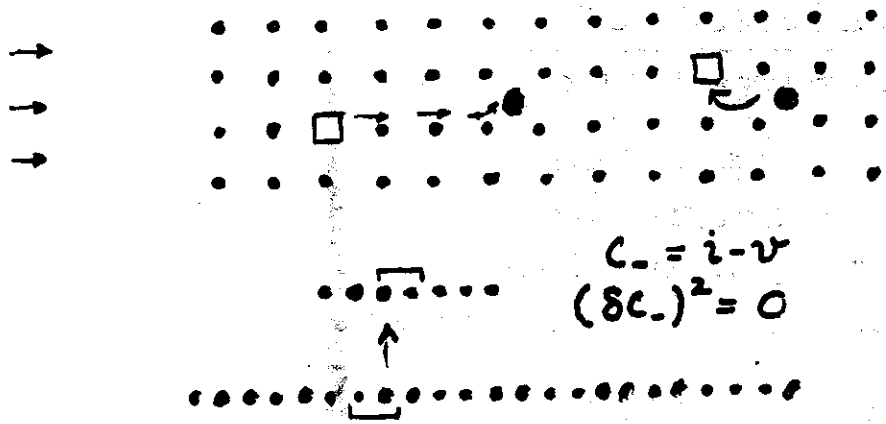
$$\frac{di}{dt} = K_i - \alpha i v - \beta_i i$$

$$\frac{dv}{dt} = K_v - \alpha i v - \beta_v v$$

$$i_0 = \frac{1}{2\alpha\beta_i}\left[(-\beta_i\beta_v + \alpha K_-) + \left\{(\beta_i\beta_v - \alpha K_-)^2 - 4\alpha\beta_i\beta_v K_i\right\}^{1/2}\right]$$

$$v_0 = \frac{1}{2\alpha\beta}\left[(-\beta_i\beta_v - \alpha K_-) + \left\{(\beta_i\beta_v + \alpha K_-)^2 - 4\alpha\beta_i\beta_v K_v\right\}^{1/2}\right]$$

FLUCTUATIONS / CORRELATED AND UNCORRELATED REACTIONS

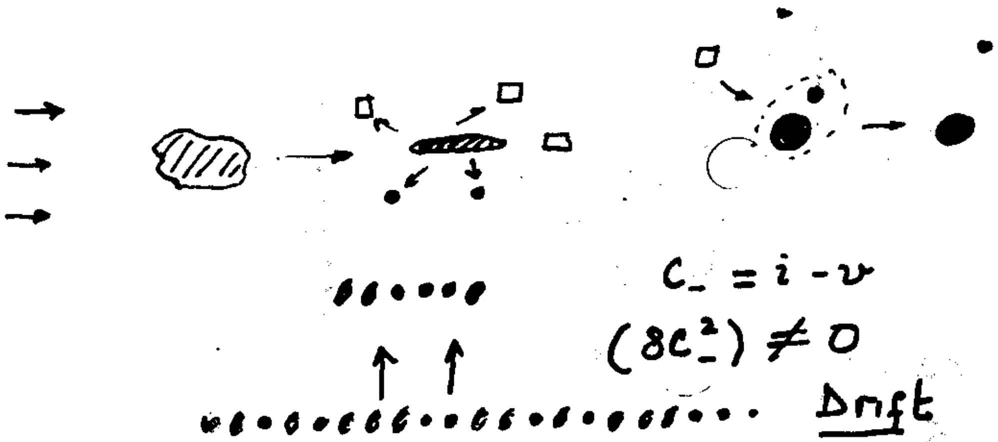


$$C_- = i - v$$

$$(\delta C_-)^2 = 0$$

$$\frac{dv}{dt} = K - \alpha v i$$

$$\frac{di}{dt} = K - \alpha v i$$



$$C_- = i - v$$

$$(\delta C_-^2) \neq 0$$

Drift

→ Removal of a Constraint.

2. FLUCTUATIONS AND DEVIATION IN CONCENTRATION IN THE PRESENCE OF SOFT MODES

CORRELATED & UNCORRELATED REACTIONS.

1. Correlated reactions

$S \longrightarrow$ Source term $\langle s \rangle = 0$

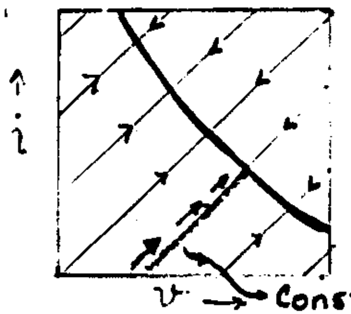
$S \xrightarrow{K} i + v$ Production in pairs

$i + v \xrightarrow{\alpha} S$ Recombination in pairs

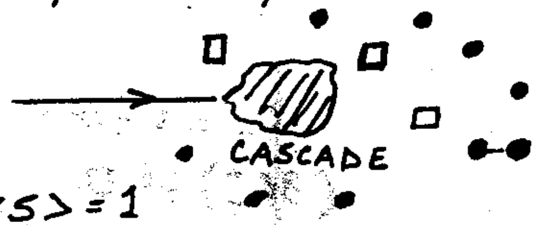
$\delta i = i - \langle i \rangle$, $\langle \delta i^2 \rangle = ?$

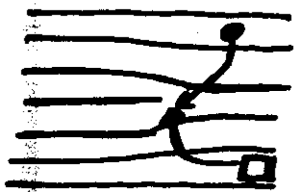
$\delta v = v - \langle v \rangle$, $\langle \delta v^2 \rangle = ?$

$$C = \begin{pmatrix} \langle \delta v^2 \rangle & \langle \delta v \delta i \rangle \\ \langle \delta i \delta v \rangle & \langle \delta i^2 \rangle \end{pmatrix} = 0$$



2. Uncorrelated reactions - actual Physical systems.





EDGE DISLOC.

$\langle s \rangle = 1$

$S \xrightarrow{K} i$

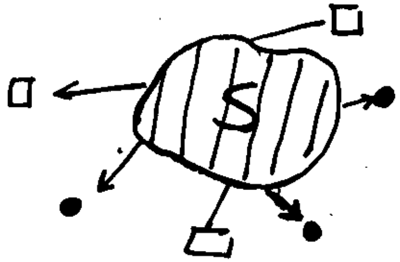
$S \xrightarrow{K} v$

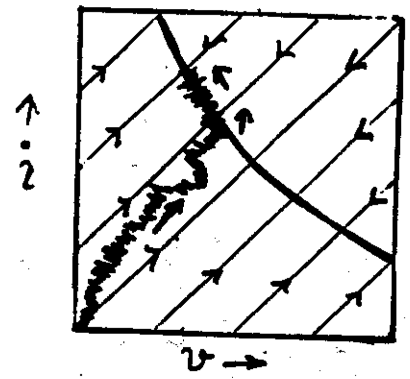
$i + v \xrightarrow{\alpha} S$

$$\frac{d\langle i \rangle}{dt} = K\langle s \rangle - \alpha\langle i \rangle\langle v \rangle$$

$$\frac{d\langle v \rangle}{dt} = K\langle s \rangle - \alpha\langle i \rangle\langle v \rangle$$

Uncorrelated Reactions - contd.





$\langle \delta c_-^2 \rangle \sim t$

CALCULATION OF THE CORRELATION MATRIX C - Keizers' Method (J. Chem 63, 1975, 398, 50

• Example of correlated reactions.

$$\frac{di}{dt} = k - \alpha i v \qquad \frac{d\delta i}{dt} = -\alpha i \delta v - \alpha v \delta i$$

$$\frac{dv}{dt} = k - \alpha i v \qquad \frac{dv}{dt} = -\alpha i \delta v - \alpha v \delta i$$

$$\frac{d\,\delta S}{dt} = \underset{\approx}{G}\, \delta \underset{\sim}{S} + F(t)$$

where $F(t)$ is the noise term

$$\langle F(t) F^T(s) \rangle = \underset{\approx}{\yen}(s)\, \delta(t-s)$$

$\underset{\approx}{\yen} \rightarrow$ Strength of the fluctuations - fluctuation dissipation theorem. $\rightarrow$ procedure Keizer

$$\underset{\approx}{C} = \langle \delta\varsigma^2 \rangle = \int_0^t e^{\underset{\approx}{G}(t-s)}\, \underset{\approx}{F}\, e^{\underset{\approx}{G}^T(t-s)}\, ds$$

In order to conveniently evaluate $\underset{\approx}{C}$ we use

$$e^{\underset{\approx}{G} t} = a_{n-1}(t)\underset{\approx}{G}^{n-1} + a_{n-2}\underset{\approx}{G}^{n-2} \cdots a_0(t)\underset{\approx}{I} = p(\underset{\approx}{G})$$

where $a_n(t)$ are evaluated from the n characteristic equations $p(\lambda_n) = \exp(\lambda_n t)$. For example if $\underset{\approx}{G}$ is a 2×2 matrix, then

$$\underset{\approx}{C}(t) = \underset{\approx}{F}\int_0^t a_0^2(t-s)\,ds + (\underset{\approx}{G}\underset{\approx}{F} + \underset{\approx}{F}\underset{\approx}{G}^T)\int_0^t a_0(t-s)\,a_1(t-s)\,ds + \underset{\approx}{G}\underset{\approx}{F}\underset{\approx}{G}^T\int_0^t a_1^2(t-s)\,ds.$$

Evaluation of the terms:

			$i=1$	$i=2$
$S \xrightarrow{K} i + v$	$k=1$		$\frac{di}{dt} = K$	$\frac{dv}{dt} = K$
$i + v \xrightarrow{\alpha} S$	$k=2$		$\frac{di}{dt} = -\alpha i v$	$\frac{dv}{dt} = -\alpha i v$

$$\underset{\approx}{G} = -\alpha\begin{pmatrix} i & v \\ i & v \end{pmatrix} \qquad \begin{cases} \lambda_1 = 0 \\ \lambda_2 = -\alpha(i+v) \end{cases}$$

$$\underset{\approx}{F} = \frac{\Omega}{\Delta V}\sum_{k=1}^{n} \nu_{kj}\,(V_k^+ + V_k^-)\,\nu_{ki}$$

ν_i: → Stochiometric Co-efficients.

	ν_{ki}	$k=1$	$k=2$
$i=1$	i	1	−1
$i=2$	v	1	−1

$$\underset{\approx}{F} = \alpha i v \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$$

$$\boxed{\begin{aligned} e^{\lambda_1 t} &= a_0 + a_1\lambda_1 \\ e^{\lambda_2 t} &= a_0 + a_2\lambda_2 \\ a_0(t) &= \frac{\lambda_2 e^{\lambda_1 t} - \lambda_1 e^{\lambda_2 t}}{\lambda_2 - \lambda_1} \\ a_1(t) &= \frac{e^{\lambda_1 t} - e^{\lambda_2 t}}{\lambda_1 - \lambda_2} \end{aligned}}$$

For the case $\lambda_1 \to 0$ $|\lambda_1 t| \ll 1$ we get

$$A_1 = \int_0^t a_0^2(t-s) = t$$

$$A_2 = \int_0^t a_0(t-s)\,a_1(t-s)\,ds = \frac{e^{\lambda_2 t}}{\lambda_2^2} - \frac{1}{\lambda_2^2} - \frac{t}{\lambda_2}$$

$$A_3 = \int_0^t a_1^2(t-s)\,ds = \frac{e^{2\lambda_2 t}}{2\lambda_2^3} - \frac{2e^{\lambda_2 t}}{\lambda_2^3} + \frac{3}{2\lambda_2^3} + \frac{t}{\lambda_2^2}$$

$$\begin{pmatrix} \langle \delta i^2 \rangle & \langle \delta i \delta v \rangle \\ \langle \delta v \delta i \rangle & \langle \delta v^2 \rangle \end{pmatrix} = A_1\underset{\approx}{F} + (\underset{\approx}{G}\underset{\approx}{F} + \underset{\approx}{F}\underset{\approx}{G}^T)A_2 + \underset{\approx}{G}\underset{\approx}{F}\underset{\approx}{G}^T A_3$$

We can now evaluate $\langle \delta C_-^2 \rangle$

$$\langle \delta C_-^2 \rangle = \langle \delta v^2 \rangle + \langle \delta i^2 \rangle - 2 \langle \delta i \delta v \rangle \equiv 0$$

$\therefore$ Though we have a soft mode $\lambda_1 = 0$ the fluctuations are unable to drive the system due to correlated reactions in this model.

