VIII. - MARTENSITIC TRANSFORMATIONS. PRETRANSITIONAL PHENOMENA VOID LATTICES AND OTHER RADIATION INDUCED PERIODIC STRUCTURES

G. Martin

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VOID LATTICES AND OTHER RADIATION INDUCED PERIODIC STRUCTURES

G. MARTIN

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Résumé. — Les conditions dans lesquelles les réseaux de cavités ont été formés sont résumées ainsi que les divers modèles proposés pour expliquer la stabilité de ces réseaux. Plusieurs mécanismes de formation de ces réseaux sont présentés. Faute d’observations en continu de la formation de ces réseaux, le choix entre ces divers modèles reste ambigu.

Il en est de même du mécanisme de formation des autres structures périodiques produites par l’irradiation, exception faite des alignements de tétraèdres de défauts d’empilement où un mécanisme de germination croissance non aléatoire a été mis en évidence récemment.

Abstract. — The conditions under which void lattices have been formed are summarized. The various models proposed to account for the stability of void lattices are briefly presented. Several mechanisms for the formation of the void lattice are reviewed. Due to the lack of in situ observations, these mechanisms are still speculative.

The same is true for the formation of other radiation induced periodic structures, except for the build up of alignments of stacking fault tetrahedra which has recently been shown to result from a selective nucleation and growth process.

Void lattices, and other radiation induced periodic structures have been often reported since Evans’s first observation of an almost perfect BCC void lattice in N⁺ irradiated Molybdenum [1].

One of the many interesting aspects of these periodic arrangements of points defect sinks, is that they appear, develop and are stable under irradiation, i.e. while point defects are being continuously produced inside the solid and eliminated on these sinks.

Several review articles have dealt with the void lattice problem (e.g. [2-5]). Nevertheless new results have been reported and new ideas have been proposed recently, so that it is not useless to review this field again.

In the next paragraphs we will concentrate on the following points:

— What are the experimental evidences for the occurrence of void lattices?
— Which models of void lattice stability have been proposed up to now?
— What about the mechanism of void lattice formation?
— What other radiation induced periodic structures have been observed?

1. The experimental observations of void lattices. — The available data on void lattices observations are summarized in table I.

It must be emphasized that void lattices with a high degree of perfection are extremely rare: these are the void lattices observed by Evans in N⁺ irradiated Mo(1) (the reproducibility of this experiment turned out to be very poor [6]), and the void lattices formed in Nb and NbO under Ta⁺, Ni⁺ or V⁺ bombardment [7-9]. These void lattices are homothetic of the host lattice and present many types of defects: missing void, several voids per lattice site, dislocation in the void lattice (Fig. 1).

All other void lattices seem to be highly imperfect: the proportion of void lattice sites which are indeed

![Fig. 1. — Void lattice in Nb after 7.5 MeV Ta⁺⁺⁺ irradiation at 800 °C, 10⁻² dpa s⁻¹ to 300 dpa (from ref. [7]). The black arrows point to dislocations in the void lattice; other defects (extra voids, missing voids) are visible.](image-url)
Experimental evidences for void lattices

\( r = \text{void radius, except for}^* \) which refers to void size in case of marked void facetting:

\( a = \text{void lattice spacing} \)

