phys. stat. sol. (b) **154**, 105 (1989)

Subject classification: 62.20; 61.80; 65.50

*Departamento Materiales, Comisión Nacional de Energía Atómica, Buenos Aires*[1])

# Thermodynamics of Deformation under Irradiation

By

A. SARCE and E. J. SAVINO[2])

An irreversible thermodynamic model is proposed for describing the deformation of a crystal under stress and irradiation. A thermodynamic inequality is found to relate the lattice straining and stress with the irreversible part of the free energy density. As an application of the model the case of straight dislocation climbing under irradiation is studied.

Un modèle thermodynamique irreversible est proposé pour décrire la déformation d'un cristal sous contrainte et irradiation. Une inégalité thermodynamique est trouvée qui rattache la déformation et les contraintes du réseau avec la partie irreversible de la densité d'energie libre. Comme application du modèle on étudie le cas de la montée d'une dislocation coin sous irradiation.

## 1. Introduction

The macroscopic constitutive equations of plasticity must be consistent with the thermodynamics of irreversible processes in a continuum medium, i.e. continuum thermodynamics [1]. Plastic deformation constitutive equations result in the continuum as an average of the dynamic behaviour of microstructural lattice defects (mainly dislocations). One of the main goals of studying the statics and dynamics of lattice defects is to relate those constitutive equations of the continuum medium to the microstructure of the crystalline medium (see for example: Rice [2], Savino and Harriague [3], Gittus et al. [4] for applications). However, seldom is any discussion found in the literature on the thermodynamic validity of the assumptions used for establishing that relationship. For example, when rate theory is used for solving the recovery of point defects under irradiation and the resulting plastic deformation due to dislocation climb and/or glide [5, 6], in general no test is performed to prove that the corresponding constitutive equation deduced by that procedure can be framed within the theory of continuum thermodynamics. In general, relating microscale to macroscale behaviour in real crystals and understanding the thermodynamics behind that relation is a major task even under quite simplifying assumptions. Germain et al. [1], Rice [2], Mrôz [7], and Stolz [8], establish general thermodynamic relations between micro- and macro-behaviour of materials. However, not clear from those works is the synergetic influence of, for example, more than one micro-process being involved in that behaviour. We shall try in this paper the thermodynamic description of a crystal being mechanically stressed and irradiated by energetic particles. That is, we shall assume energy "pumping" into the system through the bombardment with a flux $\varphi$ of particles, which modify the crystal defect population, and by the action of external forces which impose the existence of a stress field $\varepsilon$ within the crystal. Under those combined effects a strain field $\varepsilon$ is established which will be in general composed of a reversible component $\varepsilon^{R}$ that goes instantaneously to zero when the external effects disappear, and viscoelastic or plastic ones which are either permanent

---

[1]) Avda. del Libertodor 8250, 1429 Buenos Aires, Argentina.

[2]) Present address: Department of Materials Engineering, Virginia Polytechnic Institute and State University, Virginia, Blacksburg 24061, USA.

or require some finite time for recovery. We shall take in what follows these latter strains as composing the irreversible crystal straining $\varepsilon^{\mathrm{I}}$. At the microstructural level, the reversible straining is related to small displacements of the atoms within their energy well at the lattice, while the irreversible one is related to the density and distribution of lattice defects, the so-called plastic state $H$ of the crystal [2].