UNCORRELATED REACTIONS.

$s \xrightarrow{k} i$	$\frac{di}{dt} = ks$	$\frac{dv}{dt} = 0$	$\frac{ds}{dt} = -ks$
$s \xrightarrow{k} v$	$\frac{di}{dt} = 0$	$\frac{dv}{dt} = ks$	$\frac{ds}{dt} = -ks$
$i + v \xrightarrow{\alpha} s$	$\frac{di}{dt} = -\alpha i v$	$\frac{dv}{dt} = -\alpha i v$	$\frac{ds}{dt} = \alpha i v$

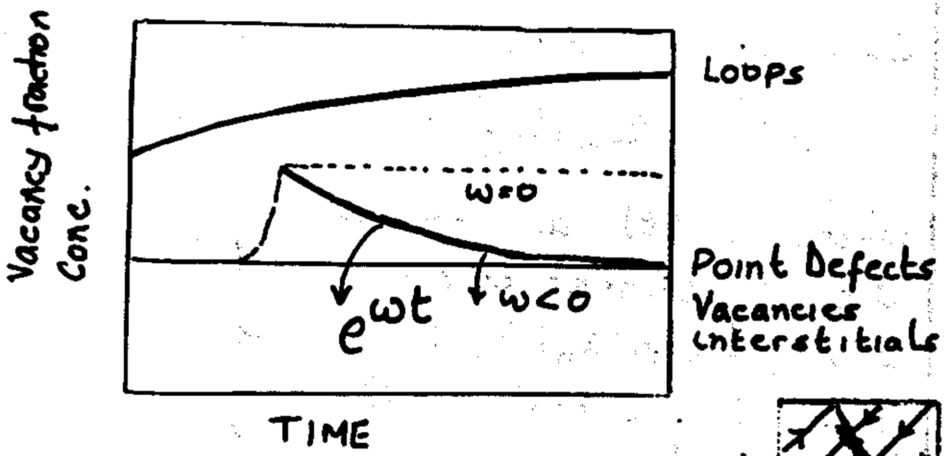
$$\not\equiv = \frac{\Omega}{\Delta V} \sum_k \nu_{kj} (V_k^+ + V_k^-) \nu_{ki}$$

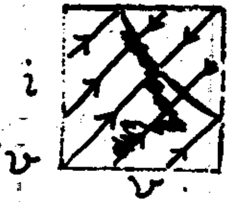
$$\langle \delta C_-^2 \rangle = \left(\frac{\Omega}{\Delta V} \right) k t .$$

Physical Process:

By introducing the source term S we have introduced one more mechanism for the dissipation of fluctuations. This removes an important constraint on the system

FLUCTUATIONS & STABILITY





$$\frac{dv}{dt} = k_v - \beta_v v - \alpha v i + D_v \nabla^2 v$$

$$\frac{di}{dt} = k_i - \beta_i i - \alpha v i + D_i \nabla^2 i$$

CORRELATED REACTIONS $\xrightarrow[\text{Const 1.}]{\text{Relax}}$ UNCORRELATED REACTIONS

$\beta_i = \beta_v = 0$

$\omega_1 = 0$, $C_- = i = v$

$(\delta C_-)^2 \equiv 0$

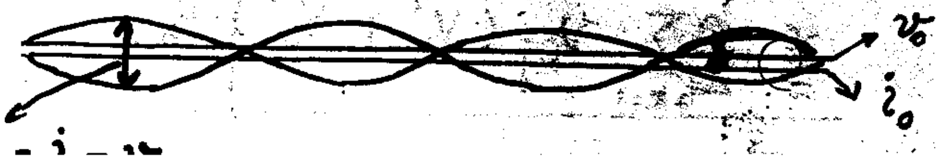
$\omega_1 = 0$, $C_- = i - v$

$(\delta C_-)^2 \propto kt$

Const 2

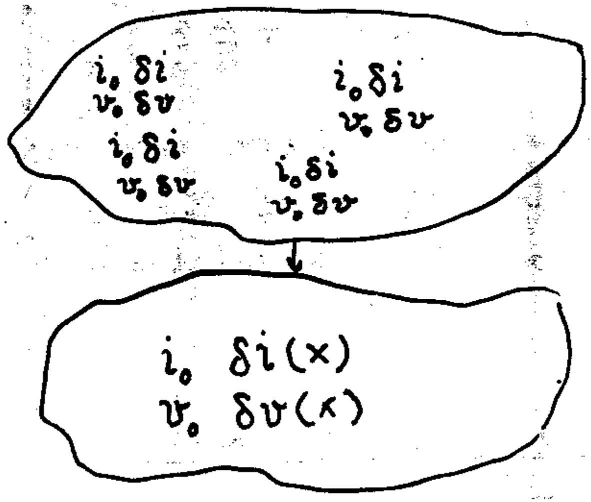
SPATIAL VARIATIONS

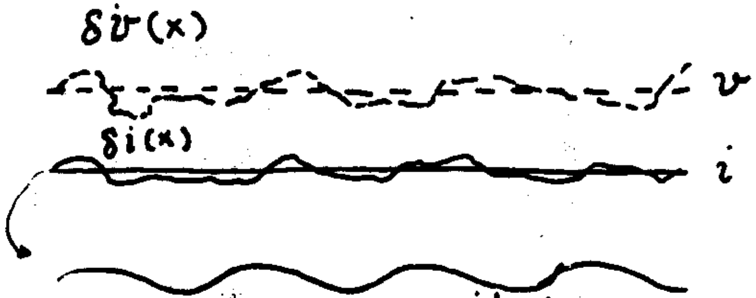
$\beta_i , \beta_v \to$ Const.



$C_- = i - v$

3. DIFFUSION AND STABILITY



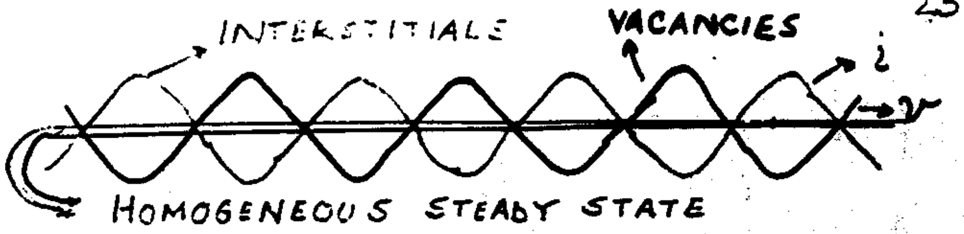


$$i = i_0 + \delta i' e^{ikx} e^{\omega t} \qquad k = \frac{2\pi}{\lambda}$$

$$\frac{di}{dt} = K - \beta_i i - \alpha i v + D_i \nabla^2 i$$

$$\frac{dv}{dt} = K - \beta_v v - \alpha i v + \underbrace{D_v \nabla^2 v}_{\text{Diffusion term}}$$

β and β = Constant



$$\frac{di}{dt} = K_i - \beta_i i - \alpha i v + D_i \nabla^2 i$$

$$\frac{dv}{dt} = K_v - \beta_v v - \alpha i v + D_v \nabla^2 v$$

steady state solution can be obtained from $\frac{d(i,v)}{dt} = K_{(i,v)} - \beta_{i,v}(i,v) - \alpha i v = 0$

$$\boxed{\begin{array}{l} \text{Homogeneous Steady State } (i_0, v_0) \\ i = i_0 + \delta i(\bar{x},t) = i_0 + \delta i' e^{+\omega t} e^{i\underline{k}\cdot\underline{r}} \\ v = v_0 + \delta v(\bar{x},t) = v_0 + \delta v' e^{+\omega t} e^{i\underline{k}\cdot\underline{r}} \end{array}}$$

$$\frac{d}{dt}\begin{pmatrix} \delta i(\vec{r},t) \\ \delta v(\vec{r},t) \end{pmatrix} = \begin{pmatrix} -\beta_i - \alpha v + D_i \nabla^2 & -\alpha i \\ -\alpha v & -\beta_v - \alpha i + D_v \nabla^2 \end{pmatrix} \begin{pmatrix} \delta i(\vec{r},t) \\ \delta v(\vec{r},t) \end{pmatrix}$$

substituting
$\delta i(\vec{r},t) = \delta i' e^{\omega t} e^{i\underline{k}\cdot\underline{r}}$
$\delta v(\vec{r},t) = \delta v' e^{\omega t} e^{i\underline{k}\cdot\underline{r}}$

we get.

$$\begin{pmatrix} -\beta_i-\alpha v_0-D_i k^2-\omega & -\alpha i_0 \\ -\alpha v_0 & -\beta_v-\alpha i_0-D_v k^2-\omega \end{pmatrix}\begin{pmatrix}\delta i' \\ \delta v'\end{pmatrix}=0$$

A solution exists only if

$$\det\begin{vmatrix} -\beta_i-\alpha v_0-D_i k^2-\omega & -\alpha i_0 \\ -\alpha v_0 & -\beta_i-\alpha i_0-D_v k^2-\omega \end{vmatrix}=0$$

or

$$\boxed{\begin{aligned} &\omega^2+\omega\left[k^2(D_i+D_v)+(\beta_v+\beta_i+\alpha v_0+\alpha i_0)\right] \\ &\quad+\left[k^4 D_i D_v+k^2(D_v\alpha v_0+D_i\alpha i_0+D_i\beta_v+D_v\beta_i) \right. \\ &\quad\left.+(\beta_i\alpha i_0+\beta_v\alpha v_0+\beta_i\beta_v)\right]=0 \end{aligned}}$$

We observe that all the terms are positive for $k^2>0$

1. $\therefore$ $\omega=\begin{cases}\lambda_1<0 \\ \lambda_2<0\end{cases}$ and there is therefore no instability possible.

2. The only condition for which $\omega=0$ is $\beta_i=\beta_v=0$ and $k^2=0$ thus the only stable state is the homogeneous state

3. If we put $\omega=0$ we get an

equation

$$k^4 D_v D_i+k^2(D_v\alpha v+D_i\alpha i+D_i\beta_v+D_v\beta_i)+(\beta_i\alpha i+\beta_v\alpha v+\beta_i\beta_v)=0$$

We observe that there are no physical acceptable values of the parameters D, α, β for which a solution $k^2>0$ exists.

4 RADIATION INDUCED INSTABILITY – BASIC APPROACH.

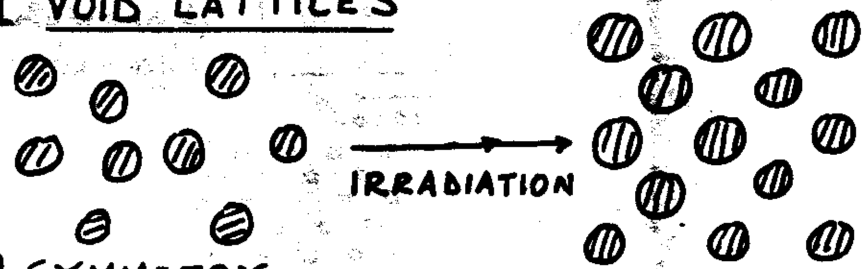
There are two approaches which can be followed to obtain the conditions for which an instability arises

1 : Coupling with microstructural Defects

2 : More careful examination of the defect diffusion co-efficients and fluxes.

EXPERIMENTAL OBSERVATIONS ON MICROSTRUCTURAL ORDERING AND 'SPINODAL' TYPE' ORDERING IN ALLOYS DURING IRRADIATION

1 VOID LATTICES



① SYMMETRY

HAVE THE SAME SYMMETRY AS THAT OF THE HOST LATTICE

Mo, Nb, Ta, W, Cr	bcc
Al, Ni	fcc
Mg	hcp

② RADIATION

Produced by cascade producing radiation → neutrons, ion
seldom formed by electron irradiation

③ DOSE RATE EFFECT

Not very sensitive to dose rate.