<table>
<thead>
<tr>
<th>Projectile</th>
<th>Flux dpa s(^{-1})</th>
<th>Dose dpa</th>
<th>( T ) °C</th>
<th>( r ) Å</th>
<th>( a ) Å</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(^{+})</td>
<td>2.7 MeV</td>
<td>2.8 ( \times 10^{-3} )</td>
<td>20</td>
<td>800</td>
<td>28</td>
<td>310</td>
<td>At 2 dpa no void ordering is observed (cuboidal shape)</td>
</tr>
<tr>
<td>Ni(^{+})</td>
<td>5 MeV</td>
<td>2 ( \times 10^{-2} )</td>
<td>6</td>
<td>900</td>
<td>38*</td>
<td>50</td>
<td>Islands of large ordered cavities among smaller randomly distributed cavities</td>
</tr>
<tr>
<td>N(^{+})</td>
<td>2 MeV</td>
<td>7 ( \times 10^{-3} )</td>
<td>100</td>
<td>870</td>
<td>25</td>
<td>220</td>
<td>Void lattice with a high degree of perfection Poor reproducibility</td>
</tr>
<tr>
<td>He(^{+})</td>
<td>36 keV</td>
<td>ions cm(^{-2}) ( \times 10^{17} )</td>
<td>20</td>
<td>37</td>
<td></td>
<td>The He bubble superlattice produces ( e^- ) diffraction spots of low index</td>
<td>[12a]</td>
</tr>
<tr>
<td>He(^{+})</td>
<td>36 keV</td>
<td>( 10^{18} )</td>
<td>20</td>
<td></td>
<td></td>
<td>Black dots He bubbles on a BCC superlattice He bubbles Blisters</td>
<td>[60]</td>
</tr>
</tbody>
</table>

**Remarks**

- Void alignments
- Void alignments formed during post irradiation annealing. Depends on preannealing treatment. Not observed for N\(^{+}\) irradiation
- Void ordering at doses larger than 3 dpa. No saturation of void swelling
- Islands of large ordered cavities among smaller randomly distributed cavities
- Void lattice with a high degree of perfection Poor reproducibility
- Void ordering at doses larger than 3 dpa. No saturation of void swelling
- Islands of large ordered cavities among smaller randomly distributed cavities
- Void ordering at doses larger than 3 dpa. No saturation of void swelling
- Islands of large ordered cavities among smaller randomly distributed cavities
- The He bubble superlattice produces \( e^- \) diffraction spots of low index
- Black dots He bubbles on a BCC superlattice He bubbles Blisters
Table I (suite)

<table>
<thead>
<tr>
<th>Projectile</th>
<th>Flux dpa s⁻¹</th>
<th>Dose dpa</th>
<th>T °C</th>
<th>r Å</th>
<th>a Å</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>He⁺</td>
<td>2 × 10⁻⁷</td>
<td>20</td>
<td>35</td>
<td>He bubbles on a BCC superlattice with ( d_{110} = 35 ) Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>25 to 60 keV</td>
<td>100 to 700</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>250 to 700</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>750</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ In situ \] observation shows that the formation of the bubble superlattice follows that of bubbles up to 250 °C. Above 250 °C BCC superlattice is directly observed. The second order superlattice spots are visible. No BCC superlattice

<table>
<thead>
<tr>
<th>MOLYBDENUM ALLOYS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy</td>
</tr>
<tr>
<td>TZM (*)</td>
</tr>
<tr>
<td>Mo⁺ 0.5 % Ti</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>(*) TZM : Mo 0.5 wt % Ti + 0.1 wt % Zr</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>NIOBIUM and NIOBIUM ALLOYS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target</td>
</tr>
<tr>
<td>Nb</td>
</tr>
<tr>
<td>Nb</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Nb</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Nb and Nb 1% Zr doped with oxygen</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

[12], [59], [62], [52], [15], [63], [56], [7], [8], [9], [64]
### OTHER BCC METALS

<table>
<thead>
<tr>
<th>Target</th>
<th>Projectile</th>
<th>Flux dpa s⁻¹</th>
<th>Dose dpa</th>
<th>T °C</th>
<th>r Å</th>
<th>a Å</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta</td>
<td>n</td>
<td>25</td>
<td>14</td>
<td>475</td>
<td>41</td>
<td>30</td>
<td>1.9 × 10¹⁷ void cm⁻³</td>
<td>[10, 52]</td>
</tr>
<tr>
<td>V</td>
<td>n</td>
<td>14</td>
<td>20</td>
<td>475</td>
<td>41</td>
<td>30</td>
<td>1.06 × 10¹⁶ void cm⁻³</td>
<td>[52]</td>
</tr>
<tr>
<td>W</td>
<td>n</td>
<td>16</td>
<td>20</td>
<td>550</td>
<td>41</td>
<td>600</td>
<td>0.59 × 10¹⁶ void cm⁻³</td>
<td>[52]</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>16</td>
<td>20</td>
<td>550</td>
<td>41</td>
<td>600</td>
<td>0.2 × 10¹⁶ void cm⁻³</td>
<td>[52]</td>
</tr>
</tbody>
</table>