Within the general problem described above we shall show in the following section the existence and evolution of a free energy function $\Phi_{\mathrm{I}}$, which relates the external variables: (i) particle flux $\varphi$ and (ii) external stress $\sigma_e$, or the equivalent internal ones: (i) crystal damage $n_\varphi$, via production of Frenkel pairs, and (ii) the internal stress field $\sigma$ induced by $\sigma_e$ ($\sigma$ is assumed to be homogeneous and $\sigma = \sigma_e$), with the plastic state $H$ and strain $\varepsilon$. As an example of the application of our approach, in subsequent sections we shall deduce from that free energy function $\Phi_{\mathrm{I}}$ the constitutive equation of a medium under irradiation and stress, when this medium is modelled under a set of simplifying assumptions. Specifically, in the example we shall assume the plastic state of the crystal to be determined by the vacancy and interstitial point defect concentration, $c_{\mathrm{v}}$ and $c_{\mathrm{i}}$, respectively, i.e. $n_\varphi = (c_{\mathrm{v}}, c_{\mathrm{i}})$, and only a single line defect type: straight edge dislocations. The irreversible straining will be taken as induced solely by dislocation climbing, i.e., $H$ is related to the space distribution of these dislocations. The thermodynamic forces that act on each dislocation in the presence of the point defect population and the homogeneous stress field will be shown. These forces agree with those deduced in the classical literature on dislocation theory [9, 10]. However, for the sake of simplicity we shall not enter into a detailed treatment of the problem of dislocation climbing as extensively developed by Balluffi [11]. In Balluffi's approach the climbing rate is determined by the point defect diffusion to jogs in the dislocation line and the subsequent jog migration within the line. We consider, however, that it is illuminating to see how in the simple case treated below, the forces acting over straight dislocations, once explicitly replaced in the time evolution of the free energy function, $\dot{\Phi}_{\mathrm{I}}$, allow to relate the dislocation climbing rate, and therefore the resulting irreversible straining, with point defect absorption and emission and long-range diffusion. That is, the classical equations (see Hirth and Lothe [9] and Friedel [10]) of dislocations climbing under stress and irradiation result, in the example, by solving the time evolution of the function $\Phi_{\mathrm{I}}$.

## 2. Free Energy and Plastic Work

According to Germain et al. [1], the rate of production of local entropy $\dot{\eta}^*$ at a point $r$ and time $t$ under a heat flux $q$, can be written as

$$\varrho T\dot{\eta}^*(r,t) = \varrho[T\dot{s}(r,t) - \dot{e}(r,t)] + \mathrm{Tr}\,(\boldsymbol{\sigma}^{\mathrm{T}} \cdot \dot{\boldsymbol{\epsilon}}) - \boldsymbol{q} \cdot \nabla(\ln T)\,, \tag{1}$$

where $T$ stands for temperature, $\varrho$ for density (assumed to be constant), $s$ for specific entropy (per unit mass), $e$ for internal energy (also per unit mass), the stress $\boldsymbol{\sigma}$ and strain $\boldsymbol{\epsilon}$ fields have been defined in the Introduction, and $\boldsymbol{\sigma}^{\mathrm{T}}$ is the transpose of the stress tensor $\boldsymbol{\sigma}$. Through all the paper dotted variables indicate time rates.

The Clausius-Duhem inequality imposes

$$\varrho T\dot{\eta}^*(r,t) \geqq 0\,. \tag{2}$$

If the free energy per unit mass,

$$\psi = e - Ts\,, \tag{3}$$

and the condition (2) are replaced into (1), we obtain at constant temperature $T$ for the evolution of that free energy density

$$-\varrho\dot{\psi}(r,t) + \mathrm{Tr}\,(\boldsymbol{\sigma}^{\mathrm{T}} \cdot \dot{\boldsymbol{\epsilon}}) \geqq 0\,. \tag{4}$$

In what follows we shall always take the constant temperature case plus the following general assumptions:

(i) the free energy density function $\psi(\varepsilon, n_\varphi, H, T)$ can always be defined at a point $(r, t)$ in the continuum;

(ii) under a change of stress $\boldsymbol{\sigma}$ a reversible strain $\boldsymbol{\epsilon}^\mathrm{R}$ (elastic strain) always appears;

(iii) this reversible reaction depends linearly on the stress,

$$\varepsilon^\mathrm{R}_{ij} = S_{ijkl}\sigma_{kl}\;; \tag{5}$$

(iv) in addition, although this is not the most general case (see Hill [12] and Kocks [13]), we shall take the compliance $S_{ijkl}$ as independent of the other variables of the system $n_\varphi$, $H$, $T$;

(v) we shall also assume that the strain can always be written as

$$\boldsymbol{\epsilon} = \boldsymbol{\epsilon}^\mathrm{R} + \boldsymbol{\epsilon}^\mathrm{I}\,, \tag{6}$$

where $\boldsymbol{\epsilon}^\mathrm{I}$ is the irreversible part of it (i.e., does not recover under instantaneous changes of $\sigma$);

(vi) finally, the relation between microstructure and continuum medium will be established by an embedding procedure [14, 15]. The idea of this approach is as follows: for one type of inhomogeneity distributed randomly, an equivalent homogeneous medium is assumed to exist. The macroscopic properties of this medium must be the same as those of the composite formed by replacing a volume region of the continuum medium by the appropriate defect core region. For the case of the straight dislocation, for example, this will be a cylindrical volume of radius $\approx b$ (Burgers vector and approximately the radius of dislocation core).

