

*In Memoriam Adelina Georgescu*

# MATERIAL ELEMENT MODEL FOR EXTRINSIC SEMICONDUCTORS WITH DEFECTS OF DISLOCATION\*

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## Abstract

In a previous paper we outlined a geometric model for the thermodynamic description of extrinsic semiconductors with defects of dislocation. Applying a geometrization technique, within the rational extended irreversible thermodynamics with internal variables, the dynamical system for *simple material elements* of these media, the expressions of the entropy function and the entropy 1-form were obtained. In this contribution we deepen the study of this geometric model. We give a detailed description of the defective media under consideration and of the dislocation core tensor, we introduce the transformation induced by the process and, applying the closure conditions for the entropy 1-form, we derive the necessary conditions for the existence of the entropy function. These and other results are new in the paper. The derivation of the relevant entropy 1-form is the starting point to introduce an extended thermodynamical phase space.

MSC: 73B20,73B99.

**keywords:** Extended and rational irreversible thermodynamics, extrinsic semiconductors, solids with defects, dislocations.

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\*Accepted for publication on January 20, 2011.

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## Introduction

Since in nature there exist no ideal crystals without defects, the aim of this paper is to study the behavior of deformable extrinsic semiconductors with defects of dislocation. The dislocation lines disturb the periodicity of the crystal lattice (see [10] and [22]) and their structure resembles a network of infinitesimally thin channels. The models for defective extrinsic semiconductors may have relevance in several fundamentals technological sectors as electronic microscopy, nanotechnology and technology for integrated circuits VLSI (Very Large Scale Integration).

Semiconductor crystals, as germanium and silicon, are tetravalent elements [11]. In Fig.1<sub>a</sub> we have the representation of a germanium crystal that has a behaviour of an insulator at a temperature of  $0^\circ K$ . But at room temperature,  $300^\circ K$  (see Fig.1<sub>b</sub>), electrons of the crystal can gain enough thermal energy to jump to the conduction band.

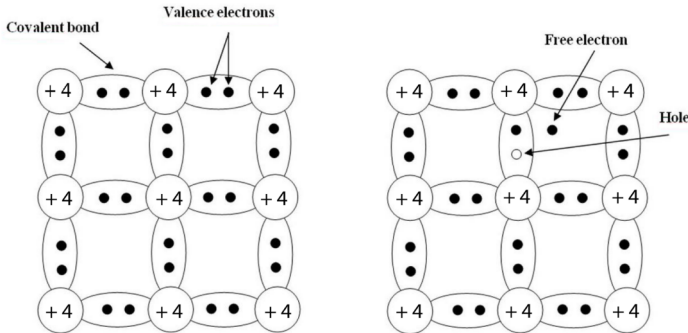


Figure 1: A symbolic representation in 2D of a germanium crystal structure: (a) at  $0^\circ K$  and (b) at  $300^\circ K$  with a broken covalent bond

To modify the electrical conductivity of an intrinsic semiconductor, impurity atoms adding one electron or one hole are introduced inside the crystal, by means of different techniques of "doping". Using pentavalent impurities, as antimony, a n-type extrinsic semiconductor is obtained, having more free electrons that may flow (see Fig.2<sub>a</sub>). By trivalent impurities, as indium, a p-type extrinsic semiconductor crystal is achieved, having more holes that may flow freely (see Fig.2<sub>b</sub>).

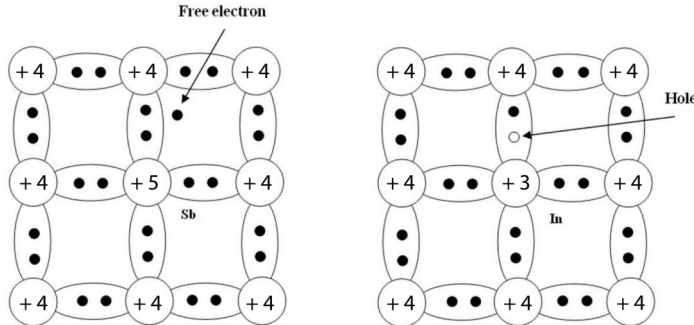


Figure 2: A symbolic representation in 2D of a germanium crystal structure:(a) doped by an atom of a pentavalent impurity (Antimony); (b) doped by an atom of a trivalent impurity (Indium)

In a previous paper [27], in the framework of the rational extended irreversible thermodynamics with internal variables [20], a thermodynamical model for defective extrinsic semiconductors was developed, introducing a dislocation density tensor à la Maruszewski [16] and its flux as internal variables. In [17] taking into account the results obtained in [27], a thermodynamical geometric model was outlined for simple material elements (see [2], [3], [4], [5], [23], [24] and [25]) of these media. The dynamical system and the expressions for the entropy function and the entropy 1-form were obtained. In this paper we deepen the study of this geometric model. In Section 1 we introduce the dislocation core tensor which describes the dislocation lines distribution. In Section 2 we give a detailed thermodynamical description of the defective media under consideration, taking into account the densities and the currents of the free electrons and holes coming from the intrinsic base. Finally, in Section 3 we introduce the transformation induced by the process and, applying the closure conditions for the entropy 1-form, we obtain the necessary conditions for the existence of the entropy function. The derivation of the entropy 1-form is the starting point to introduce a thermodynamical phase space [26]. Furthermore, from the necessary conditions for the existence of the entropy function, constitutive laws can be obtained by a suitable method [7].

In [1], [6], [8], [9], [15] and [18] geometric models for perfect extrinsic

semiconductors, for defective piezoelectric media, for high  $T_c$  superconductors of type-II, for porous structures, for polarizable media with internal variables and for deformable dielectrics with a non-Euclidean structure, respectively, were derived in the same geometrized framework.

## 1 The dislocation core tensor model

In extrinsic semiconductor crystals with defects of dislocation the geometry of the internal structure of these materials can influence the physical fields occurring in the body. These defects, acquired during a process of fabrication, can self propagate, because of changed and favorable surrounding conditions. Thus, they can provoke a premature fracture. The dislocation lines disturb the periodicity of the lattice of the crystal and their structure resembles a network of capillary channels inside the elastic solid (see [11], [16] and [22]). The interatomic distances are not conserved in the direct neighborhood of the dislocation lines in comparison to the distances in the remaining part of the lattice (see Fig.3<sub>a</sub>).