④ DOSE DEPENDENCE

There seem to be some evidence of a critical dose for ordering but the values are very different from metal to metal. Also some threshold gas concentration can influence the value

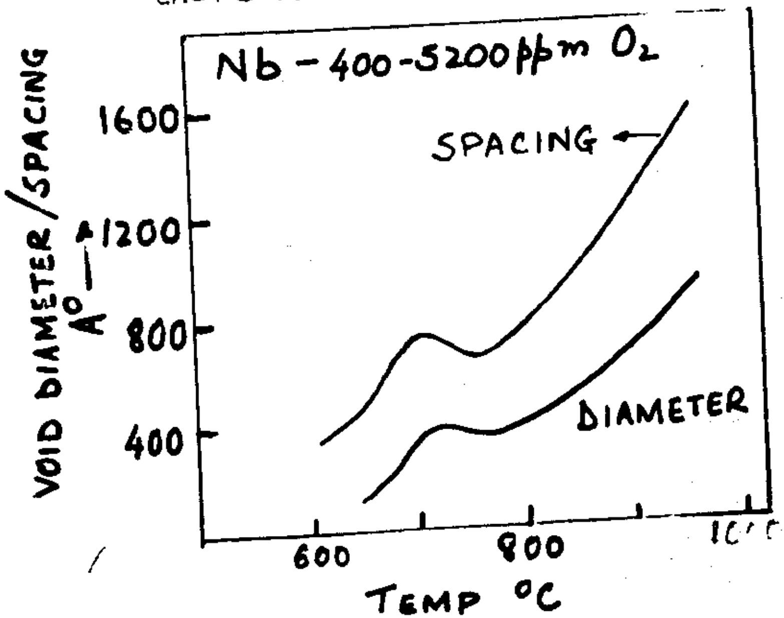
Ni ~ 350 - 400 dpa
Al ~ 40 - 80 dpa
Nb, Mo ~ 5 dpa

⑤ Alloy COMPOSITION

Weak dependence.

⑥ Temperature dependence

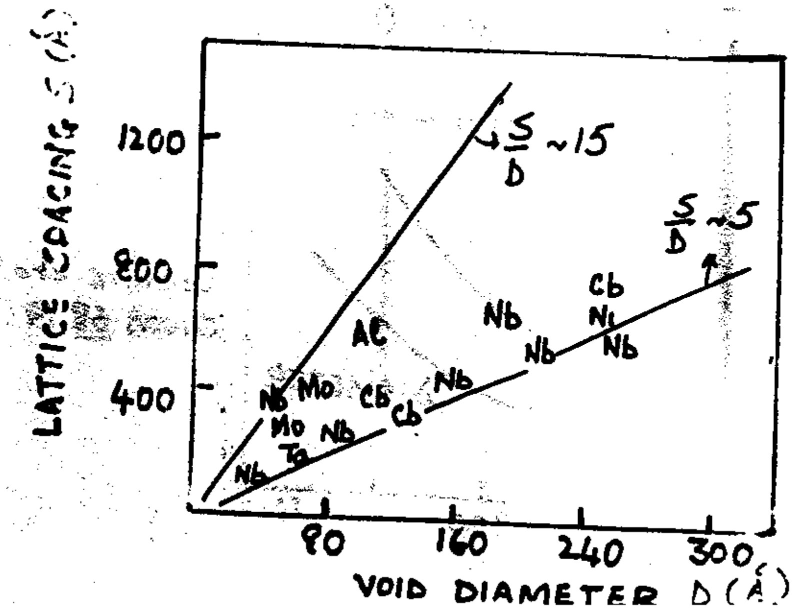
- Very few systematic investigations
- Void diameter & void spacing increase with temperature.



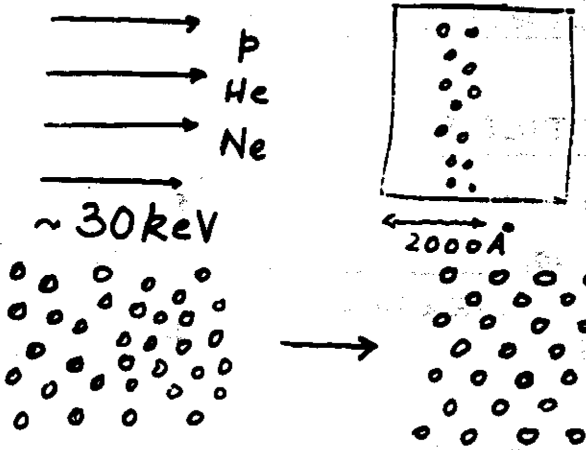
Loomis et al
JNM 68 19 (197

7 SOME TYPICAL DATA ON VOID LATTICES

MATERIAL	PROJECTILE Energy MeV	TEMP. °C	DOSE d.p.a	SPACING Å	DIAMETER Å
Ta	n >·1	585	20	205	61
W	n >·1	550	16	195	30
	n >·1	880	15	250	40
Mo	n >·1	585	36	265	64
	N 2	870	100	220	40
Nb	n >·1	790	34	665	186
	Ni 5	800	5	350	45
Ni	Ni 5	525	360	620	250
Al	Al ·4	50	40	600	100
Mg	n >·1	55	3-6	imperfect	



2 FORMATION OF GAS BUBBLE SUPERLATTICES IN METALS



- Room Temp
- 30 – 70 Å latt parameter
- diameter ~2

1. SIMILARITY WITH VOID LATTICE

1. Crystallographic symmetry and orientat is the same as the host matrix
2. Bubble Lattice spacing/diameter ~5-15
3. Stages of ordering are similar

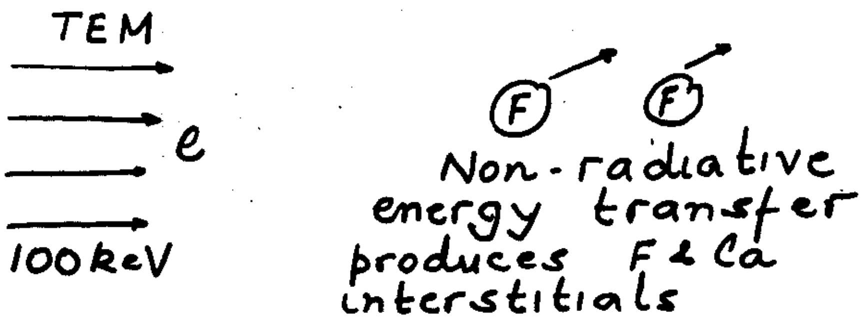
2. DIFFERENCES WITH VOID LATTICE

1. Lattice spacing & diameter ~1/10 void Latt.
2. Formed at room temperature
3. Temperature is lower than vacancy migration temperature
4. No strong temperature dependence
5. No significant cascade effects are possible at 30 keV.

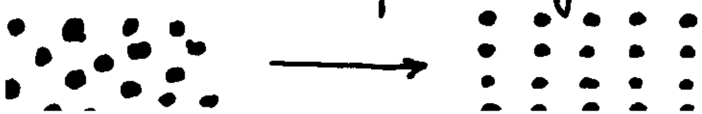
SOME TYPICAL BUBBLE LATTICE DATA

terial	Projectile Energy KeV	Temp °C	Dose ions/cm²	Spacing Å	Dia. Å
	He 36	RT	1×10^{17}	37	
		500	2×10^{17}	36	
		700	2×10^{17}	35	~24
	He 25	250	4.5×10^{17}	32	
	He 60	400	5×10^{17}	36	
	Ne 100	550	1×10^{17}	36	—
	He 30	RT	4×10^{17}	77	20
	H 16	RT	1.3×10^{17}	Not well defined	
316	He 30	RT	4×10^{17}	65	20
	He 30	RT	1.5×10^{18}	90	30

ORDERING IN COMPOUNDS CaF_2/SrF_2



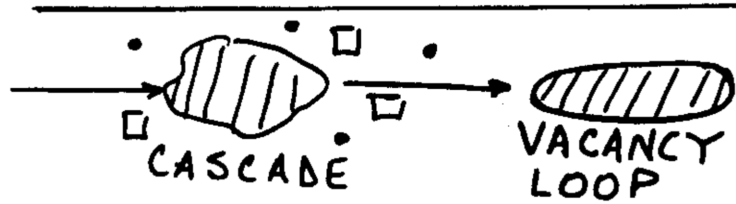
Ca → precipitates are formed which subsequently order

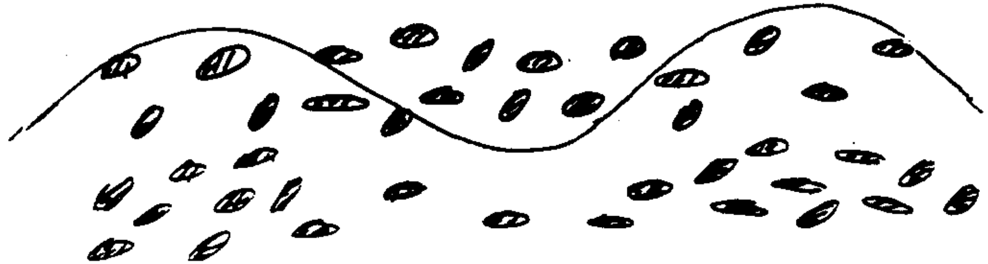


IMPORTANT FEATURES ARE

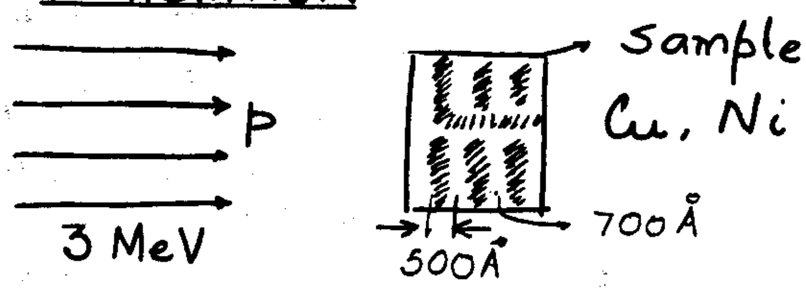
1. Ca ppts are coherent with CaF_2 structure and form a perfect lattice : A less perfect lattice is formed in SrF_2 because of a small difference in the lattice parameter of Sr and SrF_2. No ordering is observed in BaF_2 due to incoherent precipitation
2. Supperlattice in the flourite is simple cubic though the overall structure is f.c.c. However the flourite sublattice is simple cubic
3. Room Temp/spacing ~190 - 280 Å and diameter 30 - 40 Å.