The real material will be considered to be composed by "representative volume elements" (RVE) [15], and the above embedding procedure is used within each RVE for obtaining the internal variables $n_\varphi$ and $H$ at the corresponding position $r$ in the equivalent continuum medium.

The RVE should be taken as infinitesimal in the continuum limit, but they must be relatively large compared with lattice parameter or defect core region.

An additional simplifying assumption is to take the function $\psi$ as constant as a function of position, i.e., all RVE are identical in the medium. This approach avoids any influence of the gradient of the continuum medium on the problem and the subsequent difficulty in its treatment within the embedded approach. Therefore, this approximation will be taken throughout this paper.

The total free energy $F$ of the crystal results, in the above approximation, as

$$F(\varepsilon, n_\varphi, H, T) = V\varrho\psi(\varepsilon, n_\varphi, H, T)\,, \tag{7}$$

where $V$ is the volume of the crystal.

Under the above assumptions

$$\varrho[\mathrm{d}\psi(\varepsilon, n_\varphi, H, T)]_{n_\varphi, H, T} = \mathrm{d}W_\mathrm{R} = \sigma_{ij}\,\mathrm{d}\varepsilon^\mathrm{R}_{ij}\,, \tag{8}$$

where $W_\mathrm{R}$ is the reversible work. From (8) the function $\psi$ is obtained,

$$\varrho\psi(\varepsilon, n_\varphi, H, T) = \tfrac{1}{2}\,S_{ijkl}\sigma_{ij}\sigma_{kl} + \Phi_\mathrm{R}(T) + \Phi_\mathrm{I}(n_\varphi, H, T)\,, \tag{9}$$

where the integration constant is divided into two parts, a reversible one $\Phi_\mathrm{R}$, related to the temperature, and an irreversible one $\Phi_\mathrm{I}$ that is related also to the temperature and to the plastic state $H$ and point defect concentration $n_\varphi$. By replacing the time derivative of (9) and (6) into (4), we find

$$\mathrm{Tr}\,(\boldsymbol{\sigma}^\mathrm{T}\cdot\dot{\boldsymbol{\epsilon}}^\mathrm{I}) \geq \dot{\Phi}_\mathrm{I}(n_\varphi, H, T)\,. \tag{10}$$

Furthermore, from (9), at constant $T$

$$\varrho\dot{\psi} = \sigma_{ij}\dot{\varepsilon}^{\mathrm{R}}_{ij} + \dot{\Phi}_{\mathrm{I}} = \varrho\dot{e} - \varrho T(\dot{S}^{\mathrm{R}} + \dot{S}^{\mathrm{I}}) ,$$

where $\dot{S}^{\mathrm{R}}$, $\dot{S}^{\mathrm{I}}$ stand, respectively, for the rate of change of the reversible and irreversible parts of the entropy. By energy conservation $\dot{e} = 0$, and then

$$-\dot{\Phi}_{\mathrm{I}} = \varrho T\dot{S}^{\mathrm{I}} \geqq 0 . \tag{11}$$

Therefore $\dot{\Phi}_{\mathrm{I}}$ is related to the irreversible part of the entropy and it must be negative. From (10) and (11), we conclude that it is thermodynamically feasable that the irreversible straining of the lattice $\boldsymbol{\epsilon}^{\mathrm{I}}$, and then the total straining $\boldsymbol{\epsilon}$, due to the evolution of the plastic state and/or defect population and/or temperature, may be in a direction opposite to the external stress. Hence the local plastic work can be negative: $\mathrm{Tr}\,(\boldsymbol{\sigma}^{\mathrm{T}} \cdot \dot{\boldsymbol{\epsilon}}) \leqq 0$. Equation (10) is still valid when $H$, $n_{\varphi}$, or $T$ are themselves stress dependent.

## 3. Microstructure — Macrostructure Relation

Consistent with the hypothesis (vi) and (7) of the previous section we shall define the thermodynamics of the crystal via the function $\varrho\psi$ that except for the volume term $V$ assumed to be constant, agrees with $F$. We shall define at each representative volume element the thermodynamic forces $f_{\alpha}$ as the conjugate ones to the set of incremental internal variables $\mathrm{d}\xi_{\alpha}$, that are local changes of type $\alpha$, being related to a microstructural defect configuration, such that $\mathrm{d}\xi_{\alpha} = (\mathrm{d}n_{\varphi}, \mathrm{d}H)_{\alpha}$.

