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On the contribution of the mexican school to extended irreversible thermodynamics*

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ABSTRACT. The postulates and methodology of the version of extended irreversible thermodynamics developed in Mexico are presented. Mention is made of the main features which make it different from other existing versions. The ionized gas modeled as a binary mixture is discussed to illustrate the approach. Some limitations and perspectives are also pointed out.

RESUMEN. Se presentan los postulados y la metodología de la versión de la Termodinámica Irreversible Extendida desarrollada en México. Se hace mención de las principales características que la hacen diferente de otras versiones. Para ilustrar el enfoque se discute brevemente el caso de un gas ionizado modelado como una mezcla binaria. Finalmente, se señalan las limitaciones y perspectivas de esta versión.

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1. INTRODUCTION

The thermodynamic description of non-equilibrium systems is as yet an unresolved challenge for theoretical physics. Perhaps the most successful theory in this respect is linear irreversible thermodynamics (LIT), as presented for instance in the monograph of de Groot and Mazur [1], which nevertheless presents some well known limitations [2]. This has prompted in the last twenty five years efforts addressed to generalize LIT in order to extend its range of applicability. Many of these efforts [3,4,5,7] have become referred to in the literature under the common name of extended irreversible thermodynamics (EIT) in spite of the fact that, while sharing similar goals, they differ both in physical content and specific methodology. The differences between particular versions have already

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*This paper is dedicated to Prof. L.S. García-Colín on the occasion of his sixtieth birthday.

been touched upon (albeit not very deeply) by other authors [4,6,7,8]. It is the major aim of this paper to provide a systematic account of the version developed in Mexico by Prof. L.S. García-Colín and some of his collaborators (for which the name Mexican version of EIT (M-EIT) has already been introduced [9] in the literature), pointing out the most important contributions and commenting on the main discrepancies with other formulations.

The paper is organized as follows. In Sect. 2, we outline the postulates, rules and methodology of the M-EIT; in Sect. 3, we deal with an specific example, namely that of an ionized gas immersed in an electromagnetic field. Finally we close the paper in Sect. 4 with a short discussion and some concluding remarks.

2. THE MEXICAN EIT FORMALISM

The basic idea underlying all versions of EIT is the enlargement of the thermodynamic space G, so that $G = C \cup R$, where C represents the set of the usual variables of LIT and R is the set of new variables. The number and nature of the R-variables depend on the particular system and the non-equilibrium states one wants to describe and on the EIT version that one has chosen. In the M-EIT such variables are taken to be those quantities appearing in the usual balance equations for which a "constitutive" relationship is required in order to obtain a closed description of the time evolution of the system.

Formally, the postulates of EIT are two, namely:

i) There exists a continuous non-equilibrium thermodynamic potential η [10], depending on all the variables in G, whose time evolution is governed by a generalized Gibbs equation. The partial derivatives of η with respect to the G variables constitute generalized equations of state and in particular those with respect to the C variables reduce in the proper limit to their local equilibrium or equilibrium expressions. Thus the physical interpretation of η as an extension of the usual potential of LIT beyond the local equilibrium assumption naturally follows.

ii) η also obeys a balance equation of the form

$$\rho \frac{d\eta}{dt} = -\nabla \cdot J + \sigma, \tag{1}$$

where ρ is the mass density of the system, J and σ are the flux and production of η respectively. It should be stressed that once again J and σ depend on the EIT version and it is their actual forms which give physical content to this second postulate. For, the expression for $\frac{\rho d\eta}{dt}$ as obtained from Eq. (1) should be wholly compatible with the one stemming out of the generalized Gibbs equation. Clearly, in view of the fact that this latter equation contains the time derivatives of all variables in G, such compatibility implies that any assumption or restriction imposed on J or σ will show eventually in the equations governing the time evolution of the system. In particular (and it must be stressed that perhaps the most important physical difference between the M-EIT and other EIT versions resides on the assumption made on the semipositive definite character of σ), in the M-EIT the condition $\sigma \geq 0$ is not *a priori* imposed, although of course given the interpretation of η as the Shanon-Jaynes entropy provided in Ref. [10], in any particular non-equilibrium process in wich the system evolves from initial equilibrium state to another final equilibrium state, the global change in η should be positive as required by the second law of thermodynamics. Nevertheless, some important physical content in the construction of η, to be specified below, is included in the choice for σ in M-EIT. A discussion of the differences between the M-EIT and the wave approach to EIT [3] concerning this point and the choice of the R-variables has been given in Ref. [6]. On the other hand, both the Liege-Barcelona and the German schools (Refs. [4] and [5]) impose the restriction $\sigma \geq 0$ from the beginning and, rather than constructing J as the most general vector in G as done in M-EIT, they construct the flux of η to comply with the requirement of a semipositive definite σ. This point of view has far reaching consequences for the final form of the time evolution equations for the R-variables (and hence also for the time evolution of the system as a whole) that in our opinion may only be sustained within the range of validity of LIT.

Before engaging in the description of the methodology adopted in the M-EIT, a few comments are pertinent. Since EIT is aimed at generalizing LIT, the compatibility of both theories in the appropriate limit is a requirement and not a success of the former. On the other hand, it should be a matter of principle that the rules and methods in the formalism should be clearly stated and followed from the beginning, avoiding *ad hoc* changes from problem to problem. Also, as in any phenomenological theory, many unknown coefficients will arise in the developments and it is clearly necessary that either they are interpreted in terms of a more fundamental or microscopic theory or of precise experimentally determinable quantities. Finally, care must be exercised to choose systems and propose experiments where the theoretical predictions may be critically tested. A brief overview of the work generated by the Mexican group (*cf.* Ref. [7] and references therein) will suffice to demonstrate that all of these points have been seriously considered by the group. Noteworthy aspects whose details may be found in the original sources include the search for compatibility with microscopic theories, the consideration of systems such as viscoelastic fluids, fluids with internal degrees of freedom and porous media, the suggestion of experimental setups such as light or neutron scattering or the measurement of different rheological properties in particular conditions in order to check specific theoretical predictions, and the major concern to clarify and set limits of validity to the formal aspects of the theory.