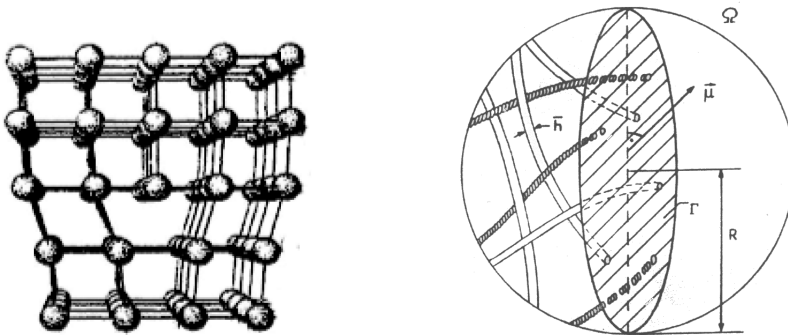


Figure 3: (a) An edge dislocation structure; (b) Characteristics of the pore-core structure ( $\bar{h} \ll R$ ) (after [16])

Moreover, the dislocation lines have their intrinsic orientation, which means, among others, that two dislocations of opposite signs annihilate when lines come close to each other. Their existence should not be omitted in the analysis of such kinetic processes as diffusion of mass or charges, transport of heat, recombination of charge carriers, etc. Thus, we introduce a dislocation

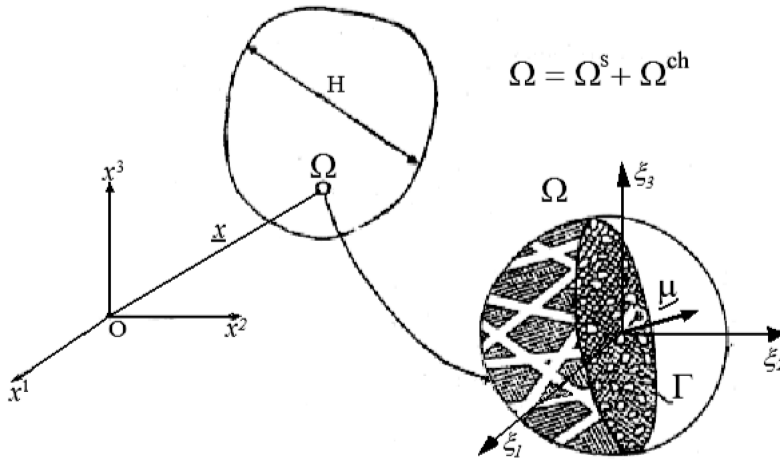


Figure 4: Averaging scheme. Characteristics of a channel structure (see [12])

core tensor à la Maruszewski [16] and its flux in the thermodynamical state space of independent variables for describing these defects. The definition and the introduction of the dislocation core tensor is based (see Fig. 3<sub>b</sub>) on a Kubik's geometrical model for porous channels. In [12] Kubik considers a representative elementary sphere volume  $\Omega$  of a porous structure having capillary tubes, large enough to provide a representation of all the statistical properties of the channel space  $\Omega^{ch}$  (see Fig. 4).  $\Omega = \Omega^s + \Omega^{ch}$ , where  $\Omega^s$  is the solid space. Since all the channels are considered to be interconnected the *effective volume porosity* is completely defined as  $f_v = \frac{\Omega^{ch}}{\Omega}$ . The analysis is restricted to media which are homogeneous with respect to volume porosity  $f_v$ , i.e.  $f_v$  remains constant in the medium. To avoid confusion all the microscopic quantities are written with respect to the coordinate system  $\xi_i$ , whereas all the macroscopic quantities are written with respect to the coordinate system  $x_i$ . Let  $\alpha(\xi)$  be any scalar, vectorial or second order tensorial quantity describing a microscopic property of the flux of some physical field flowing through the channel space  $\Omega^{ch}$  and written with respect to a coordinate system  $\xi_i$ . We assume that such quantity is zero in the solid space  $\Omega^s$ .

The volume averaging procedures give

$$\hat{\alpha}(\mathbf{x}) = \frac{1}{\Omega^{ch}} \int_{\Omega^{ch}} \alpha(\boldsymbol{\xi}) d\Omega, \quad \bar{\alpha}(\mathbf{x}) = \frac{1}{\Omega} \int_{\Omega^{ch}} \alpha(\boldsymbol{\xi}) d\Omega, \quad (1)$$

where the quantities  $\hat{\alpha}(\mathbf{x})$  and  $\bar{\alpha}(\mathbf{x})$  (written with respect to the a coordinate system  $x_i$ ) describe at macroscopic level the same property of the flux of the physical field under consideration. They are averaged quantities on the channel-volume and on the bulk-volume, respectively. Similarly, we define the averaged quantity  $\alpha(\boldsymbol{\xi})$  on the channel-area as follows

$$\overset{*}{\alpha}(\mathbf{x}, \boldsymbol{\mu}) = \frac{1}{\Gamma^{ch}} \int_{\Gamma} \alpha(\boldsymbol{\xi}) d\Gamma, \quad (2)$$

where  $\Gamma$  is the central sphere section and  $\Gamma^{ch}$  represents the channel-area of  $\Gamma$ . The orientation of  $\Gamma$  in  $\Omega$  is given by the normal vector  $\boldsymbol{\mu}$ .  $\Gamma = \Gamma^s + \Gamma^{ch}$ , where  $\Gamma^s$  is the solid-area. By definition the quantity  $\alpha(\boldsymbol{\xi})$  is zero on the solid-surface  $\Gamma^s$ . In such a medium, following [12], Maruszewski defines the so called *dislocation tensor*, as follows

$$\bar{\alpha}(\mathbf{x})_i = \mathcal{R}_{ij}(\mathbf{x}, \boldsymbol{\mu}) \overset{*}{\alpha}_j(\mathbf{x}, \boldsymbol{\mu}). \quad (3)$$

Eq. (3) gives a linear mapping between the averaged quantity on the bulk-volume  $\bar{\alpha}(\mathbf{x})$  and the average of the same quantity on the channel-area  $\overset{*}{\alpha}(\mathbf{x}, \boldsymbol{\mu})$ . In [12] Kubik gives an interpretation of  $\mathcal{R}_{ij}$  considering the flux of a quantity  $\bar{\alpha}(\mathbf{x})$  on a bulk-volume as a superposition of three unidimensional fluxes (along three mutually perpendicular channels) having average values  $\overset{*}{\alpha}_i(\mathbf{x}, \boldsymbol{\mu})$  on the orthogonal section areas of these channels. In [16] a new tensor, that refers  $\mathcal{R}_{ij}$  to the central sphere section  $\Gamma$ , is defined in the following way

$$\mathcal{R}_{ij}(\mathbf{x}, \boldsymbol{\mu}) = \Gamma a_{ij}(\mathbf{x}, \boldsymbol{\mu}).$$

$a_{ij}$  is called *dislocation core tensor* and its unit is  $m^{-2}$ . The components of  $a_{ij}$  form a kind of continuous representation of the number of dislocations which cross the surface  $\Gamma$ . Investigations show that  $a_{ij}$  is also dependent on time.