Although this approach is very similar to the one of Rice [2], it differs from it by the use of hypothesis (vi) above, which implies an effectively homogeneous medium and by the fact that in Rice's work the corresponding internal variables $\xi$ depend on the location within the medium. Actually, one of the purposes of his work is to arrive at a thermodynamic description of the continuum medium when those variables depend on the position in the medium.

From (9) the forces $f_{\alpha}$ are defined by

$$\sum_{\alpha} f_{\alpha}(\varepsilon, n_{\varphi}, H)\,\frac{\mathrm{d}\xi_{\alpha}}{\mathrm{d}t} = -\frac{\mathrm{d}^{\mathrm{P}}\Phi_{\mathrm{I}}}{\mathrm{d}t}\,(n_{\varphi}, H) , \tag{12}$$

where

$$\mathrm{d}^{\mathrm{P}}\Phi_{\mathrm{I}}(n_{\varphi}, H) = \Phi_{\mathrm{I}}(n_{\varphi} + \mathrm{d}n_{\varphi}, H + \mathrm{d}H) - \Phi_{\mathrm{I}}(n_{\varphi}, H) .$$

In the case of interest of a medium under irradiation and mechanically stressed, the defect concentration $n_{\varphi}$ is given by the one of vacancies $c_{\mathrm{v}}$ and interstitials $c_{\mathrm{i}}$ in the medium and the irreversible free energy rate can be written at any point as [16]

$$\frac{\mathrm{d}^{\mathrm{P}}\Phi_{\mathrm{I}}}{\mathrm{d}t} = -f_{\mathrm{c}}\,\frac{\mathrm{d}\xi_{\mathrm{c}}}{\mathrm{d}t} + \nabla\mu_{\mathrm{i}} \cdot \boldsymbol{J}_{\mathrm{i}} + \nabla\mu_{\mathrm{v}} \cdot \boldsymbol{J}_{\mathrm{v}} + \mu_{\mathrm{i}}K_{\mathrm{i}} + \mu_{\mathrm{v}}K_{\mathrm{v}} , \tag{13}$$

where $\nabla\mu_{\mathrm{i}}$ and $\nabla\mu_{\mathrm{v}}$ are the thermodynamic forces due to the non-uniform interstitial and vacancy concentrations, $\mu$ being the corresponding chemical potential. $K_{\mathrm{i}}$ and $K_{\mathrm{v}}$ are the rates of production of interstitials and vacancies, assumed to be equal. $\boldsymbol{J}_{\mathrm{i}}$ and $\boldsymbol{J}_{\mathrm{v}}$ are the interstitial and vacancy fluxes, respectively. The first term on the right-hand side of (13) is the irreversible free energy rate associated, for example, to the climbing of dislocations. The assumption (vi) of Section 2 implies the free energy rate to be the same for every point in the continuum. Equations (10) and (13) will describe therefore the evolution of the system and relate macrostructural stress/strain states with microstructural plastic state, defect concentration, and production.

## 4. Application to Dislocation Climbing

The climbing of dislocations in a medium under stress and with a defect concentration in excess of the equilibrium one, is due to the defect absorption and emission at the dislocation core. This essentially depends on two main effects: the availability of defects in the dislocation core neighbourhood, and the feasibility of that absorption of a defect at the core itself. As we shall see below, those two rate limiting factors are represented separately in (13). For the sake of showing this fact we shall first solve, in Section 4.1, the case of simultaneous interstitial and vacancy absorption and emission (including recombination) from a straight dislocation with given constant concentrations $c_i$, $c_v$ of interstitials and vacancies in the medium. At the dislocation core the concentration of defects is taken as zero. The effect of jogs and dislocation core configuration is not explicitly included. The rate controlling effect is taken here to be the last jump of the point defect to the straight dislocation core (therefore the name "jump method" used by Goesele [17] for this method for solving the reaction volume). This in general can be taken as a simplifying assumption of the effectively much more complex physical situation.

In Section 4.2 we solve the case where every defect that reaches the core neighbourhood is instantaneously absorbed. For that case the long-range diffusion of defects determines the climbing rate.