We are now in a position to describe the usual procedure of the M-EIT. To begin with, the partial derivatives of η with respect to the variables in G as well as J and σ are constructed, depending on their particular tensorial character, using the so called representation theorems of linear algebra [11]. Concerning the construction of σ, a particularly distinctive feature of the M-EIT is what has been called the "closure assumption" (discussed at length in Ref. [12] to which the reader is referred for a deeper insight) namely, it may incorporate parameters outside G which are nonetheless relevant to the description of the non-equilibrium state of the system. It must be pointed out that this closure assumption, which as far as we know has only been considered within the M-EIT, is crucial in order to obtain compatibility with kinetic theory as discussed for instance in Ref. [9]. Here again, as in the case of the R-variables, a judicious choice of the adequate parameters in any particular problem is likely to be suggested by the balance equations obeyed by the C-variables. The aforementioned constructions yield two different but wholly equivalent expressions for $\rho\frac{d\eta}{dt}$, one arising from the generalized Gibbs equation and containing the unknown time derivatives of the R-variables, and the other one corresponding to the balance Eq. (1). Equating these two expressions in principle would allow to obtain some information on the time evolution of the R-variables, but the process is hampered by the remaining scalars which still depend on invariants containing such variables. Hence, a natural step to take is to develop these scalars in a Taylor series around a reference state in which the R-variables are zero. The series are subsequently truncated according to the R-variables order criterion [9], in which C-variables are of order zero, R-variables are of order one and neither time nor spatial derivatives contribute to the order of a given term. This criterion does not impose any bias on the importance of either time or spatial inhomogeneities, which seems adequate for a general scheme in which extra information concerning such an importance is not available from the outset. Finally, the time evolution equations for the R-variables are derived consistently up to any desired order of approximation. It must be emphasized that in order to go beyond LIT, one requires to carry out the computations at least up to second order in the terms appearing in both expressions for $\rho\frac{d\eta}{dt}$.

While the procedure sketched above has been rather successful and widely used, another important contribution to the consolidation of the M-EIT which provides an alternative methodology and a possible route to systematically study the effect of fluctuations in a mesoscopic level, is the variational principle originally formulated by Vázquez and del Río [13] and recently generalized [13a]. In this principle one takes as the functional to be varied

$$\int \left(\rho\frac{d\eta}{dt} + \nabla\cdot\mathbf{J} - \sigma\right) dV, \tag{2}$$

where $\rho\frac{d\eta}{dt}$ is given by the generalized Gibbs equation, $\mathbf{J}$ is the most general vector in G and σ is constructed using the representation theorems and the closure assumption. The integral in Eq. (2) is taken over the volume V of the system. At the same time, the balance equations for the C-variables as well as the generalized equations of state are taken as subsidiary restrictions and the variations are performed on the R-variables only. This form of variation is of the same kind as the one used by Onsager [14] within LIT. In our case, such scheme leads to general forms for the time evolution equations of the R-variables. Of course, if one develops once again the remaining scalars and uses the R-variables order criterion, the results of the usual procedure are easily recovered. But the variational approach opens up the possibility of considering non-analytic expressions for the generalized equations of state and other phenomenological coefficients (which in the standard procedure at this stage has not been possible) as well as providing a numerical method for the solution of the equations stemming out of the formulation. In the next section we will illustrate the results of both methods in the case of an ionized gas.

3. THE IONIZED GAS IN M-EIT

The case of an ionized gas has been already dealt with within the M-EIT [15,16]. However, apart from the fact that the R-variables have been chosen differently in these two references, the system has been analyzed from the perspective of a simple fluid, which poses some difficulties when examining the compatibility with LIT. Therefore we find it instructive to consider this system here, but taking a binary mixture model where the above mentioned difficulties are avoided. In this model one has a binary gas mixture of electrons and one kind of positive ions subjected to an external electromagnetic field. For the C-variables then we take u, the total internal energy density, ρ, the total mass density, and c_e, the electron mass fraction, which are the same variables taken in LIT [1]. Of course, linear momentum is also conserved, but since a global uniform motion of the system has no effect on its thermodynamic macroscopic properties, η cannot depend on the hydrodynamic velocity, $\mathbf{v}$. Nevertheless, as it also occurs in LIT, the dynamic description must also include it as a relevant variable, which will be reflected in the equations governing the time evolution of the system.