### FCC METALS

<table>
<thead>
<tr>
<th>Target</th>
<th>Projectile</th>
<th>Flux dpa s⁻¹</th>
<th>Dose dpa</th>
<th>T °C</th>
<th>r Å</th>
<th>a Å</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>Al¹⁺ 400 keV</td>
<td>8 × 10⁻³</td>
<td>40</td>
<td>50</td>
<td>600</td>
<td>600 to 800</td>
<td>3.4 × 10¹⁶ void cm⁻³</td>
<td>[60]</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>10⁻⁶</td>
<td>6</td>
<td>55</td>
<td>40 to 400</td>
<td>Void alignments along (110) (4 × 10¹⁴ void cm⁻³)</td>
<td>[67]</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>Ni¹⁺ 5 MeV</td>
<td>10⁻²</td>
<td>360</td>
<td>525</td>
<td>250</td>
<td>260*</td>
<td>4.2 × 10¹⁵ void cm⁻³</td>
<td>[68]</td>
</tr>
<tr>
<td></td>
<td>Se¹⁺ 6-11 MeV</td>
<td>3 × 10⁻²</td>
<td>400</td>
<td>525</td>
<td>90</td>
<td>660</td>
<td>1.4 × 10¹⁶ void cm⁻³</td>
<td>[16]</td>
</tr>
<tr>
<td>Stainless Steel 20/25 + Ti</td>
<td>e⁻ 1 MeV</td>
<td>500</td>
<td>20</td>
<td>250</td>
<td>Void alignments in N doped samples. N increases void number density and void size regularity</td>
<td>[14]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### HCP METALS

<table>
<thead>
<tr>
<th>Target</th>
<th>Projectile</th>
<th>Flux dpa s⁻¹</th>
<th>Dose dpa</th>
<th>T °C</th>
<th>r Å</th>
<th>a Å</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>n</td>
<td>10⁻⁶</td>
<td>3</td>
<td>55</td>
<td>Void stratification in the basal plane</td>
<td>[67]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
occupied by voids is small (e.g. [10, 52]) Ill-positioned
voids are frequent [11] : electron diffraction patterns
from the void lattice show only low index, first order
diffraction spots [12]. Such imperfect void lattices
may be described as void alignments along the dense
rows of the host matrix as shown recently by Thomas
de Montpreville [13]. This is true both for BCC
and FCC matrices. In the latter case, alignments are
observed along <110> directions rather than <100>
as shown by the detailed discussion given in [13].

As shown by table I, such imperfect void lattices
have been observed in many metals after neutron, ion
and even electron [14] bombardment.

The most evident common feature to all these
imperfect void lattices is that they only occur for void
number densities in the range of $10^{15}$cm$^{-3}$ or higher,
that is when voids are some hundred Angstroms
apart ($\tau$). This is the case in the low temperature
part of the swelling peak ($\approx 0.3$ Tm). However, this latter
statement is not absolute since void ordering has been
observed in neutron irradiated Nb at 800 °C and not
between 430 and 700 °C for similar doses and dose
rates [15]. A high void number density may be achieved
by a proper impurity doping. Indeed the formation
of void lattices in NbO alloys has been shown to occur
only above a temperature dependent oxygen concentra-
tion threshold [9].

An often reported feature of void lattices is that
the void lattice spacing is of the order of 10 times
the void radius, which suggests a saturation of
void swelling at a level of $\sim 10^{-5}$ when void lattices
form. Some evidences of such a saturation have been
reported [8, 9, 16].