## 2 Governing equations for extrinsic semiconductors with defects of dislocation

Now, we introduce a thermodynamic model for a defective extrinsic semiconductor developed in [27] by one of us (L.R.) in the framework of Thermodynamics of irreversible processes with internal variables. In this paper, we deepen the thermodynamic description of this medium taking into account the densities and currents of the free electrons and holes that come from the intrinsic base of the semiconductor. Furthermore, we derive a set of constitutive relations. We use the standard Cartesian tensor notation in rectangular coordinate systems. We refer the motion of our material system to a current Eulerian configuration  $\mathcal{K}_t$ . We assume that in defective, extrinsic, thermoelastic semiconductors the following fields interact with each other: *the elastic field* described by the total stress tensor  $T_{ij}$  and the small-strain tensor  $\varepsilon_{ij}$ ; *the thermal field* described by the temperature  $\theta$ , its gradient and the heat flux  $q_i$ ; *the electromagnetic field* described by the electromotive intensity  $\mathcal{E}_i$  (that represents, in the Galilean approximation, the electric field referred to an element of the matter at time  $t$ , i.e. to the so called comoving frame  $\mathcal{K}_c$ ) and the magnetic induction  $B_i$  per unit volume; *the charge carrier fields* described by the densities of electrons  $n$  and holes  $p$ , their gradients and their fluxes  $j_i^n$  and  $j_i^p$ ; *the dislocation field* described by the dislocation core tensor  $a_{ij}$ , its gradient and the dislocation flux  $\mathcal{V}_{ijk}$ .

The independent variables are represented by the set

$$C = \{\varepsilon_{ij}, \mathcal{E}_i, B_i, n, p, \theta, a_{ij}, \mathcal{V}_{ijk}, j_i^n, j_i^p, q_i, n_{,i}, p_{,i}, \theta_{,i}, a_{ij,k}\}. \quad (4)$$

All the processes, occurring in the considered body, are governed by the following laws:

*Maxwell's equations* having the form:

$$\varepsilon_{ijk} E_{k,j} + \frac{\partial B_i}{\partial t} = 0, \quad D_{i,i} - \rho Z = 0, \quad (5)$$

$$\varepsilon_{ijk} H_{k,j} - j_i^Z - \frac{\partial D_i}{\partial t} = 0, \quad B_{i,i} = 0, \quad (6)$$

where  $\mathbf{E}$ ,  $\mathbf{B}$ ,  $\mathbf{D}$  and  $\mathbf{H}$  denote the electric field, the magnetic induction, the electric displacement and the magnetic field, respectively. Furthermore,

$$H_i = \frac{1}{\mu_0} B_i, \quad E_i = \frac{1}{\varepsilon_0} (D_i - P_i), \quad (7)$$

where  $\varepsilon_0$  and  $\mu_0$  denote the permittivity and permeability of vacuum and  $\mathbf{P}$  is the polarization per unit volume. The magnetization  $\mathbf{M}$  is assumed to be zero.

The total charge density  $Z$  and the density of the total current  $\mathbf{j}^Z$  are defined as follows:

$$Z = n + \bar{n} + p + \bar{p},$$

$$j_i^Z = \rho n v_i^n + \rho \bar{n} v_i^{\bar{n}} + \rho p v_i^p + \rho \bar{p} v_i^{\bar{p}} = \rho Z v_i + j_i^n + j_i^{\bar{n}} + j_i^p + j_i^{\bar{p}},$$

where  $n < 0$ ,  $\bar{n} < 0$ ,  $p > 0$ ,  $\bar{p} > 0$ ,  $j_i^n = \rho n (v_i^n - v_i)$ ,  $j_i^{\bar{n}} = 0$  (being  $v_i^{\bar{n}} = v_i$ ),  $j_i^p = \rho p (v_i^p - v_i)$ ,  $j_i^{\bar{p}} = 0$  (being  $v_i^{\bar{p}} = v_i$ ),  $\rho$  denotes the mass density,  $v_i$  are the components of the barycentric velocity of the body,  $v_i^n$ ,  $v_i^{\bar{n}}$ ,  $v_i^p$ ,  $v_i^{\bar{p}}$ , are the velocities of the electric charges  $n$ ,  $\bar{n}$ ,  $p$ ,  $\bar{p}$ , respectively, and  $j_i^n$ ,  $j_i^{\bar{n}}$ ,  $j_i^p$ ,  $j_i^{\bar{p}}$  their conduction currents, i.e. the electric currents due to the relative motion of the electric charges respect to the barycentric motion of the body.  $\rho Z v_i$  is the electric current due to the convection.

In particular,  $n$  is a total negative electric charge density coming from: the density of free electrons created doping the semiconductor by pentavalent impurities, denoted by  $N$  (see Fig. 2<sub>a</sub>), and the density of free electrons coming from the intrinsic base of the semiconductor, denoted by  $n^*$  (see Fig. 1<sub>b</sub>).  $\bar{n}$  is the charge density of the fixed and negative ionized atoms of doping tetravalent impurities, having velocity  $\mathbf{v}$  (i.e. they are comoving with the body). Thus, we have the following charge conservation laws

$$\rho \dot{N} + j_{i,i}^N = g^N, \quad \rho \dot{n}^* + j_{i,i}^{n^*} = g^{n^*}, \quad \rho \dot{\bar{n}} = \bar{g}^{\bar{n}} \quad \rho \dot{n} + j_{i,i}^n = g^n, \quad (8)$$

where the superimposed dot denotes the material derivative,  $\rho$  is the mass density,  $n = N + n^*$ ,  $j_{i,i}^n = j_{i,i}^N + j_{i,i}^{n^*}$ ,  $j_{i,i}^{\bar{n}} = 0$  and  $g^n = g^N + g^{n^*}$ .