In the present problem the balance equations are

$$\rho \frac{d\nu}{dt} = \nabla \cdot \mathbf{v}, \tag{3a}$$

$$\rho \frac{dc}{dt}_{e} = -\nabla \cdot \mathbf{j}_e, \tag{3b}$$

$$\rho \frac{d\mathbf{v}}{dt} = \nabla p - \nabla \cdot \overleftrightarrow{\tau} + \rho z(E + \mathbf{v} \times \mathbf{B}) + \mathbf{i} \times \mathbf{B}, \tag{3c}$$

$$\rho \frac{du}{dt} = -\nabla \cdot \mathbf{q} - \rho p \frac{d\nu}{dt} - \overleftrightarrow{\tau} : \nabla \mathbf{v} + \mathbf{i} \cdot (\mathbf{E} + \mathbf{v} \times \mathbf{B}), \tag{3d}$$

where $\nu = \rho^{-1}$ is the specific volume, $\mathbf{j}_e$ is the electron mass flux, p is the pressure, $\overleftrightarrow{\tau}$ is the (symmetric) viscous stress tensor, z is the total charge per unit mass, $\mathbf{E}$ and $\mathbf{B}$ are the electric field and the magnetic induction respectively, $\mathbf{i}$ is the electric conduction current density and $\mathbf{q}$ is the heat flux. Eqs. (3) together with Maxwell's equations (which will not be written down but must certainly be taken into account) clearly do not constitute a closed set. In order to have a complete set of equations we take as our R-variables $\mathbf{q}$, $\overleftrightarrow{\tau}$ and $\mathbf{j}_e$. It should be emphasized that $\mathbf{i}$ and $\mathbf{j}_e$ are related through $\mathbf{i} = (z_e - z_i)\mathbf{j}_e$ where the subindex on the charge z indicates either electrons or ions, so one could have equally chosen $\mathbf{i}$ instead of $\mathbf{j}_e$. Finally, for the construction of σ we introduce as parameters

$$p_1 = \nabla \cdot \mathbf{v}, \qquad \overleftrightarrow{p}_2 = (\nabla \mathbf{v})^s, \qquad \overleftrightarrow{p}_3 = (\nabla \mathbf{v})^a,$$
$$\mathbf{p}_4 = \mathbf{E} + \mathbf{v} \times \mathbf{B}, \qquad \mathbf{p}_5 = \mathbf{i} \times \mathbf{B}. \tag{4}$$

In Eqs. (4) the superindexes a and s indicate the antisymmetric and symmetric part of the corresponding traceless tensor. The choice of the first three parameters instead of $\nabla \mathbf{v}$ (which is the quantity that appears explicitly in the balance equations) is due to their different symmetry properties which, given the presence of the electromagnetic field, do play an important role in the formulation of the present problem.

From the preceding statements it should be clear that $\eta \equiv \eta(u, \rho, c_e, \mathbf{q}, \mathbf{j}_e, \overleftrightarrow{\tau})$ in this case. Using this η and Eqs. (4), we have derived the time evolution equations for the R-variables using both the standard procedure and the variational principle. The algebraic details are sketched in the Appendix. The results of the standard procedure up to second order are then

$$\begin{aligned}\gamma_1 \frac{d\mathbf{i}}{dt} = &-\mathbf{i} + \gamma_2(\mathbf{E} + \mathbf{v} \times \mathbf{B}) + \gamma_3 \mathbf{i} \times \mathbf{B} + \gamma_4 (\nabla \mathbf{v})^s \cdot \mathbf{i} + \gamma_6 (\nabla \mathbf{v})^a \cdot \mathbf{i} \\ &+ \gamma_7 \nabla T + \gamma_8 \nabla(\mu) + \gamma_9 \mathbf{q} + \gamma_{10}(\nabla \cdot \mathbf{v})\mathbf{q} + \gamma_{11}(\nabla \mathbf{v})^s \cdot \mathbf{q} \\ &+ \gamma_{12}(\nabla \mathbf{v})^a \cdot \mathbf{q} + \gamma_{13} \overleftrightarrow{\tau} \cdot (\mathbf{E} + \mathbf{v} \times \mathbf{B}) + \gamma_{14} \nabla \cdot \overleftrightarrow{\tau} + \gamma_{15} \overleftrightarrow{\tau} \cdot \nabla \gamma_{16},\end{aligned} \tag{5a}$$

$$\begin{aligned}\lambda_1 \frac{d\mathbf{q}}{dt} = &\lambda_2 \nabla T^{-1} + \lambda_3 \nabla (T^{-1} \mu_e) + \mathbf{q} + \lambda_4 (\nabla \cdot \mathbf{v})\mathbf{q} + \lambda_5 (\nabla \mathbf{v})^s \cdot \mathbf{q} + \lambda_6 (\nabla \mathbf{v})^a \cdot \mathbf{q} \\ &+ \lambda_7 T^{-1}(\mathbf{E} + \mathbf{v} \times \mathbf{B}) + \lambda_8 \mathbf{v}\mathbf{i} \times \mathbf{B} + \lambda_9 \mathbf{i} + \lambda_{10}(\nabla \cdot \mathbf{v})\mathbf{i} + \lambda_{11}(\nabla \mathbf{v})^s \cdot \mathbf{i} \\ &+ \lambda_{12}(\nabla \mathbf{v})^a \cdot \mathbf{i} + \lambda_{13} \nabla \cdot \overleftrightarrow{\tau} + \lambda_{14} \overleftrightarrow{\tau} \cdot (\mathbf{E} + \mathbf{v} \times \mathbf{B}),\end{aligned} \tag{5b}$$

$$\begin{aligned}\xi_1 \frac{d\overleftrightarrow{\tau}}{dt} = &\overleftrightarrow{\tau} + \xi_2 (\nabla \cdot \mathbf{v})\overleftrightarrow{\tau} + \xi_3 \overleftrightarrow{\tau} \cdot \nabla \mathbf{v} + \xi_4 T^{-1} \nabla \mathbf{q} + \xi_6 (\mathbf{E} + \mathbf{v} \times \mathbf{B})\mathbf{q} \\ &+ \xi_7 \nabla \mathbf{i} + \xi_8 (\mathbf{E} + \mathbf{v} \times \mathbf{B})\mathbf{i},\end{aligned} \tag{5c}$$