2. The models for void lattice stability. — A crystal
under irradiation which contains a void lattice is an
open system (Frenkel pairs are being continuously
produced inside the crystal), which is maintained in a
quasi steady state. Indeed energy is being injected
into the crystal by the production of Frenkel pairs:
most of this energy is dissipated into heat by Frenkel
pair recombination (mutual annihilation or recombi-
nation on defect sinks like void surfaces), the remain-
ing part is stored (point defect supersaturation, surface
energy plus interaction energy of the voids). Changing
the void configuration (void spatial configuration,
size distribution and volume fraction) both changes
the dissipative properties of the system under irradia-
tion and the amount of energy stored in the crystal.

The characteristics of the void lattices must result
from some sort of optimisation of both effects, that is
from some balance between static (minimum energy
storage) and kinetic (maximum defect capture) mechani-

2.1 Static models. — The most extensive work
has dealt with void-void interaction energy, following
the pioneer work of Mallen and Bullough [17].

2.1.1 Void-void interaction energy. — The elastic
interaction energy between voids has been estimated
by several authors. As can be seen in table II, the
conclusions reached depend on the type of approxi-
mation used in the computation:

— if the voids are treated as misfitting spher-
ical inclusions [17-20] the elastic anisotropy of
the host matrix dictates the structure of the most
stable void lattice : a BCC void lattice is expected if
$2C_{41}-C_{11}+C_{12}<0$ and a simple cubic void
lattice is expected in the reverse case. No interaction
is found in elastic isotropic materials. The ratio of the
void lattice parameter to the void radius has been
computed for Mo and is too small by a factor of 2 to 3.
This ratio may be increased if void facetting is taken
into account [17-19]. Such models cannot however
account for the observation of a void lattice in
Tungsten [21] which is elastically isotropic;

### Table I (suite)

<table>
<thead>
<tr>
<th>FLUORIDES</th>
<th>$\gamma$</th>
<th>room</th>
<th>25 to 50</th>
<th>190 to 280</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaF$_2$</td>
<td>$\gamma^{+}$ 100 keV</td>
<td></td>
<td></td>
<td></td>
<td>Simple cubic void lattice (homothetic of the F sublattice).</td>
</tr>
<tr>
<td>SrF$_2$</td>
<td>—</td>
<td>—</td>
<td></td>
<td></td>
<td>Does form after a Brownian like motion of voids.</td>
</tr>
<tr>
<td>BaF$_2$</td>
<td>—</td>
<td>—</td>
<td></td>
<td></td>
<td>Does not form at 50 or 150 °C One observation of highly imperfect void ordering. No void ordering in BaF$_2$.</td>
</tr>
</tbody>
</table>
| N.B. Void refers to a cluster of vacant sites in the alkali earth fluoride lattice. 
| The void radius, which suggests a saturation of void swelling at a level of $\sim 10^{-5}$ when void lattices form. Some evidences of such a saturation have been reported [8, 9, 16]. |

(1) Void alignments have also been observed during post irradiation annealing of Mo [17]. Although the conditions for void formation were not well identified, void alignments were reported in the samples which exhibited the highest density of voids.
TABLE II  

Void-void elastic interaction energy calculations (a/r = void lattice spacing to void radius ratio)  