Both in Sections 4.1 and 4.2, the "effective" continuum medium is determined by solving the problem within a "representative volume element" where the dislocation is embedded. Either a constant defect concentration or a condition on the defect flux may be assumed as boundary condition. A single dislocation type will be considered to exist.

### *4.1 Jump method*

We shall assume a medium under stress and irradiation. Identical straight dislocations are homogeneously distributed in it. The point defect concentration is taken as constant except at the dislocation core, and as being composed by vacancies and interstitials, i.e., $n_\varphi = (c_v, c_i)$. In this section only the first and last two terms on the right-hand side of (13) will be considered, i.e., $\boldsymbol{J}_v = \boldsymbol{J}_i = \boldsymbol{0}$ except at the singular points at the boundary of the dislocation core [17].

A dislocation unit segment will climb a lattice distance $b$ when a vacancy or interstitial is either absorbed or emitted at its core. Finding the force acting on the dislocation follows quite closely the deduction in basic textbooks (for example, Weertman and Weertman [18]). By integrating (13) and considering only vacancy emission, one obtains the thermodynamic force $\boldsymbol{f}_{c_1}$ for climbing from

$$-(\boldsymbol{\sigma} \cdot \boldsymbol{b}) \cdot \boldsymbol{b} + Q_v - TS_v + P\,\Delta V_v - \frac{kT}{b} \ln \frac{c}{c_v} = \boldsymbol{f}_{c_1} \cdot (\hat{\boldsymbol{n}} \times \boldsymbol{b})\,. \qquad (14)$$

where $\hat{\boldsymbol{n}}$ is the dislocation line direction, $\boldsymbol{b}$ the Burgers vector assumed to be equal to a lattice parameter, $\hat{\boldsymbol{n}} \times \boldsymbol{b}$ the positive climbing of a lattice parameter, $\boldsymbol{f}_{c_1}$ the thermodynamic force per unit dislocation length, $Q_v$, $S_v$, $\Delta V_v$ are energy, entropy, and volume expansion, respectively, due to the creation of a vacancy per unit dislocation length, $c$ is the density of lattice sites.

Equation (14) can be written as

$$\boldsymbol{f}_{c_1} = \frac{(\hat{\boldsymbol{n}} \times \boldsymbol{b})}{b^2} \left[ (\boldsymbol{\sigma} \cdot \boldsymbol{b}) \cdot \boldsymbol{b} + \frac{kT}{b} \ln \frac{N_v^0}{c_v} \right], \qquad (15)$$

where $N_v^0$ is the concentration of vacancies in thermal equilibrium in the perfect lattice,

$$N_v^0 = c \exp\left[-\frac{Q_v - TS_v + P\,\Delta V_v}{kT}\right]. \tag{16}$$

If $c_i$ interstitials and $c_v$ vacancies are included as independent defects (i.e., as non-interacting one with the other), (15) transforms into

$$\boldsymbol{f}_{c_z} = \frac{(\hat{\boldsymbol{n}} \times \boldsymbol{b})}{b^2}\left[2(\boldsymbol{\sigma} \cdot \boldsymbol{b}) \cdot \boldsymbol{b} + \frac{kT}{b} \ln \frac{N_v^0 c_i}{N_i^0 c_v}\right], \tag{17}$$

where $N_i^0$ is the thermal equilibrium concentration of interstitials.

The dislocation climbing rate per unit length, conjugate to the force (17), can be obtained by considering that climbing results from: a) interstitial trapping at the dislocation core, b) vacancy trapping, and c) vacancy emission. The processes a) to c) are sketched in Fig. 1 for a dislocation in a simple square lattice. Under the simplifying assumption that the dislocation climbs rigidly as a straight line (no jogs or defect diffusion at the core are explicitly treated), the climbing rate is deduced for a given concentration $c_i$, $c_v$ of point defects in its neighbourhood. By examining Fig. 1, this rate can be shown to be

$$\dot{\boldsymbol{\xi}}_c = \frac{(\hat{\boldsymbol{n}} \times \boldsymbol{b})}{b^2}\,(n_i D_i c_i - n_v D_v c_v + N_v^* D_v)\,, \tag{18}$$

where the point defect trapping a) and b) are given by the first two terms on the right side of (18). $D_i$, $D_v$ are the self-interstitial and vacancy diffusivity in the neighbourhood of the dislocation, and $n_i$ and $n_v$ are numerical values that depend on the number of interstitial sites per lattice site and the lattice symmetry. For the simple square lattice of Fig. 1, $n_i = 3/4$, $n_v = 1$. The third term gives the vacancy emission term with