Similarly,  $p$  are the positive electric charge density coming from: the density of holes created doping the semiconductor by tetravalent impurities, denoted by  $P$  (see Fig. 2<sub>b</sub>), and the density of holes coming from the intrinsic base of the semiconductor denoted by  $p^*$  (see Fig.1<sub>b</sub>).  $\bar{p}$  is the charge density of the fixed and positive ionized atoms of doping pentavalent impurities, having velocity  $\mathbf{v}$  (i.e. they are comoving with the body). Thus, we have the following charge conservation laws

$$\rho \dot{P} + j_{i,i}^P = g^P, \quad \rho \dot{p}^* + j_{i,i}^{p^*} = g^{p^*}, \quad \rho \dot{\bar{p}} = \bar{g}^{\bar{p}} \quad \rho \dot{p} + j_{i,i}^p = g^p, \quad (9)$$

where  $p = P + p^*$ ,  $j_{i,i}^p = j_{i,i}^P + j_{i,i}^{p^*}$ ,  $j_{i,i}^{\bar{p}} = 0$  and  $g^p = g^P + g^{p^*}$ . Furthermore, we assume that the concentrations  $\bar{n}$  and  $\bar{p}$  are practically constant. Hence,



$$\dot{\bar{n}} = \dot{\bar{p}} = 0 \quad \text{and} \quad \bar{g}^n = \bar{g}^p = 0. \quad (10)$$

$g^n$  and  $g^p$  describe the recombination of electrons and holes and satisfy the equation

$$g^n + g^p = 0. \quad (11)$$

Also, we have

*the evolution equations for the electron, hole and heat fluxes* having the form:

$$\dot{j}_i^n = J_i^n(C), \quad \dot{j}_i^p = J_i^p(C), \quad \dot{q}_i = Q_i(C), \quad (12)$$

where  $\mathbf{J}^n$ ,  $\mathbf{J}^p$  and  $\mathbf{Q}$  are the electron, hole and heat flux sources;

*the continuity equation:*

$$\dot{\rho} + \rho v_{i,i} = 0, \quad (13)$$

where the mass charge carriers have been neglected compared to  $\rho$  (see the final remark about it in Section 3);

*the momentum balance:*

$$\rho \dot{v}_i - T_{ji,j} - \rho Z \mathcal{E}_i - \varepsilon_{ijk} \left( j_j^n + j_j^p + \overset{\Delta}{P}_j \right) B_k - P_j \mathcal{E}_{i,j} - f_i = 0, \quad (14)$$

where

$$\overset{\Delta}{P}_i = \dot{P}_i + P_i v_{k,k} - P_k v_{i,k}, \quad \mathcal{E}_i = E_i + \varepsilon_{ijk} v_j B_k, \quad (15)$$

$T_{ij}$  denotes the total stress tensor and  $f_i$  is the body force;

*the momentum of momentum balance:*

$$\varepsilon_{ijk} T_{jk} + c_i = 0. \quad (16)$$

In [27] it was demonstrated that the couple  $c_i$  for unit volume is vanishing, so that the stress tensor  $T_{ij}$  is symmetric;

*the internal energy balance:*

$$\rho \dot{e} - T_{ji} v_{i,j} - \left( j_j^n + j_j^p \right) \mathcal{E}_j - \rho \mathcal{E}_i \dot{P}_i + q_{i,i} - \rho r = 0, \quad (17)$$

where  $v_i$  are the components of the barycentric velocity of the body,  $e$  is the internal energy density,  $r$  is the heat source distribution per unit volume,  $P_i = \rho \mathcal{P}_i$  and  $v_{i,j}$  is the velocity gradient given by

$$v_{i,j} = L_{ij} = \dot{F}_{ik} (F_{kj})^{-1},$$

where  $F_{ij}$  denotes the deformation gradient;

the evolution equations for the dislocation density and the dislocation flux:

$$\dot{a}_{ij} + \mathcal{V}_{ijk,k} - A_{ij}(C) = 0, \quad \dot{\mathcal{V}}_{ijk} - \mathcal{V}_{ijk}(C) = 0, \quad (18)$$

where  $A_{ij}$  and  $\mathcal{V}_{ijk}$  are the dislocation density and the dislocation flux sources.

All the admissible solutions of the proposed evolution equations should be restricted by the following *entropy inequality*:

$$\rho \dot{S} + J_{Sk,k} - \frac{\rho r}{\theta} \geq 0, \quad (19)$$

where  $S$  denotes the entropy per unit mass and  $\mathbf{J}_S$  is the entropy flux associated with the fields of the set  $C$ .  $\mathbf{J}_S$  is defined by

$$\mathbf{J}_S = \frac{1}{\theta} \mathbf{q} + \mathbf{k}, \quad (20)$$

with  $\mathbf{k}$  an additional term called *extra entropy flux density*.

In [27] in order to close the balance equation system the entropy inequality was analyzed by Liu's theorem [14]. For the entropy extra flux  $\mathbf{k}$  the following form was obtained

$$k_k = -q_k + \mu^n j_k^n + \mu^p j_k^p + \pi_{ij} \mathcal{V}_{ijk} + \rho v_k \psi, \quad (21)$$

where  $\mu^n \equiv \frac{\partial \psi}{\partial n}$ ,  $\mu^p \equiv \frac{\partial \psi}{\partial p}$  and  $\pi_{ij} \equiv \rho \frac{\partial \psi}{\partial a_{ij}}$  are thermodynamical potentials, with  $\psi = e - \theta S - \mathcal{E}_i \mathcal{P}_i$  the free energy density. Using Smith's theorem [28], in the case of defective semiconductors only of n-type, isotropic polynomial representations, satisfying the objectivity and material frame indifference principles (see [19] and [21]), were derived for the constitutive functions, where the following forms were assumed for the quantities responsible for the dislocation field

$$a_{ij} = a \delta_{ij}, \quad A_{ij} = A \delta_{ij}, \quad \mathcal{V}_{ijk} = \mathcal{V}_k \delta_{ij}, \quad V_{ijk} = V_k \delta_{ij}. \quad (22)$$

In this paper, using the results obtained in [27] by Liu's theorem and, applying Smith's theorem, we derive the constitutive relations for n and p type semiconductors in the same above assumptions (22) for the dislocation field. In particular, we have

$$\begin{aligned} T_{ij} = & \beta_\tau^1 \delta_{ij} + \beta_\tau^2 \varepsilon_{ij} + \beta_\tau^3 \varepsilon_{ik} \varepsilon_{kj} + \beta_\tau^4 \mathcal{E}_i \mathcal{E}_j + \beta_\tau^5 (\varepsilon_{jk} \mathcal{E}_i \mathcal{E}_k + \varepsilon_{ik} \mathcal{E}_j \mathcal{E}_k) + \\ & + \beta_\tau^6 (\varepsilon_{jk} \varepsilon_{ks} \mathcal{E}_i \mathcal{E}_s + \varepsilon_{ik} \varepsilon_{ks} \mathcal{E}_s \mathcal{E}_j), \end{aligned} \quad (23)$$

$$P_i = (\beta_{\mathfrak{P}}^1 \delta_{ik} + \beta_{\mathfrak{P}}^2 \varepsilon_{ik} + \beta_{\mathfrak{P}}^3 \varepsilon_{ij} \varepsilon_{jk}) \mathcal{E}_k, \quad (24)$$