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Spatial distribution of the cavities</th>
<th>Model for the cavity</th>
<th>Type of interaction</th>
<th>Result</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discrete block (homo) homothetic to the Wigner-Seitz cell of the host lattice</td>
<td>Lattice homothetic to the host lattice</td>
<td>One missing block</td>
<td>Induced interaction included</td>
<td>Good agreement with a/r for Mo. Good estimate of the surface tension</td>
<td>[23]</td>
</tr>
<tr>
<td>Id.</td>
<td>Id.</td>
<td>Id.</td>
<td>Id.</td>
<td>Good agreement with observed results in Ta. Predicts a very strong binding energy for void lattice in V</td>
<td>[24]</td>
</tr>
<tr>
<td>Elastically anisotropic continuum</td>
<td>Pair</td>
<td>Spherical hole with hydrostatic tension</td>
<td>Inhomogeneity interaction</td>
<td>In Mo, strongest binding energy in ⟨111⟩ direction. Zero interaction force at ( \frac{a}{r} = 3.2 ) in ⟨100⟩ direction</td>
<td>[22]</td>
</tr>
<tr>
<td>Elastically anisotropic continuum</td>
<td>Lattice homothetic to the host lattice</td>
<td>Body forces with cubic symmetry</td>
<td>No inhomogeneity interaction included</td>
<td>( \frac{a}{r} ) from 2.2 to 3.1 for Mo depending on the choice of body forces. Force along ⟨100⟩ produce void-void repulsion</td>
<td>[19]</td>
</tr>
<tr>
<td>Id.</td>
<td>Pair and lattice sums to the 25th shell</td>
<td>Id</td>
<td>Id.</td>
<td>( \frac{a}{r} = 3.07 ) for spherical voids in Mo. 8.04 for faceted voids. No void lattice is predicted in elastically isotropic materials</td>
<td>[17]</td>
</tr>
<tr>
<td>Discrete (lattice statics)</td>
<td>Pair of cavities and small aggregates</td>
<td>Spherical and tetragonal distortion tensors</td>
<td>Id.</td>
<td>Spherical inclusions form a needle like aggregate with ⟨100⟩ or ⟨111⟩ (axis and simple cubic) or BCC superstructure if ( 2C_{24} - C_{11} + C_{12} &gt; 0 ) (cubic)</td>
<td>[20]</td>
</tr>
<tr>
<td>Isotropic continuum</td>
<td>Pair</td>
<td>Spherical hole with a shell of misfitting impurity</td>
<td>Inhomogeneity interaction</td>
<td>The dependance of the solute shell concentration with the void spacing results in an equilibrium distance between the voids</td>
<td>[26]</td>
</tr>
</tbody>
</table>

— if the induced (inhomogeneity) interaction between voids is included, more complex situations arise [22-24]. In particular, both induced interaction and void facetting have been taken into account by Tewary [23-24]. Correct values of the void lattice parameter to void radius ratio were computed for a BCC void lattice in Mo [1] and in Ta [10]. A high binding energy of the voids to the void lattice is predicted: 5 eV per void in Mo, 1.35 eV in Ta, 2.5 to 10 eV in V! No void lattice has however been observed in V up to now.

Several important questions related to this type of calculations have not yet been answered:

— is it possible to account for ⟨110⟩ void alignments in Ni and Al by purely elastic interaction arguments?

— what are the formation energies of the many defects which are reported in void lattices. More generally how stable is the void lattice with respect to fluctuations of the void radius, shape, position and number density? This would give some hint to how broad the void lattice attractor is in the configuration space of the voids; indeed most metals may exhibit after a proper irradiation dose, void volume fractions larger than \( 10^{-3} \), which means that during the course of irradiation the average void distance to the void radius ratio went through the value of \( 10^{-3} \) which is typical of void lattices, although no void lattice has formed. A systematic study of the energy of imperfect void lattices would shed some light on the characteristics required for a given void population to change into a void lattice.

Other contributions to the void to void interaction energies have been proposed: these are surface plasmons interactions [25] and phonon scattering by the voids [3]. The validity of these models has been discussed by Stoneham [3].
2.1.2 Other static models. — Some attempts have been made to estimate the overall energy of the crystal under irradiation, i.e. the energy of the voids plus that of the point defect supersaturation [36, 37]. Omitting the configurational entropy of the point defects and the interaction energy between the voids, Norris and Brown found that the energy goes through a very flat minimum for a void volume fraction much smaller than the observed one. This shows that either major terms have been omitted [37] or that the stability of the steady state is not controlled by a minimum energy criterion [38].

2.2 Kinetic model. — The idea that void ordering might result from a kinetic interaction between voids which are competing for the capture of point defects was first suggested in a qualitative way by Brimhall and Simonen [31]. The BCC structure of void lattices was explained with a related argument by Winter [32]: the idea is that the Wigner Seitz cell of a BCC crystal is such that the average migration distance for a point defect to be captured by a cavity is minimum. Therefore the average point defect concentration and hence the energy stored in the crystal by these defects would be lower in the presence of a BCC void lattice.