$$N_v^* = N_v^0 \left(\frac{c_i N_v}{c_v N_i}\right), \tag{19}$$

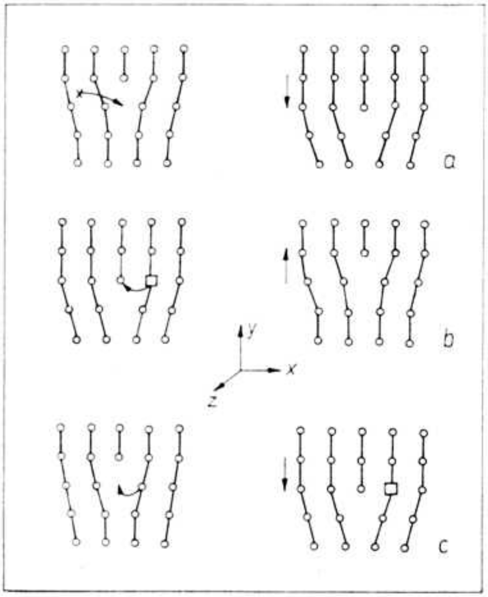

Fig. 1. Simple square lattice dislocation climbing by trapping and emission of point defects. a) Interstitial trapping, b) vacancy trapping, c) vacancy emission

where

$$N_{\mathrm{v}} = N_{\mathrm{v}}^{0} \exp \frac{[(\boldsymbol{\sigma} \cdot \boldsymbol{b}) \cdot \boldsymbol{b}]\, b}{kT} \quad \text{and} \quad N_{\mathrm{i}} = N_{\mathrm{i}}^{0} \exp - \frac{[(\boldsymbol{\sigma} \cdot \boldsymbol{b}) \cdot \boldsymbol{b}]\, b}{kT} .$$

The above equation (18) has been deduced on the basis of the last jump of the defects determining the dislocation climbing rate. As a result, this rate, and therefore $\mathrm{d}^{\mathrm{P}}\Phi_{\mathrm{I}}/\mathrm{d}t$ (13), depends on the local concentration of point defects, the local jump rate, the lattice symmetry, and the dislocation core geometry. $\mathrm{d}^{\mathrm{P}}\Phi_{\mathrm{I}}/\mathrm{d}t$ for this case, also depends on the production rate of defects, and through the thermodynamic force, on the stress field.

### *4.2 Diffusion controlled climbing*

We now look at the whole equation (13) but under the assumption that every defect that reaches the immediate neighbour sites of the dislocation core is instantaneously absorbed. The contribution of the defect population to change the irreversible free energy density,

$$\frac{\mathrm{d}^{\mathrm{P}}\Phi_{\mathrm{I}}}{\mathrm{d}t}$$

can be deduced by following the work of Dederichs and Schröder [19], Savino and Tomé [20], and Tomé et al. [21] on lattice defect diffusion. There, the defect flux is evaluated at a given lattice site $R_i$ by considering all the possible defect thermal jumps to near sites $R_j$. For the irreversible free energy at that site one must replace in (13) the defect flux deduced by the above authors,

$$\boldsymbol{J}_{\gamma}(R_i) = \frac{\nu_0}{2} \sum_j \exp\left(-\frac{Q_{ij}^{\gamma}}{kT}\right)\left[c^{\gamma}(R_j) \exp\left(\frac{E^{\gamma}(R_j)}{kT}\right) - c^{\gamma}(R_i) \exp\left(\frac{E^{\gamma}(R_i)}{kT}\right)\right] \boldsymbol{S}_{ij} , \tag{20}$$

where $\gamma$ stands for interstitials or vacancies, $c^{\gamma}(R_j)$ is the defect concentration at site $R_j$, $E(R_j)$ the energy of the lattice with the defect at site $R_j$, and $Q_{ij}^{\gamma}$ the energy with the defect at the saddle point location when jumping through the minimum energy path from $R_i$ to $R_j$ ($\boldsymbol{S}_{ij} = \boldsymbol{R}_j - \boldsymbol{R}_i$). If further we replace the chemical potentials $\mu_{\mathrm{i}}$ and $\mu_{\mathrm{v}}$ in (13) by the defect concentration $c_{\mathrm{i}}, c_{\mathrm{v}}$, we get within this approximation, for a slightly distord crystal,