4 ORDERING OF VACANCY LOOPS

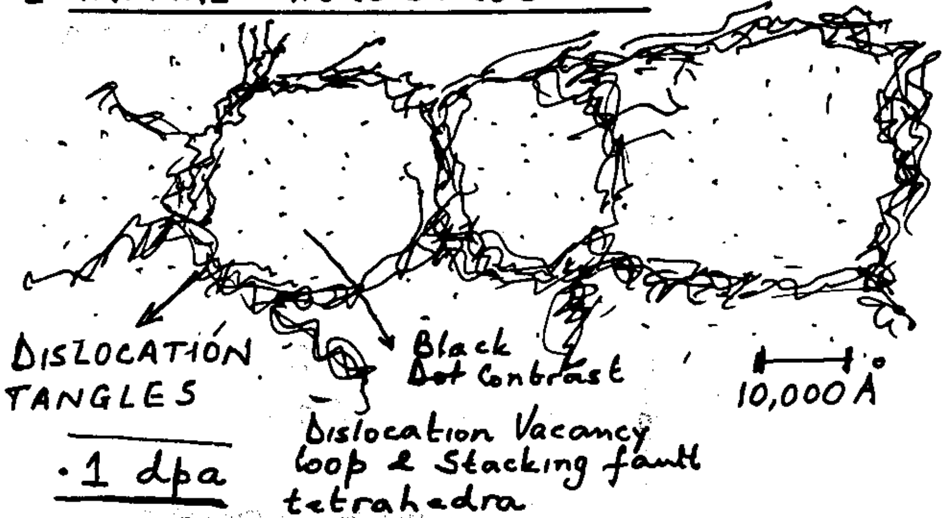


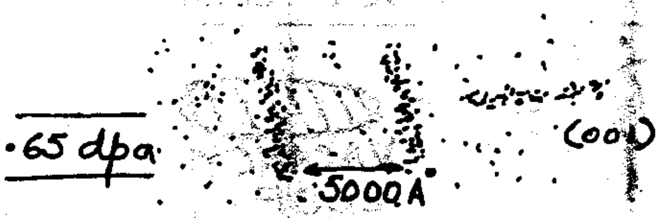


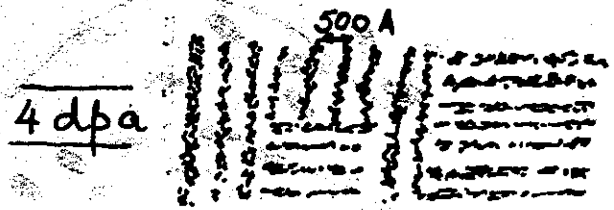
5 DISLOCATION PATTERNING DURING IRRADIATION



1 INITIAL MICROSTRUCTURE



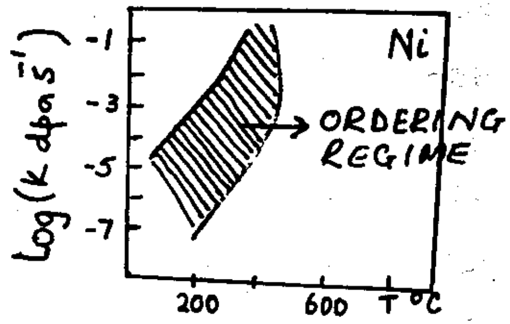




1 NATURE OF DEFECT WALLS

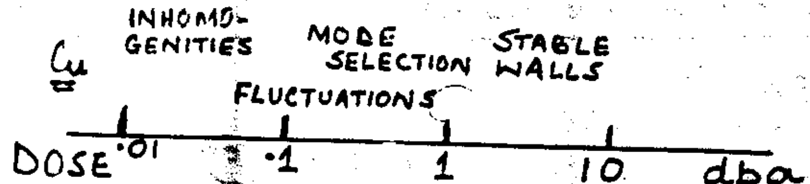
High concentration of dislocations, dislocation loops (vacancy type), stacking fault tetrahedra & a few voids

2 TEMPERATURE AND DOSE RATE REGIME

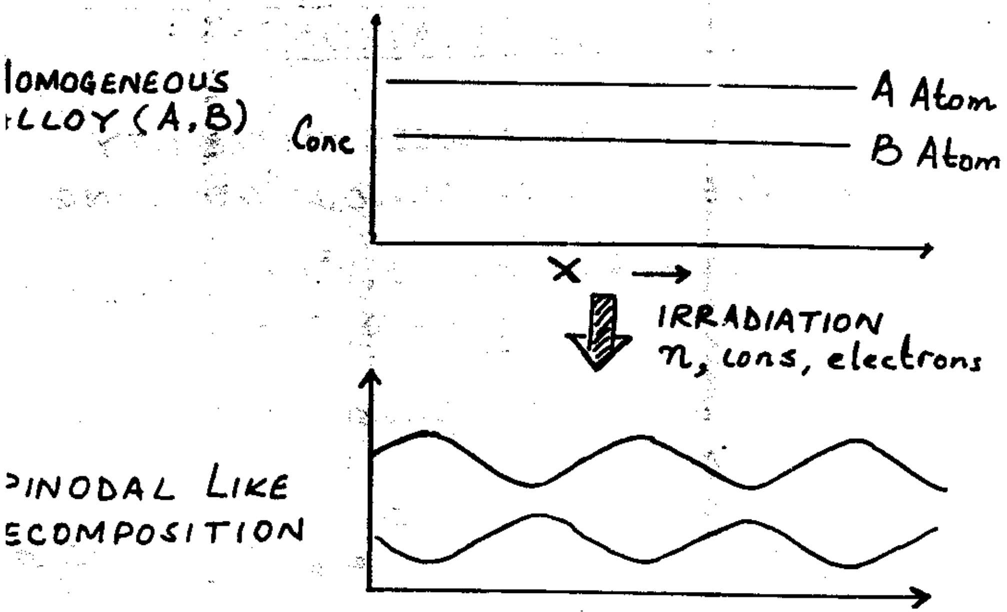


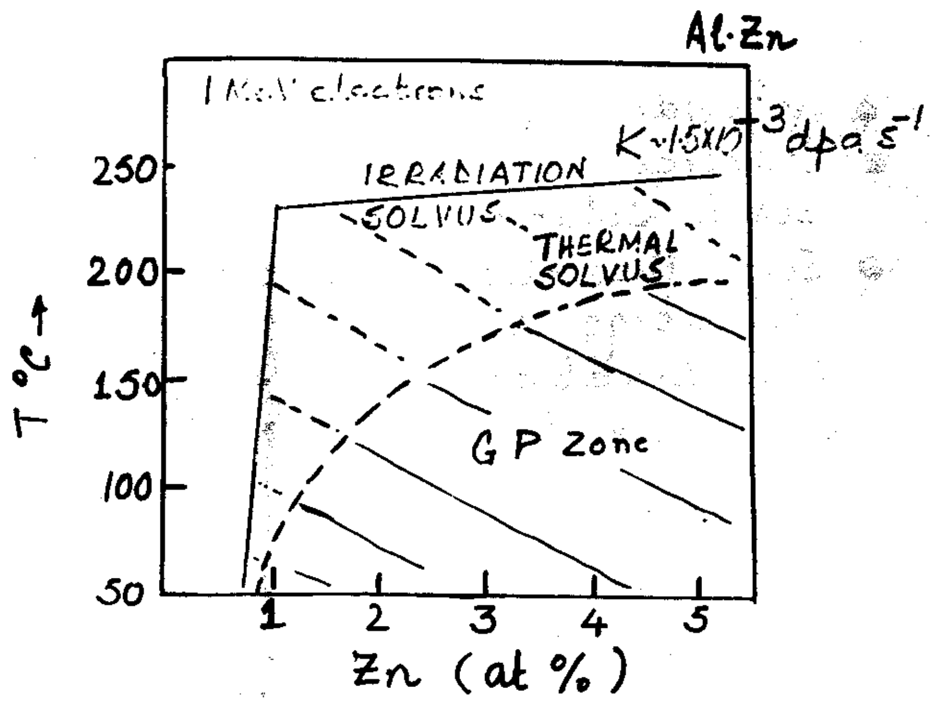
Jager et al
Non-linear Phenomena in materials Science
Trans Tech Publications
Eds Kubin & Martin

3 DOSE REGIMES



SPINODAL TYPE ORDERING OF ALLOYS





MPORTANT SYSTEMS

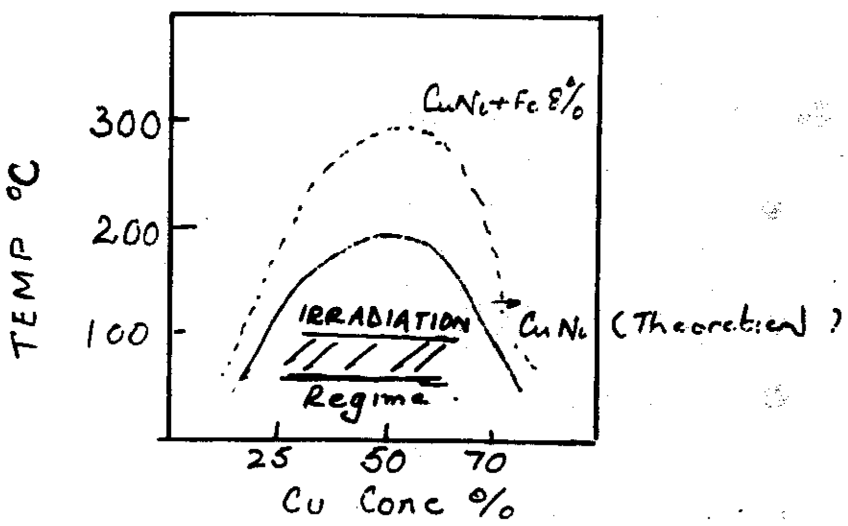
- Al-Zn (2%), Ni Be, Cu Be, W Re
- Cu Ni — Cu Ni Fe.
- Fe Ni (35%), Fe. Cr-Ni

xperimental results.

Al-Zn Alloy

Suitable quenching and aging treatments produce Zn rich G.P. zones in Al rich Al-Zn alloys. — Vacancies are needed for mass transport which can also be provided by irradiation

- Cu Ni



Cu-Ni alloy ..

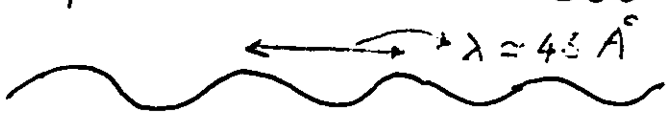
- No evidence for thermal decomposition
- Classical example of a complete solid solution.
- Some theoretical suggestions exist indicating a possible spinodal but kinetics is too sluggish at these low temperatures.

Irradiation

electron irradiation 2-3 MeV

Flux 1.6×10^{20} ions Dose $\sim 1.6 \times 10^{-2}$ dpa

Temperature 100°C ~ 300°C



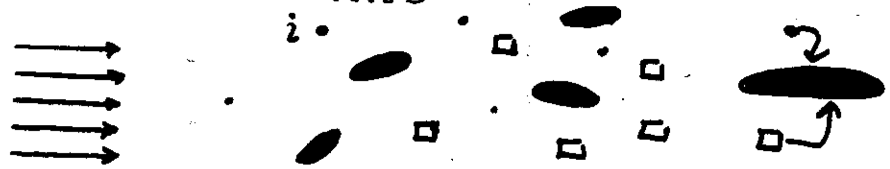
- Fe-Ni-Cr Alloys Ni ~ 30-75%
  - No evidence of thermal spinodal decomposition in these alloys.
  - $\boxed{\text{Ni}}$ — $\boxed{\text{Fe, Cr}}$
  - λ sensitive to temperature (400-650°C) λ increases with temperature
  - 5 MeV Ni^+ → till 100 dpa / Neutron Irrad.
  - Insensitive to displacement rates.

B. MICROSTRUCTURAL ORDERING DURING IRRADIATION

1 DEFECT REACTION INDUCED INSTABILITY: EXAMPLE OF SPONTANEOUS ORDERING.

$$\left.\begin{aligned} di/dt &= k_i - \beta_i i + D_i \nabla^2 i \\ dv/dt &= K_v - \beta_v v + D_v \nabla^2 v \end{aligned}\right\} \quad \alpha = 0$$

We examine the physical processes in more detail



$k_i = K$ $\quad K_v = K(1-\epsilon)$ $\quad K_{vac\ loop} = \epsilon K$

$\beta_i = z_i D_i \rho$ $\quad \beta_v = D_v \rho$

Dynamics of the vacancy loop

$$\frac{dQ}{dt} = \epsilon K + (D_v v - z_i D_i i)\rho$$

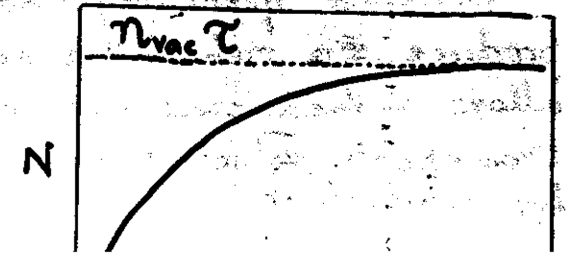
$Q = \frac{4\pi}{3} N r^3$ $\quad \rho = 2\pi N r$

$\rho = f(Q)$

$$\delta\rho = \frac{\partial f}{\partial Q}\delta Q$$

$$= f'\delta Q$$

N = Constant $= n_{vac}\tau$



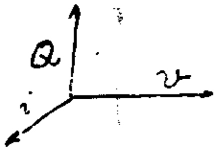
$$\frac{di}{dt} = K - Z_i D_i \rho i + D_i \nabla^2 i$$

$$\frac{dv}{dt} = K(1-\epsilon) - D_v \rho v + D_v \nabla^2 v$$

$$\frac{dQ}{dt} = \epsilon K + D_v \rho v - Z_i D_i \rho i$$

We immediately observe that one of the modes is soft for $k^2 \to 0$ since

$$\frac{dQ}{dt} = \frac{d}{dt}(i - v) \qquad \nabla^2 \text{ terms} = 0$$



We now examine the stability condition for this equation.