Benoist and Martin [33] have given a more precise treatment of this problem. Spherical voids are imbedded in a homogeneous medium where point defects are uniformly created and annihilated: the steady state point defect concentration $C_d(r)$ is governed by:

$$D V^2 C_d - \alpha C_d + g = 0$$  \hspace{1cm} (1)$$

where $D$ is the point defect diffusion coefficient, $\alpha C_d$ a linearized expression for the rate of point defect annihilation in the medium around the cavities and $g$ the production rate of point defects. The boundary condition is that $C_d = 0$ on the surface of each cavity. Using the Green’s function formalism, the flux of point defects at the surface of each cavity is obtained as a function of the configuration of the cavities (radius and spatial distribution). As shown by a perturbation calculation, the proportion of defects which are lost on the cavities goes through a maximum when the voids are arranged on a translation lattice.

The relative efficiency of BCC versus FCC void lattices for the capture of point defects depends on the relaxation length ($\sqrt{D/\alpha}$) of the point defects in the surrounding medium. BCC void lattice is the most efficient one when this length is much greater than the void lattice parameter. When the reverse is true FCC structure is favoured.

Since this maximum of capture efficiency occurs both for interstitials and vacancies, the arrangement of voids on the appropriate lattice maximises the elimination rate of Frenkel pairs i.e. the dissipation of power in the crystal under irradiation.

Finally the kinetic stability of the void lattice with respect to a fluctuation of void position has been studied. Voids tend to grow away one from the other [33]. The stability with respect to a fluctuation of the void radius is under study [34]: it depends on the conditions of irradiation (dose rate and temperature).

In its present form, this model does not predict an optimum value of the void volume fraction, nor does it give an explanation for the parallelism between the directions of the void lattice and of the host lattice. However such a parallelism might be introduced by taking into account the faceting of the voids [86].

It is interesting to notice that an interaction of the same sort has been invoked in order to account for the spatial periodicity of steps at the surface of a growing crystal [35].

2.3 Hybrid models. — The previous kinetic model ignores interaction energy consideration. The static models of section 1, on the hand ignore the existence of defect fluxes towards the voids. Nolfi has tried to include the effect of these fluxes in an elastic interaction energy calculation [26].

Indeed defect fluxes towards the voids are known to induce solute segregation of misfitting impurities at the surface of the voids [27-30, 9]. The void-void interaction would be reinforced by this shell of solute. Since the amount of segregation depends on the conditions of irradiation (temperature and dose rate [30]), the interaction energy between voids would depend on these conditions.

This model might account for the dependance of the saturation void volume fraction on the irradiation temperature observed by Loomis et al. in NbO (Fig. 2). This model has however not been developed in great detail. In its present state, it predicts that the interaction energy between voids increases with temperature whereas the perfection of the void lattice in NbO is worse at higher temperatures [9].

What type of interaction dictates the stability of the void lattices? The stability of void lattice in Mo with respect to post irradiation annealing [39, 54] suggests that the static interaction between voids is of main importance. However since the formation of void lattices is thought to be connected with a high impurity content of the matrix [6], the possibility of a stabilization of the voids by a shell of solute elements cannot be ruled out [9].

Indeed, detailed observations and calculations of voids configurations around various defects of the void lattice would give valuable informations.

3. What about the formation of the void lattices? — Several mechanisms for the formation of void lattices may be imagined:

a) void nucleation on an ordered impurity array,

b) instability of the steady state point defect population resulting in the selective amplification of certain point defect concentration waves,

c) void nucleation in preferred directions around a preexisting void.
1) The first mechanism suggested by Evans [1] has not yet received experimental confirmation. Indeed this interaction may induce point defect ordering prior to irradiation was looked for and not detected in NbO (Loomis, private communication).