where T is the local temperature, $\mu = \mu_e - \mu_i$ with μ_i and μ_e standing for the electrochemical potentials of the ions and electron respectively and the γ_i ($i = 1$ to 16), λ_i ($i = 1$ to 14) and ξ_i ($i = 1$ to 8) are phenomenological coefficients depending on the C-variables only. Notice that Eqs. (5*b*) and (5*c*) are essentially the same as those reported for the corresponding variables in Refs. [15] and [16]. Also, it is important to stress that, irrespective of the fact that at first sight some of the terms in Eq. (5*c*) seem to mix an antisymmetric tensor with a polar vector (and thus could not contribute to an equation involving the current) the phenomenological scalar coefficients are so far arbitrary. However, these coefficients may be readily identified in terms of the ones arising in the kinetic theory formulation of the same problem [17,18,19] and, as a matter of fact, in the case of a thermal plasma it follows from Eq. (28) in Ref. [19] that γ_6 should be different from zero while γ_{12} must be zero. On the other hand, the variational approach yields

$$\begin{aligned}&-\nabla \cdot \mathbf{q}\mathcal{O}_2\beta_{10} - p\nabla \circ \mathbf{v}\mathcal{O}_2\beta_{10} - \overleftrightarrow{\tau} : \nabla \mathbf{v}\mathcal{O}_2\beta_{10} + (\mathbf{E} + \mathbf{v} \times \mathbf{B}) + i \cdot (\mathbf{E} + \mathbf{v} \times \mathbf{B})\mathcal{O}_2\beta_{10} \\ &-\nabla \cdot \mathbf{v}\mathcal{O}_2\beta_{20} - \nabla \cdot \mathbf{i}\mathcal{O}_2\beta_{30} + \frac{dq}{dt} \otimes (\mathbf{q}\mathcal{O}_2\beta_{41} + \beta_{42} + \mathbf{i}\mathcal{O}_2\beta_{42} \\ &+\mathbf{q} \cdot \overleftrightarrow{\tau}\mathcal{O}_2\beta_{43} + \beta_{44}\overleftrightarrow{\tau} + \mathbf{i} \cdot \overleftrightarrow{\tau}\mathcal{O}_2\beta_{44}) + \frac{d\overleftrightarrow{\tau}}{dt} \otimes (\overleftrightarrow{\tau}\mathcal{O}_2\beta_{51} + qq\mathcal{O}_2\beta_{52} + 2\beta_{53}\mathbf{i} \\ &+\mathbf{i}i\mathcal{O}_2\beta_{53} + \beta_{54}\mathbf{q} + \mathbf{q}i\mathcal{O}_2\beta_{54} + \overleftrightarrow{\tau} \cdot \overleftrightarrow{\tau}\mathcal{O}_2\beta_{55} + 2\beta_{56}i\overleftrightarrow{\tau} + \mathbf{i}\overleftrightarrow{\tau} \cdot \mathbf{i}\mathcal{O}_2\beta_{56}\end{aligned}$$

$$\begin{aligned}
&+\mathbf{q}\overleftrightarrow{\tau}\cdot\mathbf{q}\mathcal{O}_2\beta_{57}+\beta_{58}\mathbf{q}\overleftrightarrow{\tau}+\mathbf{q}\overleftrightarrow{\tau}\cdot\mathbf{i}\mathcal{O}_2\beta_{58})+\frac{di}{dt}\otimes(\mathbf{q}\mathcal{O}_2\beta_{61}+\beta_{62}+\mathbf{i}\mathcal{O}_2\beta_{62}\\
&+\mathbf{q}\cdot\overleftrightarrow{\tau}\mathcal{O}_2\beta_{63}+\beta_{64}\overleftrightarrow{\tau}+\mathbf{i}\cdot\overleftrightarrow{\tau}\mathcal{O}_2\beta_{64})+\nabla\cdot\mathbf{q}\mathcal{O}_2\alpha_1+\nabla\cdot\mathbf{i}\mathcal{O}_2\alpha_2+\nabla\alpha_2\\
&\qquad+\nabla\cdot(\overleftrightarrow{\tau}\cdot\mathbf{q})\mathcal{O}_2\alpha_3+\nabla\cdot(\overleftrightarrow{\tau}\cdot\mathbf{i})\mathcal{O}_2\alpha_4+\alpha_4\nabla\cdot\overleftrightarrow{\tau}+\overleftrightarrow{\tau}\cdot\nabla\alpha_4-(\delta\sigma)_1=0,
\end{aligned}\tag{6a}$$