$$\begin{pmatrix} i \\ v \\ Q \end{pmatrix} = \begin{pmatrix} i_0 \\ v_0 \\ Q_0 \end{pmatrix} + \begin{pmatrix} \delta i' \\ \delta v' \\ \delta Q' \end{pmatrix} e^{\omega t} e^{i\underline{k}\cdot\underline{r}}$$

$$\det \begin{vmatrix} -(Z_i D_i \rho + D_i k^2) - \omega & 0 & -\frac{Kf'}{\rho} \\ 0 & -(D_v \rho + D_v k^2) - \omega & -\frac{K(1-\epsilon)f'}{\rho} \\ -Z_i D_i \rho & D_v \rho & -\frac{\epsilon K f'}{\rho} - \omega \end{vmatrix}$$

Solving the above determinant we get

$$\omega^3 + \omega^2 g_2(k^2) + \omega g_1(k^2) + g(k^2) = 0$$

A soft mode can arise if $g(k^2) = 0$

$$g(k^2) = \left[-\frac{\epsilon K}{\rho} + \left\{ \frac{(\epsilon Z + (Z-1))Kk^2 + \epsilon K Z \rho}{(Z\rho + k^2)(k^2 + \rho)} \right\} \right] f'$$

$$= 0$$

$$k^2 = 0$$

$$k_c^2 = \left\{ \frac{(Z-1) - \epsilon}{\epsilon} \right\} \rho$$

We therefore obtain the condition that a bifurcation to a periodic structure takes place only if

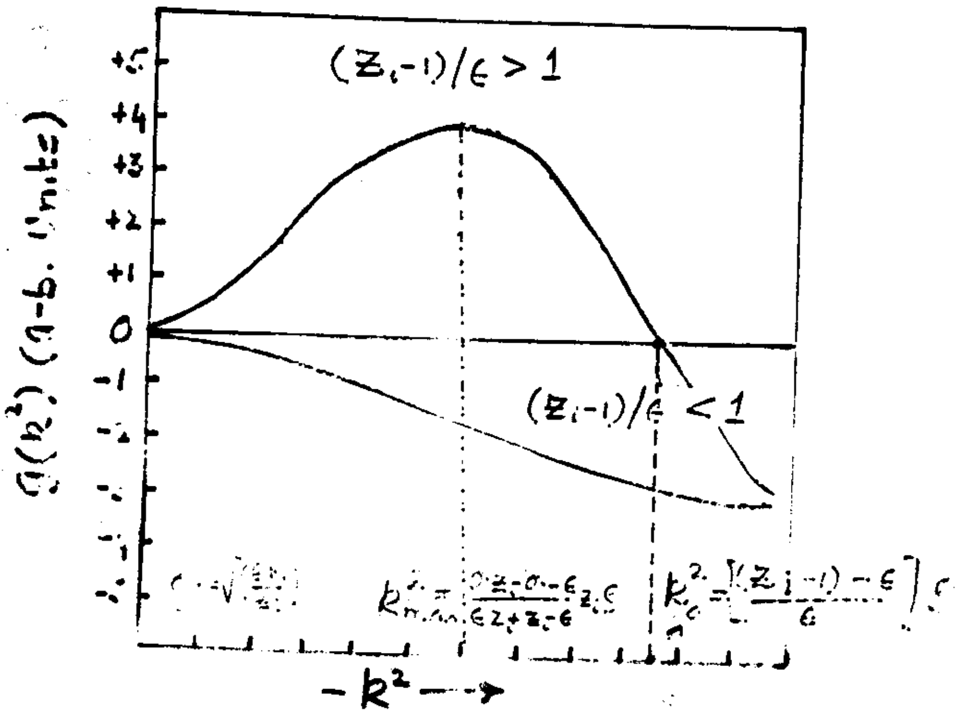
$$\frac{(Z-1)}{\epsilon} > 1$$

$$\therefore\ k^2 > k_c^2 \qquad g(k^2) < 0 \qquad \omega_3 < 0$$

$$k^2 < k_c^2 \qquad g(k^2) > 0 \qquad \omega_3 > 0$$

$\therefore$ A definite periodic structure will emerge.

PLOT OF THE AMPLIFICATION FACTOR $g(k^2)$



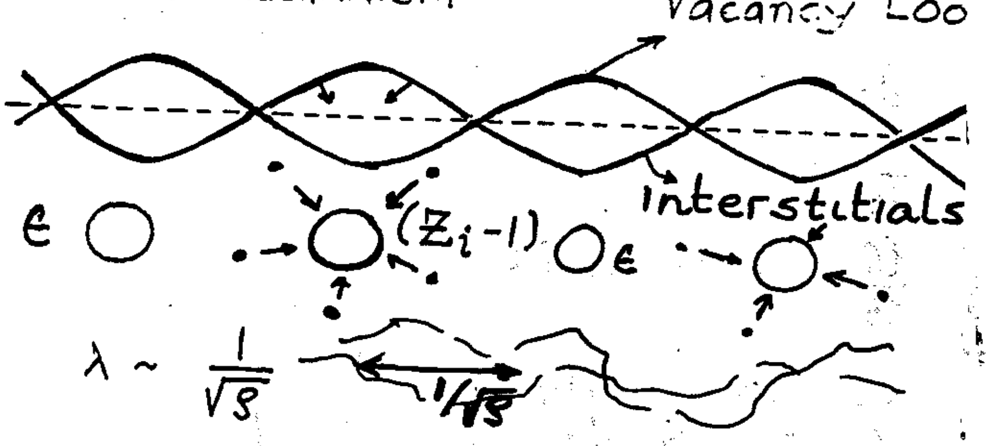
$(Z_i - 1) \sim .08$ $\qquad \epsilon \sim .04$

$k_c^2 \sim \frac{1}{2}\rho \qquad \rho = \frac{2\pi}{6} \, N \, r$, with $N = 2\times10^{18}\,cm^{-3}$, $r = 2\times10^{-7}\,cm$

$\sim 10^{12}\,cm^{-2} \qquad \approx 2\times10^{12}\,cm^{-2}$

$\lambda \sim \frac{2\pi}{k} \approx \underline{600\,Å}$

- BASIC MECHANISM



- MAIN FEATURES OF THE MODEL.

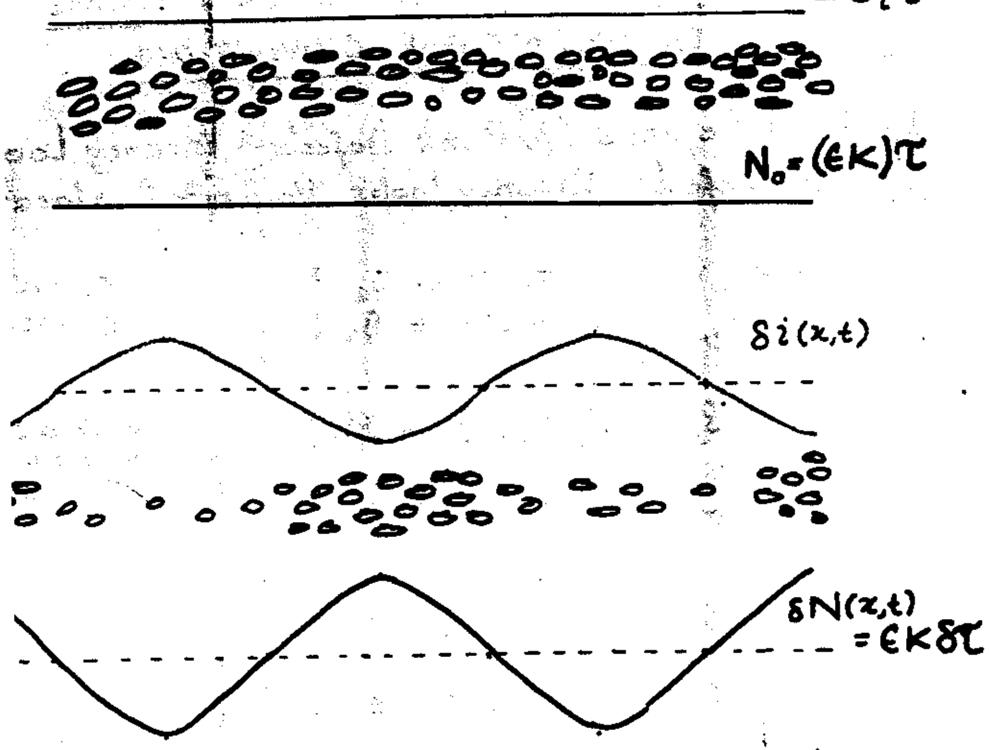
1. Approximate wave length scale
2. Temperature independence
3. Identifies the drive parameter for the bifurcation as $(Z_i-1)/\epsilon$.

- <u>LIMITATION OF THE MODEL</u>!

Spontaneous bifurcation which is unphysical.

PHYSICAL MECHANISM

$$i_0 = \frac{K}{ZD_i\rho}$$



$$\begin{bmatrix}\delta i\\ \delta v\\ \delta Q\end{bmatrix} = \left[\underset{\approx}{G}(k^2)\right]\begin{bmatrix}\delta i\\ \delta v\\ \delta Q\end{bmatrix}$$

Solutions Exist

$$\text{Det}\,\left|\underset{\approx}{G}(k^2) - \underset{\approx}{I}\,\omega\right| = 0$$

$$\frac{d}{dt}\begin{bmatrix}\delta p_1\\ \delta p_2\\ \delta p_3\end{bmatrix} = \left[\underset{\approx}{U}^{-1}\underset{\approx}{G}(k^2)\underset{\approx}{U}\right]\begin{bmatrix}\delta p_1\\ \delta p_2\\ \delta p_3\end{bmatrix} \qquad \begin{bmatrix}\delta p_1\\ \delta p_2\\ \delta p_3\end{bmatrix} = U^{-1}\begin{bmatrix}\delta i\\ \delta v\\ \delta Q\end{bmatrix}$$

$$\downarrow$$

$$\begin{bmatrix}\omega_1(k^2) & & 0\\ & \omega_2(k^2) & \\ 0 & & \omega_3(k^2)\end{bmatrix} \longrightarrow = 0$$

$p_1 = e^{\omega_1(k^2)t}$ Mode δp_3 is soft

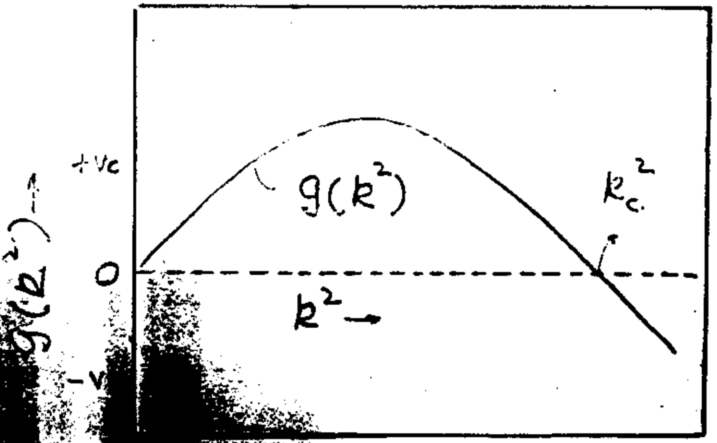
$$\text{Det}\,\left|\underset{\approx}{G}(k^2) - \underset{\approx}{I}\,\omega\right| = 0$$

$$\omega^3 + \omega^2 g_2(k^2) + \omega g_1(k^2) + g(k^2) = 0$$

$$g(k^2) = \omega_1\omega_2\omega_3$$

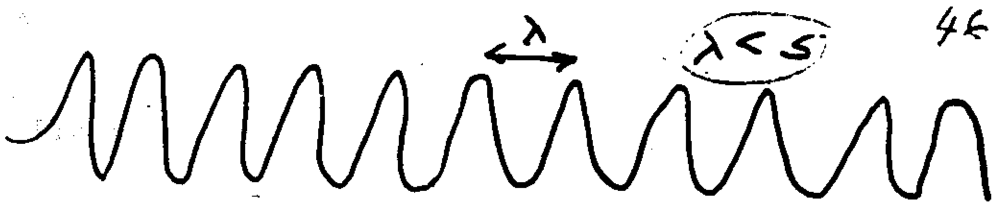
$\omega_1 < 0$ $\omega_2 < 0$ $\therefore \omega_1\omega_2 > 0$