2) A model for the second mechanism (instability of the point defect population) has been elaborated by Martin [40]: the local point defect population is governed by a set of coupled partial derivative equations of the type:

$$\frac{\partial C(r, t)}{\partial t} = \frac{\partial C}{\partial t} \left|_{\text{chem.}} + \frac{\partial C}{\partial t} \right|_{\text{diff.}}$$

where the first term of the RHS represents the production and mutual recombination rates of defects and the second term the rate of change of the local point defect concentration due to diffusion. This system of equations has a spatially uniform steady state solution. It can be shown that since the chemical reactions have no self catalytic step, the steady state point defect population is stable both with respect to an overall change in concentrations and to spatial fluctuations, except if the effect of attractive interactions between point defects are included in the diffusion term: this interaction may induce point defect up-hill diffusion which results in the amplification of certain point defect concentration waves. This happens when the irradiation flux is larger than a temperature dependant flux threshold. This phenomenon has many similarities with the spinodal decomposition of an unstable equilibrium state of a multicomponent solid solution [84, 85] in the present case, however, what is being studied is the decomposition of an unstable steady state of an open system: the presence of a chemical term in the RHS of eq. (2) results in some peculiarities which have been discussed in [40].

Although the argument has not yet been worked out in detail, the directions of the fastest growing point defect concentration waves are the directions of strongest interaction energy between the point defects which constitute these concentration waves. Since both interstitials and vacancies build up these waves, the prediction of these directions is not straightforward.

This mechanism is however not consistent with the fact that void ordering is only observed at higher doses, while at lower doses short void alignments are observed among a more or less random void population (e.g. [9]).

On the other hand, the very high void number densities which are necessary for the formation of void lattices might result from an instability of the vacancy population rather than from the standard nucleation and growth process. There is however no direct experimental proof of this suggestion.

3) The third possibility, i.e. a non random void nucleation resulting in the progressive build up of a void lattice, has not yet been studied in details. However due to the interaction energy between the voids and the point defects, the flux of point defects towards a void has not a spherical symmetry and one expects the directions of maximum vacancy flux to be distinct from those of maximum interstitial flux [41]. This might lead to directions of preferential void nucleation around preexisting voids. It is worth mentioning that non random nucleation of stacking fault tetrahedra has recently been observed in gold during e- irradiation in a HVEM [42].

4) Several mechanisms for the selective growth (decay) of well (ill) positionned voids might be imagined. The most specific one of irradiation conditions was suggested by Foreman [43]: crowdings are supposed to propagate along the dense rows of the matrix with a mean free path larger than the void to void average distance. Such crowdings would produce void alignments along the dense rows of the matrix by eliminating out of line voids. Despite the unusual properties required from the crowdings, this model gives the most straightforward explanation for the occurrence of void alignments along the dense rows of the host matrix (⟨111⟩ in BCC and ⟨110⟩ in FCC matrices) [5, 13].

Another mechanism for selective decay of ill positionned voids might simply be related to a
bias in thermal emission of vacancies from the various voids, much in the same way which results in the late stage ordering of precipitates during Ostwald ripening [44, 45]. Indeed, let us assume that two voids with volume respectively equal to $V_1$ and $V_2$ may exchange vacancies without any other modification of the surrounding system (i.e. no change of the point defect supersaturation). The excess of the overall surface energy of these two voids with respect to a single void of volume $V = V_1 + V_2$ varies with the relative size of the voids as shown on figure 3. This is the only modification of the energy of the system which accompanies the exchange of vacancies between the voids, in the absence of void-void interaction energy.

As shown on figure 3, except for the unstable equilibrium position $V_1 = V_2 = V/2$, the energy of the system decreases when one of the cavities grows at the expense of the second one. Let us now consider the effect of an interaction energy between the voids, the position of which is assumed to be fixed: by symmetry, this energy has an extremum for $V_1 = V_2 = V/2$ and cancels for $V_1 = V$ or $V_2 = V$. The excess energy of the two voids with respect to a single void of volume $V$ is schematically shown on figure 3. For voids which attract one another (negative binding energy), the equilibrium configuration $V_1 = V_2 = V/2$, is stabilized by void-void interaction energy. Unlike in the absence of the interaction energy between voids, a smaller cavity may now grow at the expense of a larger one, bringing the system into a metastable equilibrium state. The coarsening kinetics of interacting inclusions has been given a more detailed treatment by Cahn [46].