$$\begin{aligned}
&-\nabla\cdot\mathbf{q}\mathcal{O}_1\beta_{10}-p\nabla\cdot\mathbf{v}\mathcal{O}_1\beta_{10}-\overleftrightarrow{\tau}:\nabla\mathbf{v}\mathcal{O}_1\beta_{10}+\mathbf{i}\cdot(\mathbf{E}+\mathbf{v}\times\mathbf{B})\mathcal{O}_1\beta_{10}\\
&+\nabla\cdot\mathbf{v}\mathcal{O}_1\beta_{20}-\nabla\cdot\mathbf{i}\mathcal{O}_1\beta_{30}+\frac{dq}{dt}\otimes(\beta_{41}+\mathbf{i}\mathcal{O}_1\beta_{42}+\beta_{43}\overleftrightarrow{\tau}+\mathbf{q}\cdot\overleftrightarrow{\tau}\mathcal{O}_1\beta_{43}\\
&+\mathbf{i}\cdot\overleftrightarrow{\tau}\mathcal{O}_1\beta_{44})+\frac{d\overleftrightarrow{\tau}}{dt}\otimes(\overleftrightarrow{\tau}\mathcal{O}_1\beta_{51}+2\beta_{52}\mathbf{q}+\mathbf{q}q\mathcal{O}_1\beta_{52}+\mathbf{i}i\mathcal{O}_1\beta_{53}+\beta_{54}i\\
&+\mathbf{q}i\mathcal{O}_1\beta_{54}+\overleftrightarrow{\tau}\cdot\overleftrightarrow{\tau}\mathcal{O}_1\beta_{55}+\mathbf{i}\overleftrightarrow{\tau}\cdot\mathbf{i}\overleftrightarrow{\tau}\mathcal{O}_1\beta_{56}+2\beta_{57}\mathbf{q}\overleftrightarrow{\tau}+\mathbf{q}\overleftrightarrow{\tau}\cdot\mathbf{q}\mathcal{O}_1\beta_{57}+\beta_{58}\overleftrightarrow{\tau}\cdot\mathbf{i}\\
&+\mathbf{q}\overleftrightarrow{\tau}\cdot\mathbf{i}\mathcal{O}_1\beta_{58})+\frac{di}{dt}\otimes(\beta_{55}+\mathbf{i}\overleftrightarrow{\tau}\cdot\mathbf{i}\mathcal{O}_1\beta_{56}+2\beta_{57}\mathbf{q}\overleftrightarrow{\tau}+\mathbf{q}\overleftrightarrow{\tau}\cdot\mathcal{O}_1\beta_{57}+\beta_{58}\overleftrightarrow{\tau}\cdot\mathbf{i}\\
&+\mathbf{q}\overleftrightarrow{\tau}\cdot\mathbf{i}\mathcal{O}_1\beta_{58})+\frac{di}{dt}\otimes(\beta_{61}+\mathbf{q}\mathcal{O}_1\beta_{61})+\mathbf{i}\mathcal{O}_1\beta_{62}\beta_{63}\overleftrightarrow{\tau}+\mathbf{q}\cdot\overleftrightarrow{\tau}\mathcal{O}_1\beta_{63}\\
&+\mathbf{i}\cdot\overleftrightarrow{\tau}\mathcal{O}_1\beta_{64}+\nabla\cdot\mathbf{q}\mathcal{O}_1\alpha_1+\nabla\alpha_1+\nabla\cdot\mathbf{i}\mathcal{O}_1\alpha_2+\nabla\cdot(\overleftrightarrow{\tau}\cdot\mathbf{q})\mathcal{O}_1\alpha_3\\
&\qquad\qquad+\alpha_3\nabla\cdot\overleftrightarrow{\tau}+\overleftrightarrow{\tau}\cdot\nabla\alpha_3+\nabla\cdot(\overset{\leftrightarrow}{(}\tau)\cdot\mathbf{i})\mathcal{O}_1\alpha_4-(\delta\sigma)_q=0,
\end{aligned}\tag{6b}$$

$$\begin{aligned}
&\nabla\cdot\mathbf{q}\mathcal{O}_3\beta_{10}p\nabla\cdot\mathbf{v}\mathcal{O}_3\beta_{10}-\beta_{10}\nabla\mathbf{v}-\overleftrightarrow{\tau}:\nabla\mathbf{v}\mathcal{O}_3\beta_{10}+\mathbf{i}\cdot(\mathbf{E}+\mathbf{v}\times\mathbf{B})\mathcal{O}_3\beta_{10}\\
&\quad+\nabla\cdot\mathbf{v}\mathcal{O}_3\beta_{20}-\nabla\cdot\mathbf{i}\mathcal{O}_3\beta_{30}+\frac{d\mathbf{q}}{dt}\otimes(\mathbf{q}\mathcal{O}_3\beta_{42}+\beta_{43}\mathbf{q}+\mathbf{q}\cdot\overleftrightarrow{\tau}\mathcal{O}_3\beta_{43}+\beta_{44}i\\
&\quad+\mathbf{i}\cdot\overleftrightarrow{\tau}\mathcal{O}_3\beta_{44})+\frac{d\overleftrightarrow{\tau}}{dt}\otimes(\beta_{51}+\overleftrightarrow{\tau}\mathcal{O}_3\beta_{51}+\mathbf{q}q\mathcal{O}_3\beta_{53}+\mathbf{q}i\mathcal{O}_3\beta_{54}\\
&\quad+2\beta_{55}\overleftrightarrow{\tau}+\overleftrightarrow{\tau}\cdot\overleftrightarrow{\tau}\mathcal{O}_3\beta_{55}+\beta_{56}ii+\mathbf{i}\overleftrightarrow{\tau}\cdot\mathbf{i}\mathcal{O}_3\beta_{56}+\beta_{57}\mathbf{q}q+\mathbf{q}\overleftrightarrow{\tau}\cdot\mathbf{q}\mathcal{O}_3\beta_{57}+\beta_{58}\mathbf{q}i\\
&\quad+q\overleftrightarrow{\tau}\cdot\mathbf{i}\mathcal{O}_3\beta)+\frac{di}{dt}\otimes(\mathbf{q}\mathcal{O}_3\beta_{62}+\beta_{63}\mathbf{q}+\mathbf{q}\cdot\overleftrightarrow{\tau}\mathcal{O}_3\beta_{63}+\beta_{64}i\\
&\quad+\mathbf{i}\cdot\overleftrightarrow{\tau}\mathcal{O}_3\beta_{64}+\nabla\cdot\mathbf{q}\mathcal{O}_3\alpha_1+\nabla\cdot\mathbf{i}\mathcal{O}_3\alpha_2+\nabla\cdot(\overleftrightarrow{\tau}\cdot\mathbf{q})\mathcal{O}_3\alpha_3+\alpha_3\nabla\mathbf{q}\\
&\qquad\qquad+\mathbf{q}\cdot\nabla\alpha_3+\nabla\cdot(\overleftrightarrow{\tau}\cdot\mathbf{i})\mathcal{O}_3\alpha_4+\mathbf{i}\cdot\nabla\alpha_4-(\delta\sigma)_{\overleftrightarrow{\tau}}=0,
\end{aligned}\tag{6c}$$