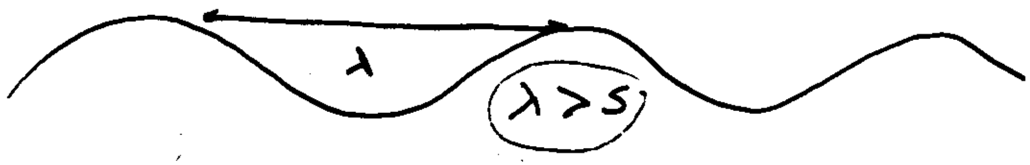
$g(k^2) > 0$	$\omega_3 > 0$
$g(k^2) = 0$	$\omega_3 = 0$
$g(k^2) < 0$	$\omega_3 < 0$



$$\delta Q = U_1(k^2)\underset{e^{\omega_1 t}}{p_1} + U_2(k^2)\underset{e^{\omega_2 t}}{p_2} + U_3(k^2)\underset{e^{\omega_3(k^2)t}}{p_3}$$

$$U_3(k^2)\,e^{\omega_3(k^2)t}\,e^{i\mathbf{k}\cdot\mathbf{r}}$$





$$k^2 = \left(\frac{\epsilon - \Delta Z}{\epsilon}\right)\rho$$

$\underline{\epsilon > \Delta Z}$ $\qquad\qquad$ $\epsilon > 0$

$$\frac{dQ}{dt} = \epsilon K + (D_v v - Z_i D_i i)\rho$$

$$\frac{d\,\delta Q}{dt} = (D_v \bar{v} - Z D_i i)\,\delta\rho + \rho(D_v \delta v - Z_i D_i \delta i)$$

$$\delta v = \frac{K(1-\epsilon)\,\delta\rho}{D_v \rho(\rho + k^2)} \qquad \bar{v} = \frac{K(1-\epsilon)}{D_v \rho}$$

2 EFFECT OF ADDITIONAL SINK TERMS ON THE BIFURCATION CONDITION.

(1) Point Defects (2) Point Defects & Vacancy Loo[ps]
(3) Point Defects, Vacancy loops, Voids & Dislocat[ions]

$$\left.\begin{aligned} di/dt &= K_i - \beta_i i - \alpha i v + D_i \nabla^2 i \\ dv/dt &= K_v - \beta_v v - \alpha i v + D_v \nabla^2 v \end{aligned}\right\} \quad \begin{aligned} K_i &= K \\ K_v &= K(\end{aligned}$$

$$\begin{aligned} \beta_i &= D_i \rho_S + Z_i D_i(\rho_L + \rho_D) \\ \beta_v &= D_v(\rho_S + \rho_L + \rho_D) \end{aligned} \quad \left\{\begin{aligned} &S \to \text{Voids} \\ &L \to \text{Vac. Lo} \\ &D \to \text{Disloc.} \end{aligned}\right.$$

$$dQ_S/dt = \rho_S(D_v v - D_i i)$$

$$dQ_L/dt = \epsilon K + \rho_L(D_v v - Z_i D_i i)$$

$$dQ_D/dt = \rho_D(Z_i D_i i - D_v v)$$

Before doing the stability analysis we examine the nature of the homogeneo[us] solution

$$\frac{di}{dt} - \frac{dv}{dt} = \frac{dQ_S}{dt} + \frac{dQ_L}{dt} - \frac{dQ_D}{dt}$$

$$\omega \to 0 \qquad k^2 \to 0$$

we set

$$\frac{di}{dt} = \frac{dv}{dt} = 0 \quad \text{and substitute in}$$

We can now eliminate the fast modes using the relations

$$i_o = \frac{K}{D_i\, B} \qquad v_o = \frac{K(1-\epsilon)}{D_v\, A}$$

$$\delta i = -\frac{K(\delta\rho_s + z\,\delta\rho_L + z\,\delta\rho_D)}{D_i B\,(B + k^2)}$$

$$\delta v = -\frac{K(1-\epsilon)(\delta\rho_s + \delta\rho_L + \delta\rho_D)}{D_v A\,(A + k^2}$$

$$A = (\rho_s + \rho_L + \rho_D)$$

$$B = \rho_s + z(\rho_L + \rho_D)$$

Evaluating δQ_s, δQ_L and δQ_D we get

$$\begin{bmatrix} Q_s \\ Q_L \\ Q_D \end{bmatrix} = \begin{bmatrix} (\rho_L+\rho_D)R_{(1)} + k^2 R_{(0)} & -\rho_s R_{(1)} & -\rho_s R_{(1)} \\ -\rho_L R_{(1)} & \rho_s R_{(1)} + \rho_D R_{(2)} + k^2 R_{(1)} & -\rho_L R_{(2)} \\ -\rho_D R_{(1)} & -\rho_D R_{(2)} & \rho_s R_{(1)} + \rho_L R_{(2)} + k^2 R_{(1)} \end{bmatrix} \begin{bmatrix} \frac{\partial \rho_s}{\partial Q_s}\delta Q_s \\ \frac{\partial \rho_L}{\partial Q_L}\delta Q_L \\ \frac{\delta \rho_D}{\partial Q_D}\delta Q_D \end{bmatrix}$$

where

$$R_{(n)} = \frac{K}{A(A+k^2)} - \frac{z_i^n K(1-\epsilon)}{B(B+k^2)}$$

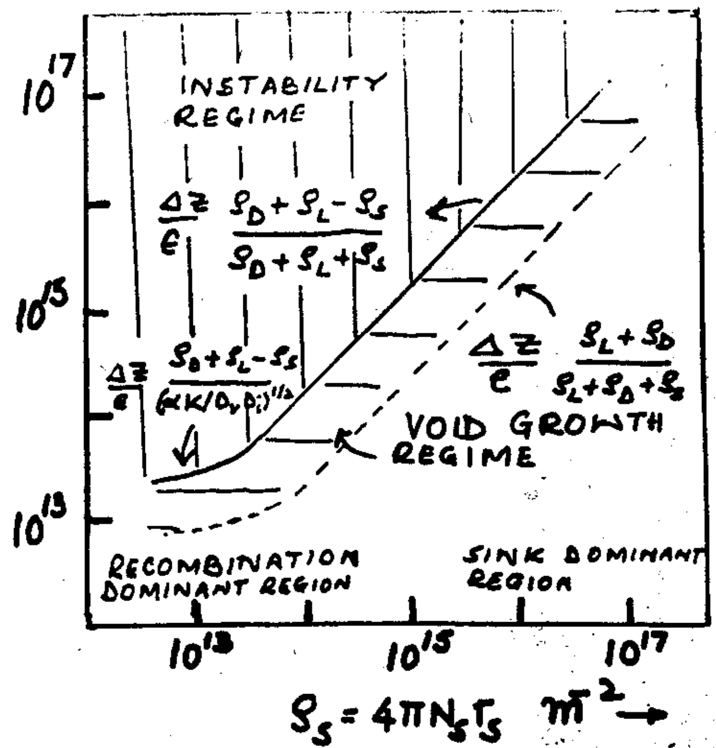
$$R_{(1)} = (Z_i - 1)K\,\frac{(\rho_L+\rho_D)^2 - \rho_s^2 - k^2\rho_s}{AB(A+k^2)(B+k^2)} - \frac{\epsilon K}{A(A+k^2)}$$

CONDITION FOR SPATIAL INSTABILITY.

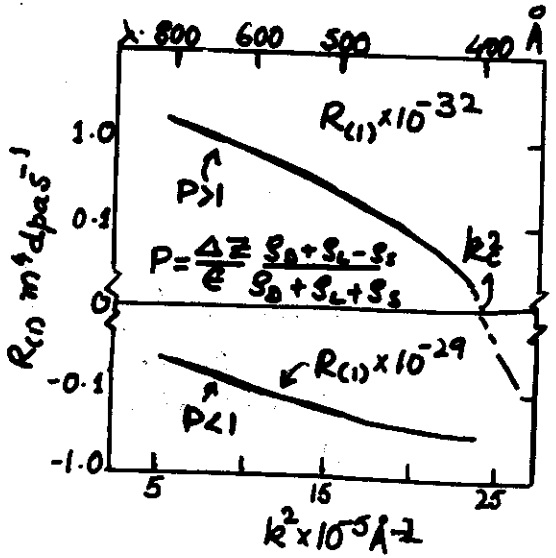
$$R_{(1)} > 0$$

$$\frac{Z_i - 1}{\epsilon}\;\frac{\rho_D + \rho_L - \rho_s}{\rho_D + \rho_L + \rho_s} > 0$$

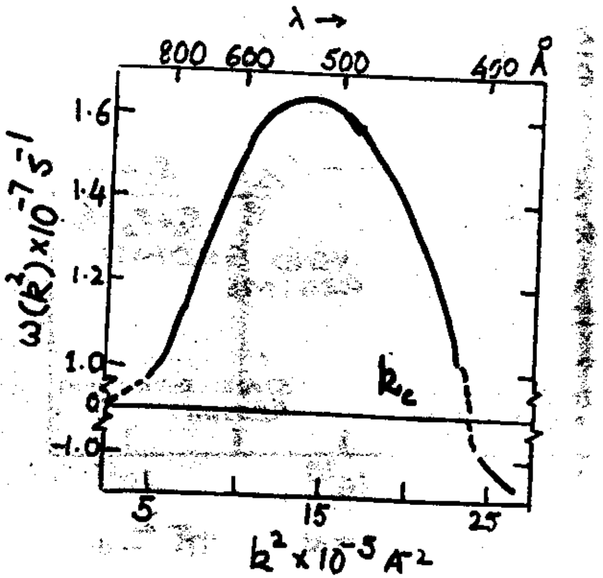
- We observe that by addition of neutral sinks like voids there is a minimum threshold dislocation density requiered and no spontaneous bifurcation occurs.



PLOT OF $R_{(1)}$ AS A FUNCTION OF k^2



PLOT OF ONE OF THE ROOTS $\omega(k^2)$.