$$\begin{aligned} \mu^n &= \beta_n^1 n + \beta_n^2 p + \beta_n^3 a + \beta_n^4 \theta + \beta_n^5 \mathcal{E}_k \mathcal{E}_k + \\ &+ (\beta_n^6 \delta_{ij} + \beta_n^7 \varepsilon_{ij} + \beta_n^8 \varepsilon_{jk} \varepsilon_{ki} + \beta_n^9 \mathcal{E}_i \mathcal{E}_j + \beta_n^{10} \varepsilon_{jk} \mathcal{E}_i \mathcal{E}_k) \varepsilon_{ij}, \end{aligned} \quad (25)$$

$$\begin{aligned} \mu^p &= \beta_p^1 n + \beta_p^2 p + \beta_p^3 a + \beta_p^4 \theta + \beta_p^5 \mathcal{E}_k \mathcal{E}_k + \\ &+ (\beta_p^6 \delta_{ij} + \beta_p^7 \varepsilon_{ij} + \beta_p^8 \varepsilon_{jk} \varepsilon_{ki} + \beta_p^9 \mathcal{E}_i \mathcal{E}_j + \beta_p^{10} \varepsilon_{jk} \mathcal{E}_i \mathcal{E}_k) \varepsilon_{ij}, \end{aligned} \quad (26)$$

$$\begin{aligned} \pi &= \beta_\pi^1 n + \beta_\pi^2 p + \beta_\pi^3 a + \beta_\pi^4 \theta + \beta_\pi^5 \mathcal{E}_k \mathcal{E}_k + \\ &+ (\beta_\pi^6 \delta_{ij} + \beta_\pi^7 \varepsilon_{ij} + \beta_\pi^8 \varepsilon_{jk} \varepsilon_{ki} + \beta_\pi^9 \mathcal{E}_i \mathcal{E}_j + \beta_\pi^{10} \varepsilon_{jk} \mathcal{E}_i \mathcal{E}_k) \varepsilon_{ij}, \end{aligned} \quad (27)$$

$$\begin{aligned} g^n &= \beta_{g^n}^1 n + \beta_{g^n}^2 p + \beta_{g^n}^3 a + \beta_{g^n}^4 \theta + \beta_{g^n}^5 \mathcal{E}_k \mathcal{E}_k + \\ &+ (\beta_{g^n}^6 \delta_{ij} + \beta_{g^n}^7 \varepsilon_{ij} + \beta_{g^n}^8 \varepsilon_{jk} \varepsilon_{ki} + \beta_{g^n}^9 \mathcal{E}_i \mathcal{E}_j + \beta_{g^n}^{10} \varepsilon_{jk} \mathcal{E}_i \mathcal{E}_k) \varepsilon_{ij}, \end{aligned} \quad (28)$$

and  $g^p = -g^n$ , where  $\beta_\alpha^\alpha$ ,  $\beta_{\mathfrak{P}}^\gamma$ ,  $\beta_n^\varepsilon$ ,  $\beta_p^\varepsilon$ ,  $\beta_\pi^\varepsilon$ ,  $\beta_{g^n}^\varepsilon$  ( $\alpha = 1, 2, \dots, 6$ ,  $\gamma = 1, 2, 3$ ,  $\varepsilon = 1, 2, \dots, 10$ ) can be functions of the following invariants

$$n, p, \theta, a, \mathcal{E}_i \mathcal{E}_i, \varepsilon_{kk}, \varepsilon_{ij} \varepsilon_{ij}, \varepsilon_{ij} \varepsilon_{jk} \varepsilon_{ki}, \varepsilon_{ij} \mathcal{E}_i \mathcal{E}_j, \varepsilon_{ij} \varepsilon_{jk} \mathcal{E}_i \mathcal{E}_k. \quad (29)$$

Furthermore, we have obtained the following approximated expressions for the evolution equations for the dislocation density, dislocation, electron, hole and heat fluxes

$$\begin{aligned} \dot{a} + \mathcal{V}_{k,k} &= \delta_a^1 \varepsilon_{kk} + \delta_a^2 n + \delta_a^3 p + \delta_a^4 \theta + \delta_a^5 a + \delta_a^6 \mathcal{E}_i + \delta_a^7 a_{,i} + \delta_a^8 n_{,i} + \\ &+ \delta_a^9 p_{,i} + \delta_a^{10} \theta_{,i} + \delta_a^{11} \mathcal{V}_i + \delta_a^{12} j_i^n + \delta_a^{13} j_i^p + \delta_a^{14} q_i, \end{aligned} \quad (30)$$

$$\dot{\mathcal{V}}_k = \delta_v^1 \mathcal{E}_k + \delta_v^2 a_{,k} + \delta_v^3 n_{,k} + \delta_v^4 p_{,k} + \delta_v^5 \theta_{,k} + \delta_v^6 \mathcal{V}_k + \delta_v^7 j_k^n + \delta_v^8 j_k^p + \delta_v^9 q_k, \quad (31)$$

$$\dot{j}_k^n = \delta_n^1 \mathcal{E}_k + \delta_n^2 a_{,k} + \delta_n^3 n_{,k} + \delta_n^4 p_{,k} + \delta_n^5 \theta_{,k} + \delta_n^6 \mathcal{V}_k + \delta_n^7 j_k^n + \delta_n^8 j_k^p + \delta_n^9 q_k, \quad (32)$$

$$\dot{j}_k^p = \delta_p^1 \mathcal{E}_k + \delta_p^2 a_{,k} + \delta_p^3 n_{,k} + \delta_p^4 p_{,k} + \delta_p^5 \theta_{,k} + \delta_p^6 \mathcal{V}_k + \delta_p^7 j_k^n + \delta_p^8 j_k^p + \delta_p^9 q_k, \quad (33)$$

$$\dot{q}_k = \delta_q^1 \mathcal{E}_k + \delta_q^2 a_{,k} + \delta_q^3 n_{,k} + \delta_q^4 p_{,k} + \delta_q^5 \theta_{,k} + \delta_q^6 \mathcal{V}_k + \delta_q^7 j_k^n + \delta_q^8 j_k^p + \delta_q^9 q_k, \quad (34)$$

where  $\delta_a^\zeta$ ,  $\delta_v^\eta$ ,  $\delta_n^\eta$ ,  $\delta_p^\eta$ ,  $\delta_q^\eta$  ( $\zeta = 1, 2, \dots, 14$ ,  $\eta = 1, 2, \dots, 9$ ) can depend on invariants built on the set C (see eq. (4)). The laws (23) - (34) are very general, but it is possible to treat special problems describing the physical reality in several situations by some simplifications.