Finally the last mechanism for ordering a randomly nucleated void population is provided by the migration of voids by surface diffusion: an order of magnitude calculation by Stoneham [4] points to the possibility of small readjustments of void positions by surface diffusion. There is however no direct observation of such a process in the case of void lattice formation in metals. In electron irradiated CaF$_2$, however, a brownian motion of the voids (or Calcium particles) prior to the superstructure formation has been reported [47].

In principle it should be possible to choose between a mechanism of type 3 (non random nucleation) and one of type 4 (selective growth): the first one would result in the formation of the void lattice while the void number density increases; the second one would lead to the opposite.

Figure 4 due to Brimhall et al. [7] shows that the formation of the void lattice in Nb may take place both during an increase or a decrease of the void number density, depending on the irradiation temperature. It is therefore difficult to choose between the previous mechanisms in the absence of in situ observations. Such observations have been reported recently for the formation of He bubble lattice during He implantation in Mo [60]. In this case (which is more similar to a standard precipitation problem, since unlike vacancies He atoms are conservative units) the formation of the bubble lattice followed a random nucleation process at least for the lower temperatures investigated.

Fig. 3. — Effect of the void-void interaction energy on the driving force for Ostwald ripening (schematic): $\Delta E = \text{Excess energy of two voids of volume } V_1 \text{ and } V - V_1$, with respect to the energy of a single void with volume $V$; ——— surface tension only; ———— surface tension plus attractive interaction between voids; + + + surface tension plus repulsive interaction between voids.

Fig. 4. — Void number density as a function of dose for Nb bombarded with 7.5 MeV Ta$^{+ +}$ ions at 800 °C (a) and 900 °C (b). The arrow points to the onset of void ordering (according to ref. [7]).

4. What about other modulated structures formed under irradiation — Other periodic structures have been formed under irradiation. These are the vacancy loop arrays in Ni produced either by ion irradiation [56, 71, 72] or neutron irradiations [73, 74], the stacking fault tetrahedra arrays produced by $e^-$ irradiation in Au [42, 48, 75, 76], Cu [77, 80], Pb [79], the modulated distribution of radiation induced precipitates in undersaturated NiSi [81] or NiBe [82] solid solutions, and of M$_{23}$C$_6$ precipitates formed during ion bombardment of FeNiCr alloys [83].
We refer to these non random morphologies as modulated structures since no lattices with a degree of a perfection similar to that of the void lattices has yet been reported. These structures are better described as alignments.

In the case of stacking fault tetrahedra, an in situ observation of the formation of SFT alignments in Au under 1.5 MeV e⁻ irradiation at room temperature has shown that alignments result from a non random nucleation and growth of the SFT [42]. The directions of alignments correspond to the directions of strongest attraction between one preexisting SFT and a smaller one [48]. For all other systems, the defect clusters have a more complicated structure, and their interaction energy has not yet been studied in detail.

5. Conclusion. — Void lattices with a high degree of perfection are rare. Most experimental studies have produced highly imperfect void lattices. Void lattices have the interesting feature of being produced under dynamical conditions by the condensation of non a conservative species (vacancies). This results in a large variety of possible interaction mechanisms between the voids.

The theory of the static properties of perfect void lattices is by far the most extensively developed one. The most detailed experimental study of void lattices does not confirm the predicted independance of the void volume fraction on irradiation temperature. The kinetic models are not sufficiently developed to allow for a detailed comparison with experiment.

The mechanism of void lattice formation is still speculative. In situ observation of the formation of void lattices would be of prime interest.

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Note added in proof: since this paper was submitted, two interesting papers concerning the kinetic interaction between voids were published: 


Brailsford, A. D. (J. Appl. Phys. 48 (1977) 4402) gives a quantitative estimate of the velocity of void migration, in the limit where the kinetic interaction is the only active interaction. The migration is shown to be much too slow to account for the overall ordering process.