EFFECT OF TEMPERATURE ON VOID LATTICE FORMATION. — inclusion of thermal emission terms

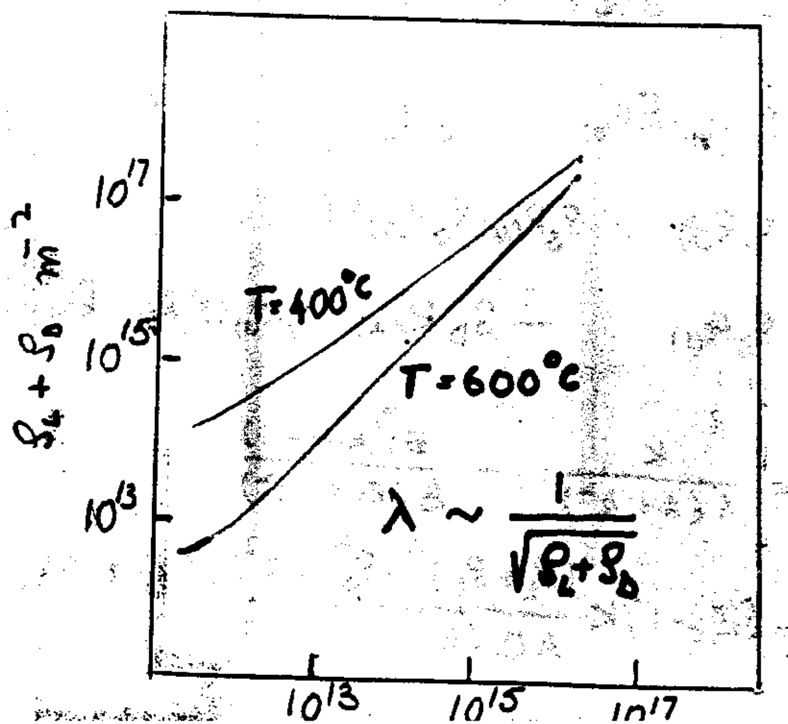
$$v_{th} = e^{-E_f/kT}$$

$$\left(\frac{dQ_s}{dt}\right)_{th} = -\rho_s D_v v_{th}\, e^{[(\frac{2\gamma}{r_s} - P_g)b^3/k_B T]}$$

$$\left(\frac{dQ_L}{dt}\right)_{th} = -\rho_L D_v v_{th}\, e^{[(\gamma_{SF} + F_{el}(r_L))b^2/k_B T]}$$

$$\left(\frac{dQ_D}{dt}\right)_{th} = +\rho_D D_v v_{th}$$

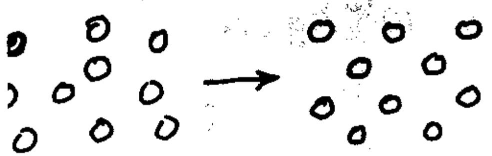
$$K_v = K(1-\epsilon) + K_{th}$$

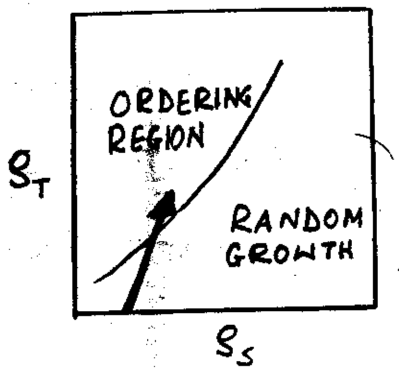


SUMMARY OF THE RESULTS FOR VOID LATTICE FORMATION

- Control Parameter

$$\frac{\lambda}{\varepsilon} \equiv \frac{\rho_D + \rho_L - \rho_S}{\rho_D + \rho_L + \rho_S} > 1$$





Wave Length or Spacing

$\lambda \sim (\text{sink strength})^{-1/2}$

Temperature dependence of λ

$\lambda \uparrow$ as $T \uparrow$

Dose Rate dependence

weak dependence

- Critical Dose

Decided by the control parameter

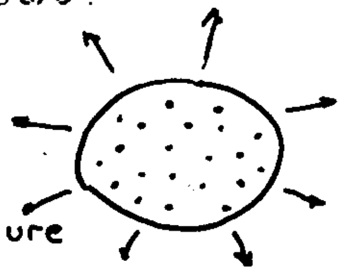
2 RELATED MODELS FOR ORDERING — BUBBLE SUPERLATTICE FORMATION.

- Bubble lattice is formed by implantation of 20 – 40 keV (H / He) ions
- At these energies there is no cascade production and hence no vacancy loops. We have to therefore look for an alternate process for an instability to develop giving rise to a periodic structure.

Process of bubble growth.

(v, g, P)

vacancies gas atoms pressure



Volume $V_b = v\Omega = \frac{4\pi}{3} r_1^3$

Surface Energy $\Big\}\ \Gamma_1 = S(v)\Gamma = 4\pi r_1^2 \Gamma$

Let us assume that the bubble acquires an additional δg gas atoms which results in further overpressurizati

$$(v, g+P) + \delta g \longrightarrow (v, g+\delta g, P+\delta P)$$

The over pressurized bubble relaxes by giving out an interstitial and increases the volume by Ω.

$$(v, g+\delta g, P+\delta P) \rightarrow (v+1, g+\delta g, P)+i$$

The new volume and surface energy become

$$V_b(v+1) = \frac{4\pi}{3} r_2^3 \quad \& \quad \Gamma_2 = \Gamma_1 + \delta\Gamma = 4\pi r_2^2 \Gamma$$

Conserving the energy, we have (E_i^F = interstitial formation energy)

$$V_b(v)\,\delta P = \delta g\, k_B T = \Omega P + \delta\Gamma + E_i^F$$

or
$$\delta g = \frac{\Omega P + \delta\Gamma + E_i^F}{k_B T}$$

Let a fraction αK gas atoms be injected in the metal per second. Then

$$\frac{dg}{dt} = \alpha K$$

$\therefore$ No of interstitials produced per sec. will be

$$\epsilon = \frac{1}{K\,\delta g}\frac{dg}{dt} = \frac{\alpha k_B T}{\Omega P + \delta\Gamma + E_i^F}$$

Bias Factor:

$$Z_d = 1 - \frac{3\mu_d\,\delta P^2}{56\, k_B T\, G^2} \qquad d = v \text{ or } i$$

μ_d = elastic polarizability $\begin{cases} \mu_v \approx -15\,\text{eV} \\ \mu_i \approx -150\,\text{eV} \end{cases}$

$$\delta P = \left\{\left(P - \frac{2\Gamma}{r}\right)\right\} \approx 2\,\text{GPa}$$

G = shear modulus $\simeq 10^{10}\,\text{kg/m}^2$

$k_B T \approx .025\,\text{eV}$

$Z_v = 1.013 \qquad Z_i = 1.13$

$\Delta Z \simeq 11\%$ (Wolfer et al ASTM STP 570 (1975) 233)

STABILITY ANALYSIS

$$\frac{dv}{dt} = K - D_v \rho v + D_v \nabla^2 v$$

$$\frac{di}{dt} = K(1+\epsilon) - Z D_i \rho i + D_i \nabla^2 i$$

$$\frac{dQ}{dt} = (D_v v - Z D_i i)\rho_v$$

$$Q = Q_0 + \delta Q' e^{\omega t} e^{i \mathbf{k}\cdot\mathbf{r}}$$

$$\omega(k^2) = -\frac{\epsilon K}{\rho_0} + \left[\frac{(Z\epsilon + Z - 1)Kk^2 + \epsilon Z K \rho_0}{(Z\rho_0 + k^2)(\rho_0 + k^2)}\right]$$

B PERIODIC DECOMPOSITION IN ALLOYS

- RADIATION ENHANCED PROCESSES
- RADIATION INDUCED MECHANISMS

Reaction Controlled — Diffusion Controlled

RADIATION ENHANCED PROCESSES

Local Conc. fluctuation
$\delta C(x,t) = [C(x,t) - C_o]$

$$\delta C(\underline{x},t) = \sum_k A(\underline{k},t)\, e^{i\underline{k}\cdot\underline{x}}$$

Equation of motion for the amplitudes is $\frac{d}{dt} A(\underline{k},t) = \alpha(\underline{k},t)\, A(\underline{k},t)$

$\alpha(k,t)$. amplification factor.

$$\therefore\ A(\underline{k},t) = \exp\left\{\int_0^t \alpha(\underline{k},t')\,dt'\right\} \cdot A(k,0)$$

If we have a multicomponent system

$$\frac{d}{dt} A_j(\underline{k},t) = \sum S_{jl}\, A_l(k,t)$$

$S_{jl} \rightarrow$ Stability matrix.

behaviour of the alloy will be given by the maximum eigenvalue of the stability matrix S

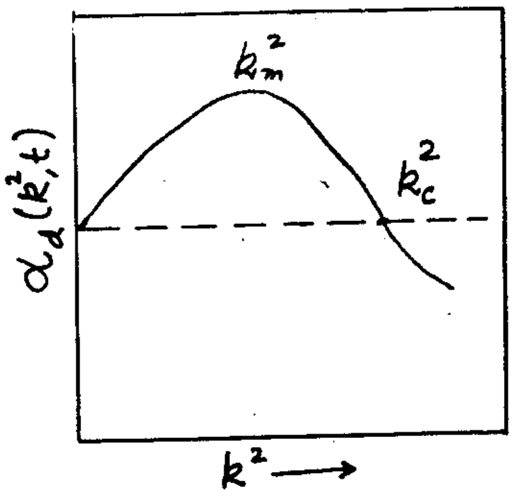
$$\alpha_{eff}(\underline{k}) = \max \omega_j(\underline{k})$$

$$\underset{\approx}{S} = \underbrace{\underset{\approx}{S}_d}_{\text{diagonal}} + \underbrace{\underset{\approx}{S}_{nd}}_{\text{non diagonal}}$$

$$\alpha_{eff} = \alpha_d + \alpha_{nd}$$

α_{nd}: Contribution from off diagonal terms.
Important for irradiation conditions.

Thermodynamic Model for spinodal decomposition



Cahn $\alpha_d = a k^2 (k_c^2 - k^2)$

Cook $= a(k,t) k^2 (k_c^2 - k^2)$

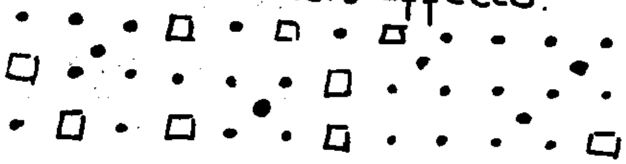
Langer et al $= a(k,t)(k_c^2(t) - k^2)$

$$\alpha_{cahn} = -M_{therm}\, k^2 (f'' + 2Gk^2)$$

$M_{therm} = G \cdot D_{therm}$; G is the gradient energy term

INFLUENCE OF RADIATION

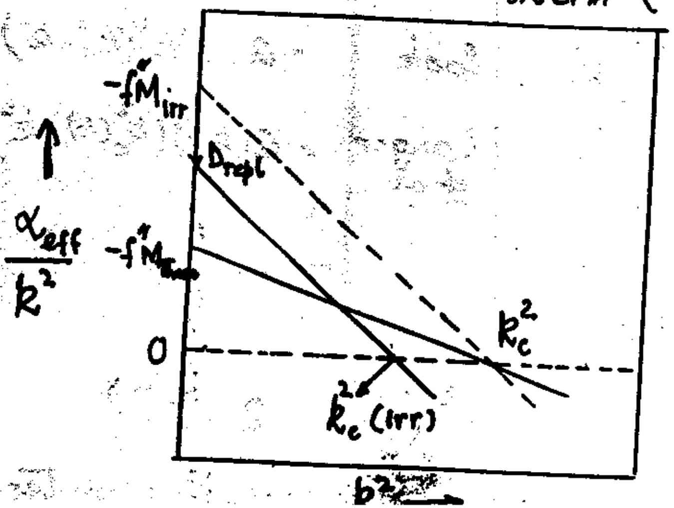
- Defect concentration effects.



(1) Free energy f and f'' is not significantly influenced by the irradiation produced defects. This is because the stored energies in the defect configurations is small as compared to the thermal phase change energie involving the atoms.

(2) However defects significantly influence the mobility due to additional transport mechanisms

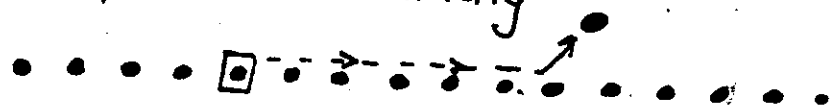
$$M_{irr} = M_{therm}\,(D_{irr}/D_{therm})$$



$$\frac{\alpha_{Cahn}}{k^2} = -M_{therm}(f''+2Kk^2)$$

λ_{max} unaffected!

- Replacement mixing



$$D_{repl} = \bar{C}_B D^A_{repl} + C_A D^B_{repl}$$

$$= \frac{1}{6} b^2 K_{repl} \langle n \rangle$$

$$D^{A,B}_{repl} = \frac{1}{2} b^2 \sum_{\alpha=1}^{z} \cos^2\alpha \; \Pi^{A,B}_{\alpha} \qquad \Pi^{A,B}_{\alpha_1} = K_{repl} \sum_{n=1}^{\infty} n\,p(n)\,p(\alpha_1) \quad \frac{1}{z}$$

$$D^{ions}_{repl} \simeq 3\cdot 10^{-14}\,cm^2\,K \qquad D^{elec}_{repl} \sim \cdot 1\, D^{ions}_{repl}$$

$$\left(\frac{d\delta C(x,t)}{dt}\right)_{repl} = D_{repl} \nabla^2 \delta C(x,t)$$

$$\frac{d}{dt} A(k,t) = -D_{repl} k^2 A(k,t)$$

$$\frac{\alpha_{eff}}{k^2} = -D_{repl} - M_{irr}\{f''+2Gk^2\}$$

- Unlike radiation enhanced diffusion replacement mixing can shift k_c^2 and k^2_{max} to lower values of k or larger λ. Thus only longer wavelengths may be stable.