### 3 A geometric model for extrinsic semiconductors with defects of dislocation

In this Section, following [2], [3], [4], [5], [23], [24] and [25], we deepen the study of the geometric model for the thermodynamics of extrinsic defective semiconductors outlined in [17], where the dynamical system for *simple material elements* of these media, the expressions of the entropy function and the entropy 1-form were obtained. In particular, we derive the transformation induced by the process and, applying the closure conditions for the entropy 1-form, the necessary conditions for the existence of the entropy function.

Consider a material element and define the state space at time  $t$  as the set  $B_t$  of all the state variables which "fit" the configuration of the element at time  $t$ .  $B_t$  is assumed to have the structure of a finite dimensional manifold. The "total state space" is the disjoint union  $\mathcal{B} = \bigcup_t \{t\} \times B_t$  with a given natural structure of fibre bundle over  $\mathbb{R}$  where time flows (see [4] and [5]). We call it the thermodynamic fiber bundle. We consider the case in which the instantaneous state space  $B_t$  does not vary in time (i.e. there is an abstract space  $B$  such that  $B_t \simeq B$  for all instants of time  $t$ ) and the state space  $\mathcal{B}$  has the topology of the Cartesian product  $\mathcal{B} \simeq \mathbb{R} \times B$ . Furthermore, we consider an abstract space of *processes* (see [2], [3], [23], [24] and [25]) i.e. a set  $\Pi$  of functions

$$P_t^i : [0, t] \rightarrow \mathcal{G},$$

where  $[0, t]$  is any time interval, the space  $\mathcal{G}$  being a suitable target space defined by the problem under consideration,  $i$  a label ranging in an unspecified index set for all allowed processes and  $t \in \mathbb{R}$  the so called *duration* of the process. For the given state space  $B$  we suppose that the set  $\Pi$  is such that the following statements hold:

- $\exists D : P_t^i \in \Pi \rightarrow D(P_t^i) \equiv D_t^i \in \mathcal{P}(B)$ .  
 $D$  is the *domain function*,  $D_t^i$  is the *domain* of the  $i$ -th process (of duration  $t$ ) and  $\mathcal{P}(B)$  is the set of all the subsets of  $B$ ;
- $\exists R : P_t^i \in \Pi \rightarrow R(P_t^i) \equiv R_t^i \in \mathcal{P}(B)$ .  $R$  is the *range function* and  $R_t^i$  is called the *range* of the  $i$ -th process (of duration  $t$ );
- considering the restrictions

$$P_t^i = P_t^i |_{[0, \tau]} \quad (\tau \leq t) \quad (35)$$

new processes, called *restricted processes*, are obtained and they satisfy the following condition:

$$\forall \tau < t \quad D(P_t^i) \subseteq D(P_\tau^i). \quad (36)$$

Incidentally, this implies that  $\bigcap_{\tau=0}^t D(P_\tau^i) = D(P_t^i)$ , where  $t$  is the maximal duration.

Then, a continuous function is defined

$$\chi : (t, P_t^i) \in \mathbb{R} \times \Pi \rightarrow \rho_t^i \in C^0(B, B) \quad (37)$$

with

$$\rho_t^i : b \in D_t^i \subseteq B \rightarrow \rho_t^i(b) = b_t \in R_t^i \subseteq B, \quad (38)$$

so that for any instant of time  $t$  and for any process  $P_t^i \in \Pi$  a continuous mapping,  $\rho_t^i$ , called *transformation induced by the process* is generated, which gives point by point a correspondence between the initial state  $b$  and the final state  $\rho_t^i(b) = b_t$ .

Moreover, if  $P_t^i$  and  $P_s^j$  are processes such that  $D_s^j \cap R_t^i \neq \emptyset$ , then the function

$$(P_s^j \circ P_t^i) : [0, t + s] \rightarrow \mathcal{G}$$

defined by

$$(P_s^j \circ P_t^i)(\tau) = \begin{cases} P_t^i(\tau), & \tau \in [0, t] \\ P_s^j(\tau - t), & \tau \in ]t, t + s] \end{cases} \quad (39)$$

is a process having the following domain

$$D(P_s^j \circ P_t^i) = (\rho_t^i)^{-1}(D_s^j \cap R_t^i) \quad (40)$$

and,  $\forall b \in D(P_s^j \circ P_t^i)$ , the transformation induced by the process  $P_s^j \circ P_t^i$  is defined by

$$\rho_{t+s}^{ij}(b) = [\rho_s^j(\rho_t^i(b))]. \quad (41)$$

Now, we introduce a function of time

$$\lambda_b^i(\tau) = \begin{cases} b & \text{if } \tau = 0 \\ \rho_t^i(b) & \text{if } \tau \in ]0, t] \end{cases} \quad \text{with } b \in D_t^i \quad (42)$$

such that the transformation for the medium is a function

$$\delta : \tau \in \mathbb{R} \longrightarrow \delta(\tau) = (\tau, \lambda_b^i(\tau)) \in \mathbb{R} \times B. \quad (43)$$

With these positions the transformation is interpreted as a curve  $\delta$  in the union of all the state spaces such that it intersects the instantaneous state space just once.

Now, we assume that the behavior of extrinsic thermoelastic semiconductors with defects of dislocation is described by the following state variables

$$\mathbf{C} = \{F_{ij}, D_i, B_i, n, p, e, a_{ij}, \mathcal{V}_{ijk}, j_i^n, j_i^p, q_i, n_{,i}, p_{,i}, \theta_{,i}, a_{ij,k}\},$$

where we have taken into consideration the gradient of deformation  $F_{ij}$  instead of the strain tensor, following standard methods. The full state space is then

$$B = Lin(\mathfrak{V}) \oplus \mathfrak{V} \oplus \mathfrak{V} \oplus \mathbb{R} \oplus \mathbb{R} \oplus \mathbb{R} \oplus \mathcal{W}_1 \oplus \mathcal{W}_2 \oplus \mathfrak{V} \oplus \mathfrak{V} \oplus \mathfrak{V} \oplus \mathfrak{V} \oplus \mathfrak{V} \oplus \mathfrak{V} \oplus \mathfrak{V} \oplus Lin(\mathcal{W}_1),$$

where  $\mathfrak{V} \simeq \mathbb{R}^3$ ,  $\mathcal{W}_1$  and  $\mathcal{W}_2$  are vector spaces accounting for the internal variables  $\mathbf{a}$  and  $\mathbf{V}$ , respectively.