where the β_{ij} ($i=1$ to 6, $j=0$ to 8) and the α_i ($i=1$ to 4) are the scalar phenomenological coefficients appearing in the expressions obtained via the representation theorems of the generalized equations of state ($i=0$ indicates that the corresponding equation of state is a scalar) and the generalized entropy flux J,respectively. The operator $\mathcal{O}_j$ ($j=1\ldots3$) is defined as $\mathcal{O}_j\epsilon\equiv\left(\frac{\partial}{\partial\mathbf{R}_j}I_i\right)\frac{\partial}{\partial I_i}\epsilon$ where $\mathbf{R}_1=\mathbf{q}$, $\mathbf{R}_2=\mathbf{i}$, $\mathbf{R}_3=\overleftrightarrow{\tau}$, ϵ is any of the scalar quantities and I_i are the scalar invariants of the extended thermodynamic space, so that $\mathcal{O}_\epsilon$ is a vector. Also $(\delta\sigma)_a$ indicates the variation of σ with respect to the variable a, where the expression for σ is given in the appendix [*cf.* Eq. (*A*5)]. Notice that the couplings present in Eqs. (6) (some of which will only appear in the usual procedure if one goes beyond the second order) evidently make derivation of a generalized Ohm's law from them look rather more complicated than the one leading to Eqs. (5), but it should be borne in mind that the former involve no approximations. For the sake of exhibiting the compatibility between the variational approach and the standard procedure, we note that, consistently with the order kept in the derivation of Eqs. (5), substituting Eqs. (*A*6), (*A*7) and the equation that results after substitution of Eq. (*A*8) in Eq. (*A*5) in Eq. (6*a*) and neglecting in the resulting expression terms of second and higher order, we obtain precisely Eq. (*A*9*a*). In a similar way, Eqs. (*A*9*b*) and (*A*9*c*) may be derived from Eqs. (6*b*) and (6*c*), respectively. Therefore, both the standard and the variational schemes lead to the same results once the order of approximation has been fixed. In particular, the derivation of the generalized Ohm's law from Eqs. (6) is achieved after decoupling Eqs. (*A*9*a*) and (*A*9*b*) as indicated in the Appendix.

4. CONCLUDING REMARKS

In this paper we have discussed the Mexican version of EIT, emphasizing the most important contributions and highlighting the main differences with the other existing versions. It is essential to stress that, apart from the methodological aspects that were discussed in the previous section, the most important physical difference between the M-EIT and other EIT formalisms, is the fact that beyond LIT σ is not assumed *a priori* to be necessarily a semipositive definite quantity. This leads to far reaching consequences for the final structure of the equations governing the time evolution of the system, since the condition $\sigma \geq 0$ restricts the possibility of many couplings between the R-variables which are allowed by M-EIT. For instance, if σ were assumed to be positive definite, all coefficients σ_4 to σ_{13} in Eq. (A7) should be zero. This would in turn imply that a term such as $\gamma_3 \mathbf{i} \times \mathbf{B}$ in Eq. (5*a*) (giving rise to the Ettinghausen effect) and all terms in Eqs. (5) involving the parameters would simply not be present in the time evolution equations for the R-variables.

The paper would not be complete if mention was not made of some of the limitations and of the perspectives for future developments. Perhaps the most serious difficulty that M-EIT is faced with, which incidentally is shared by the other EIT formulations, is the fact that there is not a unique recipe to decide which and how many R-variables and parameters are required to describe a given nonequilibrium system. In this respect, it is rather encouraging that the work in Ref. [10] may shed some light on this problem. On the other hand, so far most of the developments have been geared towards deriving known results or simple generalizations, and there have been no crucial experiments in which the basic assumptions of the theory might be tested. It is true that the amount of theoretical evidence already compatible with the M-EIT gives confidence on the validity and usefulness of the approach. But more efforts in proposing new and relatively simple experiments to test specific theoretical predictions are called for. Finally, and this may be either a merit or a limitation, the tensorial character of the variables in G and of the parameters required for closure plays a key role in the final structure of the resulting equations for the time evolution of the R-variables. This implies for instance that in any system in which the C-variables are two scalars and the R-variables are two vectors and a second rank tensor and the number and nature of the parameters in the same as the one in Eqs. (4), the structure of the time evolution equations for the R-variables up to second order will be identical to the one shown in Eqs. (5).

Concerning the perspectives, it must be stressed that the variational principle, apart from being elegant, provides some insight as to the role of η in the theory as well as offering some advantages over the usual procedure of M-EIT that have already been mentioned. In particular, it would be interesting to examine the consequences that can arise from modeling the scalars appearing in the general coupled time evolution equations for the R-variables without recourse to analytical expansions in Taylor series. Further, and perhaps more important, this approach suggests a generalization of the results of Onsager and Machlup [20] to include the study of fluctuations and enter into a mesoscopic formulation. Finally with regards to the standard procedure, the time and spatial dependence of the phenomenological coefficients through the C-variables has been largely ignored in the problem dealt with so far; but this restriction can be easily avoided and it may lead for instance to a natural inclusion of memory effects and spatial inhomogeneities not considered up until now.