$$\begin{aligned}
&\boldsymbol{f}_{c_\gamma} \frac{\mathrm{d}\xi_{\mathrm{c}}}{\mathrm{d}t} + \frac{\mathrm{d}^{\mathrm{P}}\Phi_{1}(n_{\varphi}, H)}{\mathrm{d}t} = \\
&= \frac{\nu_0}{4} \sum_{i,j,\gamma} \exp\left(-\frac{Q_{ij}^{\gamma}}{kT}\right)\left[c^{\gamma}(R_j) \exp\left(\frac{E^{\gamma}(R_j)}{kT}\right) - c^{\gamma}(R_i) \exp\left(\frac{E^{\gamma}(R_i)}{kT}\right)\right]^2 - \\
&- \sum_{\gamma} K^{\gamma} \sum_{i} c^{\gamma}(R_i) \exp\left(\frac{E^{\gamma}(R_i)}{kT}\right).
\end{aligned} \tag{21}$$

In the case of diffusion controlling, the dislocation climb rate, when the recombination is negligible, is

$$\dot{\xi}_{\mathrm{c}} = (J_{\mathrm{i}} - J_{\mathrm{v}})\, (\hat{\boldsymbol{n}} \times \boldsymbol{b}) . \tag{22}$$

With (17), (21), and (22), $\mathrm{d}^{\mathrm{P}}\Phi^{\mathrm{I}}/\mathrm{d}t$ can be obtained.

If only the single-defect case (either interstitials or vacancies) is considered in (21), we get the Lagrangian for the stationary case,

$$
\begin{aligned}
&f_{e_1}\frac{\mathrm{d}\xi_{e_1}}{\mathrm{d}t}+\frac{\mathrm{d}^{\mathrm{P}}\Phi_\mathrm{I}(n_\varphi, H)}{\mathrm{d}t}=\\
&=\frac{\nu_0}{4}\sum_{i,j}\exp\left(-\frac{Q_{ij}}{kT}\right)\left[c(R_j)\exp\left(\frac{E(R_j)}{kT}\right)-c(R_i)\exp\left(\frac{E(R_i)}{kT}\right)\right]^2-\\
&\quad-K\sum_i c(R_i)\exp\left(\frac{E(R_i)}{kT}\right),
\end{aligned}
\tag{23}
$$

where $\mathrm{d}\boldsymbol{\xi}_{e_1}/\mathrm{d}t$ is $\boldsymbol{J}(\hat{\boldsymbol{n}}\times\boldsymbol{b})$.

Equation (23) exactly agrees with the ansatz of Dederichs and Schröder [19]. Diffusion in stress field under irradiation can be deduced from (23).

Finally, in this case of long-range diffusion of defects, it can be easily proved that the maximum climbing rate is determined by the condition of no accumulation of defects in the neighbourhood of the dislocation. Thermodynamically the condition of extremum results for

$$\delta\left(\frac{\mathrm{d}^{\mathrm{P}}\Phi_\mathrm{I}}{\mathrm{d}t}\right)=0\,.$$

In turn, this lack of point defect accumulation depends on the jump rate at the dislocation core.

## 5. Summary and Conclusions

We have developed a thermodynamic framework for describing the plastic state of a crystal under stress and irradiation.

We have shown, based on an embedding procedure, the existence and evolution of the irreversible part of a free energy, $\Phi_\mathrm{I}$, which relates the external variables (i) particle flux $\varphi$ and (ii) external stress $\sigma_\mathrm{e}$; or the equivalent internal ones (i) crystal damage $n_\varphi$, via production of Frenkel pairs, and (ii) the internal stress field $\sigma$ induced by $\sigma_\mathrm{e}$, with the plastic state $H$ and strain $\varepsilon$.

As independent external variables, irradiation and stress can produce an opposite straining effect on the lattice. However, we found a thermodynamic restriction, based on the Clausius-Duhem principle, which imposes

$$\mathrm{Tr}\,(\boldsymbol{\sigma}^\mathrm{T}\cdot\dot{\boldsymbol{\epsilon}})\geqq\dot{\Phi}_\mathrm{I}\,,$$

where $\dot{\Phi}_\mathrm{I}\leqq 0$. This implies that the straining may be opposite in sign to the stress, i.e., some amount of anti-straining may exist, however, limited to a maximum value satisfying the above inequality.