Moreover, applying the usual method, we assume that for each pair  $(P_t^i, b)$  the following dynamical system holds (see [2], [3], [23], [24] and [25])

$$\left\{ \begin{array}{l} \dot{\mathbf{F}} = \mathbf{L}\mathbf{F} \\ \dot{\mathbf{D}} = \mathcal{H} \\ \dot{\mathbf{B}} = \mathbf{\Xi} \\ \rho \dot{n} = G^n \\ \rho \dot{p} = G^p \\ \rho \dot{e} = \mathbf{T} \cdot \mathbf{L} + h \\ \dot{\mathbf{a}} = \boldsymbol{\gamma} \\ \dot{\mathbf{V}} = \mathbf{V} \\ \dot{\mathbf{j}}^n = \mathbf{J}^n \\ \dot{\mathbf{j}}^p = \mathbf{J}^p \\ \dot{\mathbf{q}} = \mathbf{Q} \\ \dot{\nabla} n = \mathcal{N} \\ \dot{\nabla} p = \mathcal{P} \\ \dot{\nabla} \theta = \boldsymbol{\Theta} \\ \dot{\nabla} \mathbf{a} = \boldsymbol{\Gamma}, \end{array} \right. \quad (44)$$

where

$$\begin{aligned} \mathcal{H}_i &= \varepsilon_{ijk} H_{k,j} - (j_i^n + j_i^p) - \rho Z v_i, & \Xi_i &= -\varepsilon_{ijk} E_{k,j}, & G^n &= g^n - j_{i,i}^n, \\ G^p &= g^p - j_{i,i}^p, & h &= (j_i^n + j_i^p) \mathcal{E}_i - \frac{\dot{\rho}}{\rho} \mathcal{E}_i P_i + \mathcal{E}_i \dot{P}_i - q_{i,i} + \rho r, \\ \gamma_{ij} &= -\mathcal{V}_{ijk,k} + A_{ij}, \end{aligned} \quad (45)$$

(see eqn.s (5)<sub>1</sub>, (6)<sub>1</sub>, (8)<sub>4</sub>, (9)<sub>4</sub>, (17), (18) and (23) - (34)) and  $\delta$  is defined by eq. (43).

The constitutive functions  $\theta$ ,  $\mathbf{T}$ ,  $\mathbf{P}$ ,  $\mathbf{J}^n$ ,  $\mathbf{J}^p$ ,  $\mathbf{Q}$ ,  $\mathbf{A}$ ,  $\mathbf{V}$ ,  $g^n$  and  $g^p$  are defined in the following way

$$\begin{aligned}\theta &: \mathbb{R} \times B \rightarrow \mathbb{R}^{++}, \quad \mathbf{T} : \mathbb{R} \times B \rightarrow \text{Sym}(\mathfrak{V}), \quad \mathbf{P} : \mathbb{R} \times B \rightarrow \mathfrak{V}, \\ \mathbf{J}^n &: \mathbb{R} \times B \rightarrow \mathfrak{V}, \quad \mathbf{J}^p : \mathbb{R} \times B \rightarrow \mathfrak{V}, \quad \mathbf{Q} : \mathbb{R} \times B \rightarrow \mathfrak{V}, \quad \mathbf{A} : \mathbb{R} \times B \rightarrow \mathcal{W}_1, \\ \mathbf{V} &: \mathbb{R} \times B \rightarrow \mathcal{W}_2, \quad g^n : \mathbb{R} \times B \rightarrow \mathbb{R}, \quad g^p : \mathbb{R} \times B \rightarrow \mathbb{R}.\end{aligned}$$

The set  $(B, \Pi, \theta, \mathbf{T}, \mathbf{P}, \mathbf{J}^n, \mathbf{J}^p, \mathbf{A}, \mathbf{V}, \mathbf{Q}, g^n, g^p)$  defines the simple material element for defective extrinsic semiconductors (see [24]).

Following standard procedures (see [3], [4] and [5]), in this geometrical structure we are able to introduce an action  $s$ , called “*entropy function*”, which is related to a reversible transformation between the initial and the actual states  $b$  and  $b_t$ , respectively, in the following way:

$$s(\rho_t^i, b, t) = - \int_0^t \frac{1}{\rho} \nabla \cdot \mathbf{J}_S d\tau, \quad (46)$$

where  $\mathbf{J}_S$  is defined according to equation (20). Then, we get

$$s = \int_0^t -\frac{1}{\rho\theta} \nabla \cdot \mathbf{q} d\tau + \int_0^t \frac{1}{\rho\theta^2} \mathbf{q} \cdot \nabla \theta d\tau - \int_0^t \frac{1}{\rho} \nabla \cdot \mathbf{k} d\tau. \quad (47)$$

Using the internal energy balance equation and the relation  $\mathbf{L} = \nabla \mathbf{v} = \dot{\mathbf{F}}\mathbf{F}^{-1}$ , we obtain the following expression for  $\nabla \cdot \mathbf{q}$

$$\nabla \cdot \mathbf{q} = -\rho\dot{e} + \mathbf{T} \cdot (\dot{\mathbf{F}}\mathbf{F}^{-1}) + (\mathbf{j}^n + \mathbf{j}^p) \cdot \boldsymbol{\varepsilon} - \frac{\dot{\rho}}{\rho} \boldsymbol{\varepsilon} \cdot \mathbf{P} + \boldsymbol{\varepsilon} \cdot \dot{\mathbf{P}}, \quad (48)$$

so that the final expression for the entropy function is calculated as an integral along a path into the space  $\mathbb{R} \times B$  of all thermodynamic variables together with the independent time variable

$$s(\rho_t^i, b, t) = \int_{\delta} \Omega, \quad \text{with}$$

$$\Omega = -\frac{1}{\rho\theta} (\mathbf{T}\mathbf{F}^{-T}) \cdot d\mathbf{F} - \frac{1}{\rho\theta} \boldsymbol{\varepsilon} \cdot d\mathbf{D} + \frac{1}{\theta} de + \left[ \frac{1}{\rho\theta^2} \mathbf{q} \cdot \nabla \theta - \frac{1}{\rho\theta} (\mathbf{j}^n + \mathbf{j}^p) \cdot \boldsymbol{\varepsilon} \right]$$

$$+\frac{1}{\rho^2\theta}\dot{\rho}\boldsymbol{\varepsilon}\cdot\mathbf{P}+\frac{\varepsilon_0}{\rho\theta}\boldsymbol{\varepsilon}\cdot\dot{\mathbf{E}}-\frac{1}{\rho}\nabla\cdot\mathbf{k}\Big]d\tau, \quad (49)$$