APPENDIX

In this appendix we outline the algebra involved in the standard procedure and in the variational formulation of the M-EIT. We start with the generalized Gibbs equation. Since $\eta \equiv \eta(u, \rho, c_e, \mathbf{q}, \mathbf{i}, \overleftrightarrow{\tau})$,* this equation reads

$$\rho \frac{d\eta}{dt} = \beta_1 \frac{du}{dt} + \beta_2 \frac{d\mathbf{B}}{dt} + \beta_3 \frac{dc_e}{dt} + \beta_4 \cdot \frac{d\mathbf{q}}{dt} + \overleftrightarrow{\beta}_5 : \frac{d\overleftrightarrow{\tau}}{dt} + \beta_6 \cdot \frac{d\mathbf{i}}{dt}, \tag{A1}$$

where β_1 to β_6 are the generalized equations of state which according to their tensorial character and with the aid of the representation theorems of linear algebra may be written as

$$\begin{aligned}
&\beta_1 = \beta_1(u, \mathbf{B}, c_e, I_i), && \beta_2 = \beta_2(u, \mathbf{B}, c_e, I_i), \\
&\beta_3 = \beta_3(u, \mathbf{B}, c_e, I_i), && \beta_4 = \beta_{41}\mathbf{q} + \beta_{42}\mathbf{i} + \beta_{43}\overleftrightarrow{\tau} \cdot \mathbf{q} \\
& && \qquad + \beta_{44}\overleftrightarrow{\tau} \cdot \mathbf{i}, \qquad\qquad (A2) \\
&\overleftrightarrow{\beta}_5 = \beta_{51}\overleftrightarrow{\tau} + \beta_{52}\mathbf{q}\mathbf{q} + \beta_{53}\mathbf{i}\mathbf{i} + \beta_{54}\mathbf{i}\mathbf{q} + \beta_{55}\overleftrightarrow{\tau} \cdot \overleftrightarrow{\tau} && \beta_6 = \beta_{61}\mathbf{q} + \beta_{62}\mathbf{i} + \beta_{63}\overleftrightarrow{\tau} \cdot \mathbf{q} \\
&\qquad + \beta_{56}\mathbf{i}\overleftrightarrow{\tau} \cdot \mathbf{i} + \beta_{57}\mathbf{q}\overleftrightarrow{\tau} \cdot \mathbf{q} + \beta_{58}\mathbf{q}\overleftrightarrow{\tau} \cdot \mathbf{i}, && \qquad + \beta_{64}\overleftrightarrow{\tau} \cdot \mathbf{i}.
\end{aligned}$$

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*Notice that without loss of generality, for convenience we have chosen to take $\mathbf{i}$ rather than $\mathbf{j}_e$ as the R-variable here.

Here the I_i ($i = 1$ to 11) are the scalar invariants of the extended thermodynamic space appropriate for this problem, namely,

$$\begin{array}{lll} I_1 = \mathbf{q}\cdot\mathbf{q}, & I_2 = \mathbf{i}\cdot\mathbf{i}, & \\ I_3 = \mathbf{q}\cdot\mathbf{i}, & I_4 = tr(\overleftrightarrow{\tau}\cdot\overleftrightarrow{\tau}), & I_5 = \mathrm{tr}(\overleftrightarrow{\tau}\cdot\overleftrightarrow{\tau}\cdot\overleftrightarrow{\tau}), \\ I_6 = \mathbf{q}\cdot\overleftrightarrow{\tau}\cdot\mathbf{q}, & I_7 = \mathbf{i}\cdot\overleftrightarrow{\tau}\cdot\mathbf{i}, & I_9 = \mathbf{q}\cdot\overleftrightarrow{\tau}\cdot\mathbf{i}, \\ I_9 = \mathbf{q}\cdot(\overleftrightarrow{\tau}\cdot\overleftrightarrow{\tau})\cdot\mathbf{q}, & I_{10} = \mathbf{i}\cdot(\overleftrightarrow{\tau}\cdot\overleftrightarrow{\tau})\cdot\mathbf{i}, & I_{11} + \mathbf{q}\cdot(\overleftrightarrow{\tau}\cdot\overleftrightarrow{\tau})\cdot\mathbf{i}. \end{array} \tag{A3}$$

On the other hand, the flux $\mathbf{J}$ and the production σ of the non-equilibrium potential η appearing in eq. (1) are similarly constructed as

$$\mathbf{J}_\eta = \alpha_1\mathbf{q} + \alpha_2\mathbf{i} + \alpha_3\overleftrightarrow{\tau}\cdot\mathbf{q} + \alpha_4\overleftrightarrow{\tau}\cdot\mathbf{i}, \tag{A4}$$

$$\sigma = \sigma(u, \rho, c_e, I_i, p_i), \tag{A5}$$

where the closure assumption [12] has been invoked to include the terms containing the parameters p_1 to $\mathbf{p}_5$ [*cf.* Eq. (4)].

In order to carry out the standard procedure, we now develop all the scalars in Eqs. (*A*2), (*A*4) and (*A*5) in a Taylor series around the state with $\mathbf{i} = \mathbf{q} = \tau = 0$. Then, to derive the time evolution equations for the fast variables up to second order according to the *R*-variables order criterion [9], the quantities β_{ij}, α_i and σ_i must be approximated as

$$\begin{array}{ll} \beta_1 = T^{-1} + O(2) & \beta_2 = pT^{-1} + O(2) \\ \beta_3 = \mu T^{-1} + O(2) & \beta_{41} = \delta_{4f} + O(2) \\ \beta_{42} = \delta_{5f} + O(2) & \beta_{51} = \delta_{6f} + O(2) \\ \beta_{61} = \delta_{7f} + O(2) & \beta_{62} = \delta_{8f} + O(2) \\ \alpha_1 = \delta_{9f} + O(2) & \alpha_2 = \delta_{10f} + O(2) \\ \alpha_3 = \delta_{24f} + O(2) & \alpha_4 = \delta_{25f} + O(2) \end{array} \tag{A6}$$