- Stability of the alloy depends on Temp T through $M_{irr}(T) < f''(T)$. The phase boundary [illegible]

Compositional changes by defect reactions

Consider an A, B alloy then

$$\xi_A = \frac{n_A}{n_A + n_B} \qquad \xi_B = \frac{n_B}{n_A + n_B}$$

$$n_A + n_B + n_v = n_L = \text{Const}$$

$$\frac{d}{dt}\xi_A = \frac{\xi_B \frac{d}{dt} n_A - \xi_A \frac{d}{dt} n_B}{n_A + n_B}$$

Changes in n_A and n_B can be due to the following processes.

1) Production of a Frenkel Defect

$$n_L^{-1} \frac{d}{dt} n_{A,B} \Big|_{production} = -K^{v}_{A,B}$$

where $K^{v}_{A,B} = \sigma_{A,B} \Phi \xi_{A,B}$

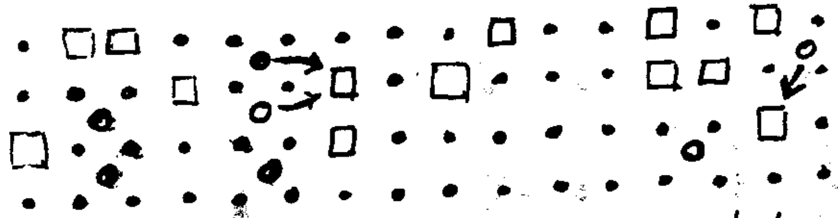
2.) Recombination

i_A, i_B interstitial Concentration

and $v = n_v / n_L$ Vacancy Concentration

$$n_L^{-1} \frac{d}{dt} n_{A,B} = \alpha_{A,B}\, i_{A,B}\, v$$

$\alpha_{A,B}$ → Recombination Constant.

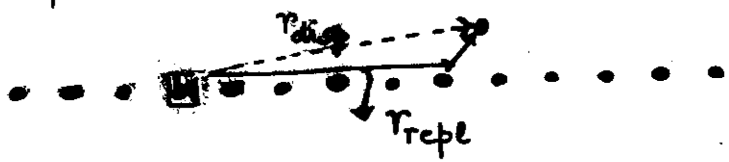


Recombination of A interstitial in A-rich region is more probable than B-interstitial in A-rich region

$$\alpha_{A,B} = \alpha^{0}_{A,B} + \gamma_{A,B}\, \xi_{A,B}$$

This can give rise to uphill diffusion processes.

(3) ~~Replacement~~ chain mixing.



$$K^{i}_{A,B}(\underline{r}) = \Phi \int \sigma_{A,B}\, \xi_{A,B}(\underline{r}')\, \omega(\underline{r} - \underline{r}')\, d\underline{r}'$$

$$\omega(r - r') \propto \delta(\underline{r}_{disp} - |r - r'|)$$

$$K^{i}_{A,B}(\underline{r}) = (1 - m) K^{V}_{A,B}(\underline{r}) + m \langle K^{v}_{A,B} \rangle$$

[illegible] r_{disp} [illegible] $- \cos(k\, r_{disp})$

(4) Interstitial exchange reactions

$$\frac{d}{dt}\, i_A \Big|_{exch.} = -\nu_A \xi_B i_A + \nu_B \xi_A i_B = -\frac{d}{dt}\, i_B \Big|_{exch}$$

$$\frac{d\xi_{A,B}}{dt}\Big|_{exch} = -\frac{d}{dt}\, i_{A,B}\Big|_{exch}$$

(5) Diffusion coupling

$$\frac{d}{dt}\, v_{diff} = D_v \nabla^2 v \, ; \quad \frac{d}{dt}\, i_{A,B}\Big|_{diff} = D_{i_{A,B}} \nabla^2 i_{A,B}$$

Rate equations

$$\frac{d}{dt}\xi_A = -\xi_B (K_A^v - \alpha_A i_A v) + \xi_A (K_B^v - \alpha_B i_B v)$$

$$\frac{di_A}{dt} = K_A^i - \alpha_A i_A v + D_{i_A} \nabla^2 i_A + \frac{\partial}{\partial t} i_A \Big|_{exch}$$

$$\frac{di_B}{dt} = K_B^i - \alpha_B i_B v + D_{i_B} \nabla^2 i_B + \frac{\partial}{\partial t} i_B \Big|_{exch}$$

$$\frac{dv}{dt} = K_A^v + K_B^v - (\alpha_A i_A + \alpha_B i_B) v + D_v \nabla^2$$

$$\underset{\approx}{S} = \begin{bmatrix} -D_{i_A} k^2 - \alpha_A \bar{v} - \nu_A \xi_B & \nu_B \xi_A & -\alpha_A \bar{i}_A & z_A - \Delta z_A \\ \nu_A \xi_B & -D_{i_B} k^2 - \alpha_B \bar{v} - \nu_B \xi_A & -\alpha_B \bar{i}_B & -(z_B - \Delta z_B \\ -\alpha_A \bar{v} & -\alpha_B \bar{v} & -D_v k^2 - (\alpha_A \bar{i}_A + \alpha_B \bar{i}_B) & (z_A - \\ (\alpha_A \bar{v} + \nu_A) \xi_B & -(\alpha_B \bar{v} + \nu_B) \xi_A & \alpha_A \bar{i}_A \xi_B - \alpha_B \bar{i}_B \xi_A & -(z_A \xi_B + \end{bmatrix}$$

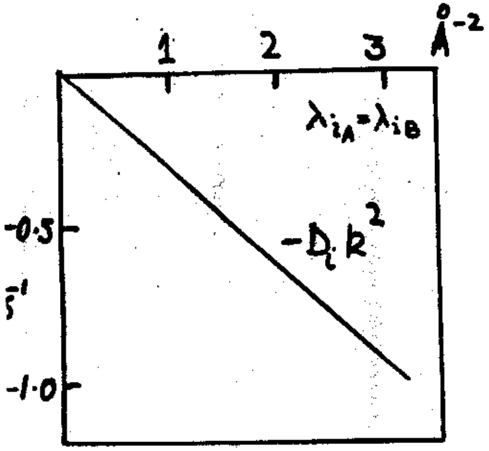
where

$$z_A = \frac{\partial}{\partial \xi_A} K_A^v - \bar{i}_A \bar{v} \frac{\partial}{\partial \xi_A} \alpha_A + \nu_A \bar{i}_A + \nu_B \bar{i}_B$$

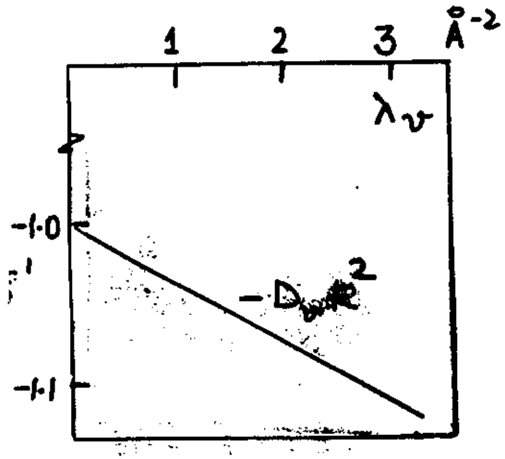
$$\Delta z_A = \frac{\partial}{\partial \xi_A} (K_A^v - K_A^i)$$

$$\| \underset{\approx}{S} \| = \lambda_{i_A} \cdot \lambda_{i_B} \cdot \lambda_v \cdot \lambda_{\xi_A}$$

k^2 – Dependence of the eigenvalues

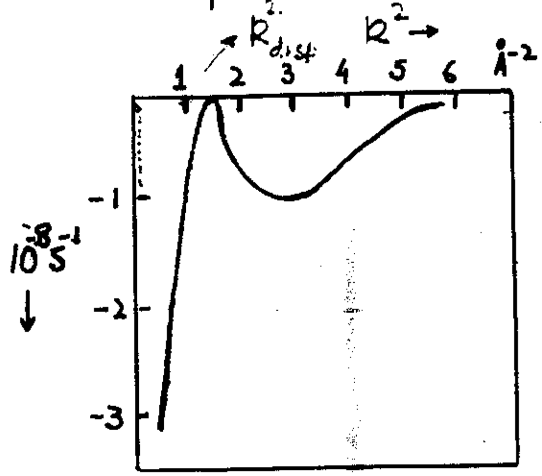


$D_{iA} = D_{iB}$

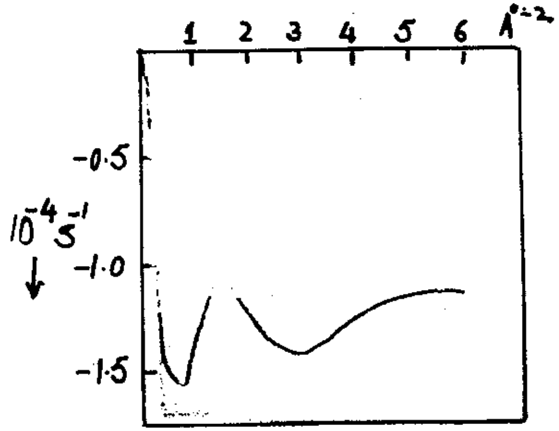


$D_{iA} = D_{iB}$

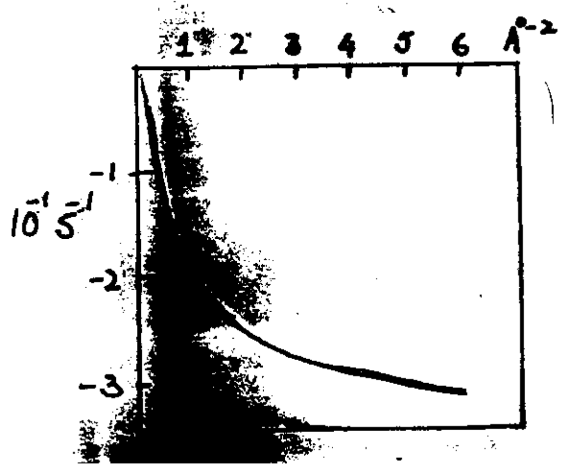
k^2 Dependence of the eigenvalue λ_{ξ_A}



$\nu_A = \nu_B = 0$



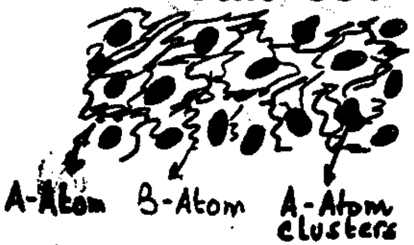
$\nu_A = 0 \quad \nu_B \neq 0$

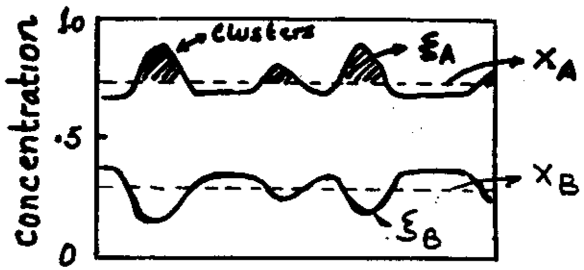


$\nu_A \neq 0 \quad \nu_B \neq 0$

A MODEL FOR CuNi

initial state





$$\eta = \frac{1}{\Omega_s}\int_{\Omega_s} (\xi_A - X_A)_{\xi_A \geq X_A} \, d\Omega$$

$$\frac{dI_A}{dt} = K_A - (\alpha_A + \gamma_A \eta) I_A V$$

$$\frac{dI_B}{dt} = K_B - (\alpha_B + \gamma_B \eta) I_B V$$

$$\frac{d\eta}{dt} = D_A (z_A \eta + \eta_s) I_A - D_B (z_B \eta + \eta_s) I_B$$

This shows a similar coupling as in the case of vacancy loops.

$\lambda \sim 60$ Å