where we have used the relation  $\mathbf{T}\cdot(\dot{\mathbf{F}}\mathbf{F}^{-1})=(\mathbf{T}\mathbf{F}^{-T})\cdot\dot{\mathbf{F}}$  (being  $\mathbf{F}^{-T}=(\mathbf{F}^{-1})^T$  and  $T$  denoting matrix transposition). In eq.(49) the entropy function defines a 1-form  $\Omega$  in  $\mathbb{R}\times B$  called the *entropy 1-form*. In components the entropy 1-form  $\Omega$  becomes:

$$\Omega=\omega_\mu dq^\mu+\omega_0 dt=\omega_A dq^A \quad (A=1,2,\dots,16),$$

where

$$q^A=(\mathbf{F},\mathbf{D},\mathbf{B},n,p,e,\mathbf{a},\boldsymbol{\nu},\mathbf{j}^n,\mathbf{j}^p,\mathbf{q},\nabla n,\nabla p,\nabla\theta,\nabla\mathbf{a},t)$$

and

$$\omega_A=\left[\left(-\frac{1}{\rho\theta}\mathbf{T}\mathbf{F}^{-T}\right),\left(\frac{1}{\rho\theta}\boldsymbol{\varepsilon}\right),0,0,0,\left(\frac{1}{\theta}\right),0,0,0,0,0,0,0,0,0,0,\left(\frac{1}{\rho\theta^2}\mathbf{q}\cdot\nabla\theta-\frac{1}{\rho\theta}(\mathbf{j}^n+\mathbf{j}^p)\cdot\boldsymbol{\varepsilon}+\frac{1}{\rho^2\theta}\dot{\rho}\boldsymbol{\varepsilon}\cdot\mathbf{P}+\frac{\varepsilon_0}{\rho\theta}\boldsymbol{\varepsilon}\cdot\dot{\mathbf{E}}-\frac{1}{\rho}\nabla\cdot\mathbf{k}\right)\right].$$

Thus, by external differentiation, a 2-form is obtained:

$$d\Omega=\frac{\partial w_A}{\partial q^B}dq^B\wedge dq^A \quad (A,B=1,2,\dots,16).$$

Since  $d\Omega$  can be written in the following form

$$\begin{aligned} d\Omega &= \sum_{B<A} \frac{\partial w_A}{\partial q^B} dq^B \wedge dq^A + \sum_{B>A} \frac{\partial w_A}{\partial q^B} dq^B \wedge dq^A \\ &= \sum_{B<A} \left( \frac{\partial w_A}{\partial q^B} - \frac{\partial w_B}{\partial q^A} \right) dq^B \wedge dq^A, \end{aligned}$$

applying the closure conditions for the entropy 1-form, we obtain the necessary conditions for the existence of the entropy function  $s$  during the processes under consideration setting

$$\frac{\partial w_A}{\partial q^B} = \frac{\partial w_B}{\partial q^A}.$$

In our case we have

$$\partial_e\left(-\frac{1}{\rho\theta}\mathbf{T}\mathbf{F}^{-T}\right)=\partial_{\mathbf{F}}\left(\frac{1}{\theta}\right), \quad \partial_{\mathbf{D}}\left(-\frac{1}{\rho\theta}\mathbf{T}\mathbf{F}^{-T}\right)=\partial_{\mathbf{F}}\left[-\frac{1}{\rho\theta}\boldsymbol{\varepsilon}\right],$$



$$\partial_{\mathbf{D}} \left( \frac{1}{\theta} \right) = \partial_e \left[ -\frac{1}{\rho\theta} \boldsymbol{\mathcal{E}} \right], \quad \frac{\partial \omega_A}{\partial \mathbf{q}^B} = 0 \quad (A = 1, 2, 6, 16; B = 3, 4, 5, 7, \dots, 15),$$

$$\partial_t \left( -\frac{1}{\rho\theta} \mathbf{T}\mathbf{F}^{-T} \right) = \partial_{\mathbf{F}} \left[ \frac{1}{\rho\theta^2} \mathbf{q} \cdot \nabla\theta - \frac{1}{\rho\theta} (\mathbf{j}^n + \mathbf{j}^p) \cdot \boldsymbol{\mathcal{E}} + \frac{1}{\rho^2\theta} \dot{\rho} \boldsymbol{\mathcal{E}} \cdot \mathbf{P} + \frac{1}{\rho\theta} \epsilon_0 \boldsymbol{\mathcal{E}} \cdot \dot{\mathbf{E}} - \frac{1}{\rho} \nabla \cdot \mathbf{k} \right],$$

$$\partial_t \left( \frac{1}{\theta} \right) = \partial_e \left[ \frac{1}{\rho\theta^2} \mathbf{q} \cdot \nabla\theta - \frac{1}{\rho\theta} (\mathbf{j}^n + \mathbf{j}^p) \cdot \boldsymbol{\mathcal{E}} + \frac{1}{\rho^2\theta} \dot{\rho} \boldsymbol{\mathcal{E}} \cdot \mathbf{P} + \frac{1}{\rho\theta} \epsilon_0 \boldsymbol{\mathcal{E}} \cdot \dot{\mathbf{E}} - \frac{1}{\rho} \nabla \cdot \mathbf{k} \right],$$

$$\partial_t \left[ -\frac{1}{\rho\theta} \boldsymbol{\mathcal{E}} \right] = \partial_{\mathbf{D}} \left[ \frac{1}{\rho\theta^2} \mathbf{q} \cdot \nabla\theta - \frac{1}{\rho\theta} (\mathbf{j}^n + \mathbf{j}^p) \cdot \boldsymbol{\mathcal{E}} + \frac{1}{\rho^2\theta} \dot{\rho} \boldsymbol{\mathcal{E}} \cdot \mathbf{P} + \frac{1}{\rho\theta} \epsilon_0 \boldsymbol{\mathcal{E}} \cdot \dot{\mathbf{E}} - \frac{1}{\rho} \nabla \cdot \mathbf{k} \right].$$

We remark that in semiconductor crystals  $\rho$  is practically constant, so that all results derived in the paper containing the time derivative of  $\rho$  can be disregarded. The above relations give the necessary conditions characterizing a sort of "irrotationality" of the entropy 1-form during the analyzed transformation. If the entropy 1-form in eq. (49) is closed and its coefficients are regular, this form is exact and the existence of an upper-potential satisfying relation  $S(b_t) - S(b) \geq s$  is ensured, for all  $P_t^i \in \Pi$ , with  $b_t = \rho_t^i(b)$  [3]. Starting from the entropy 1-form it is possible to introduce and investigate an extended thermodynamical phase space in a suitable way [26].

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