A similar conclusion as above was obtained by Rice [2] in the case of relaxating "locked-in" energy. In our case inequality (10) is due to the coexistence of more than one mechanical process. As we said in the Introduction, energy is irreversibly "pumped" into the system, both by irradiation and by the mechanical effect of an applied stress. The above result validates, for example, the case of radiation growth of anisotropic materials. In that case, the direction of the net deformation of a specimen may be independent of the direction of the stress [3]. However, even in that case, (11) must be satisfied, i.e., the maximum amount of anti-straining is thermodynamically restricted.

As an example of a simple application for the above thermodynamic approach, the problem of straight dislocation climbing under irradiation is studied by explicitly developing the irreversible part of the free energy. The dislocation line is assumed to remain always straight, and two limiting cases are studied: (i) constant concentration of defects, except at the dislocation core (defect jump method [17]) and (ii) long-range diffusion of defects. In the first case a defect jump rate restriction at the core is imposed, while in the second that jump rate is taken as infinite. The appropriate climbing rate is obtained in each case. Also in the second case, Dederichs and Schröder's ansatz [19] for point defect diffusion under stress is deduced within this thermodynamic framework and based on the microstructural defect jump rate.

***Acknowledgements***

This work was partially supported by the "Proyecto Multinacional de Investigación y Desarrollo en Materiales"OEA—CNEA (Organization of American States — National Atomic Energy Commission of Argentina) and the Materials Engineering Department, Virginia Polytechnic Institute and State University, Blacksburg, Virgina, USA.

### References

[1] P. Germain, Q. Nguyen, and P. Suquet, J. appl. Mech. **105**, 1010 (1983).
[2] J. R. Rice, in: Constitutive Equations in Plasticity, MIT Press, Cambridge/Massachusetts/London 1975 (p. 23).
[3] E. J. Savino and S. Harriague, 12th Internat. Symp. Effects of Radiation on Materials, ASTM STP870, 1985 (p. 667).
[4] J. Gittus and J. Zarka (Ed.), Modelling Small Deformation of Polycrystals, Elsevier Appl. Sci. Publ., London/New York 1986.
J. Gittus, J. Zarka, and Siavouche-Nemat-Nasser (Ed.), Large Deformations of Solids, Elsevier Appl. Sci. Publ., London/New York 1986.
[5] R. Bullough and M. R. Hayns, J. nuclear Mater. (Amsterdam) **57**, 348 (1975).
[6] J. H. Gittus and R. G. Anderson, Proc. European Conf. Irradiation Embrittlement and Creep in Fuel Cladding and Core Components, London 1972 (p. 291).
[7] Z. Mróz, in: Modelling Small Deformation of Polycrystals, Ed. J. Gittus and J. Zarka, Elsevier Appl. Sci. Publ., London/New York 1986 (p. 293).
[8] C. Stolz, see [7] (p. 89).
[9] J. Hirth and J. Lothe, Theory of Dislocations, McGraw-Hill Publ. Co., New York 1968.
[10] J. Friedel, Dislocations, Addison-Wesley Publ. Co., London 1964.
[11] R. Balluffi, phys. stat. sol. **31**, 443 (1969).
[12] R. Hill, J. Mech. Phys. Solids **13**, 89 (1965).
[13] U. F. Kocks, Physics of Strength and Plasticity, MIT Press, Cambridge (Mass.) 1969.
[14] A. D. Brailsford and R. Bullough, Roy. Phil. Trans. (London) **302**, 87 (1981).
[15] S. Nemat-Nasser, see [7] (p. 41).
[16] Y. Adda and J. Philibert, La diffusion dans les solides, Université de France Press, 1966.
[17] U. M. Goesele, Progr. Reaction Kinetics **13**, 63 (1984).
[18] J. Weertman and J. Weertman, Elementary Dislocation Theory, Macmillan Co., New York 1965.
[19] P. H. Dederichs and K. Schröder, Phys. Rev. B **17**, 2524 (1978).
[20] E. J. Savino and C. N. Tomé, J. nuclear Mater. **108/109**, 405 (1982).
[21] C. N. Tomé, H. A. Cecatto, and E. J. Savino, Phys. Rev. B **25**, 7428 (1982).

*(Received May 5, 1988; in revised form February 1, 1989)*