$$\begin{aligned} \sigma = {} & \sigma_1\mathbf{q}\cdot\mathbf{q} + \sigma_2\mathbf{i}\cdot\mathbf{i} + \sigma_3\overleftrightarrow{\tau} : \overleftrightarrow{\tau} + \sigma_4\mathbf{p}_5\cdot\mathbf{q} + \sigma_5(\overleftrightarrow{p}_2\cdot\mathbf{q})\cdot\mathbf{q} \\ & + \sigma_6(\overleftrightarrow{p}_3\cdot\mathbf{q})\cdot\mathbf{q} + \sigma_7\mathbf{p}_5\cdot\mathbf{i} + \sigma_8(\overleftrightarrow{p}_2\cdot\mathbf{i})\cdot\mathbf{i} + \sigma_9(\overleftrightarrow{p}_3\cdot\mathbf{i})\cdot\mathbf{i} \\ & + \sigma_{10}(\overleftrightarrow{\tau}\cdot\overleftrightarrow{p}_2) : \overleftrightarrow{\tau} + \sigma_{11}(\overleftrightarrow{\tau}\cdot\overleftrightarrow{p}_3) : \overleftrightarrow{\tau} + \sigma_{12}(\overleftrightarrow{\tau}\cdot\mathbf{q})\cdot\mathbf{p}_4 \\ & + \sigma_{13}(\overleftrightarrow{\tau}\cdot\mathbf{i})\cdot\mathbf{p}_4, \end{aligned} \tag{A7}$$

with

$$\begin{aligned}
\sigma_1 &= \delta_{11f} + O(2) & \sigma_2 &= \delta_{12f} + O(2) \\
\sigma_3 &= \delta_{13f} + O(2) & \sigma_4 &= \delta_{14f} + O(2) \\
\sigma_5 &= \delta_{15f} + O(2) & \sigma_6 &= \delta_{16f} + O(2) \\
\sigma_7 &= \delta_{17f} + O(2) & \sigma_8 &= \delta_{18f} + O(2) \\
\sigma_9 &= \delta_{19f} + O(2) & \sigma_{10} &= \delta_{20f} + O(2) \\
\sigma_{11} &= \delta_{21f} + O(2) & \sigma_{12} &= \delta_{22f} + O(2) \\
\sigma_{13} &= \delta_{23f} + O(2) & &
\end{aligned} \tag{A8}$$

where in order to achieve compatibility we have identified the first three equations of state with those of LIT and $\delta_{if} = \delta_{if}(u, \nu, c_e)$, i = 1 to 25, the subscript f on the δ's having been included to indicate that these coefficients are the first terms in the Taylor's series developments of the β_{ij}, α_i and σ, respectively around the state which is characterized by $\mathbf{q} = \mathbf{i} = \mathbf{0}$ and $\overleftrightarrow{\tau} = \overleftrightarrow{0}$.

Substituting Eqs. ($A2$) and ($A5$) in Eq. ($A1$) and equating the result with the one obtained from the substitution of Eqs. ($A6$–8) in Eq. (1) one obtains the following approximate set of time evolution equations for the R-variables ($\varepsilon_i + \varepsilon_{i'} = 1$, i=1,4, and the ε's are pure number):

$$\begin{aligned}
\delta_{7f} \frac{d\overleftrightarrow{\tau}}{dt} = {} & T^{-1}\nabla\mathbf{v} + \delta_{3f}\overleftrightarrow{\tau} - \delta_{24f}\nabla\mathbf{q} - \delta_{25f}\nabla\mathbf{j}_f - \epsilon_1\mathbf{q}\nabla\delta_{24f} - \epsilon_2\mathbf{j}_f\nabla\delta_{25f} \\
& - \delta_{20f}\overleftrightarrow{\tau} \cdot (\nabla\mathbf{v})^s + \delta_{21f}\overleftrightarrow{\tau} \cdot (\nabla\mathbf{v})^a + \epsilon_3\delta_{22f}\mathbf{q}(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \\
& + \epsilon_4\delta_{23f}\mathbf{i}(\mathbf{E} + \mathbf{v} \times \mathbf{B}),
\end{aligned} \tag{A9a}$$

$$\begin{aligned}
\delta_{4f}\frac{d\mathbf{q}}{dt} + \delta_{5f}\frac{d\mathbf{i}}{dt} = {} & -\nabla(T^{-1}) + \delta_{11f}\mathbf{q} - \delta_{24f}\nabla \cdot \overleftrightarrow{\tau} + \epsilon_1'\overleftrightarrow{\tau} \cdot \nabla\delta_{24f} \\
& + \epsilon_3'\delta_{24f}\overleftrightarrow{\tau} \cdot (\mathbf{E} + \mathbf{v} \times \mathbf{B}) + \delta_{14f}(\mathbf{i} \times \mathbf{B}) + \delta_{15f}(\nabla\mathbf{v})^s \cdot \mathbf{q} \\
& + \delta_{16f}(\nabla\mathbf{v})^a \cdot \mathbf{q} + \delta_{22f}(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \cdot \overleftrightarrow{\tau},
\end{aligned} \tag{A9b}$$

$$\begin{aligned}
\delta_{7f}\frac{d\mathbf{q}}{dt} + \delta_{8f}\frac{d\mathbf{i}}{dt} = {} & -\nabla(\mu T^{-1}) + \delta_{12f}\mathbf{i} - \delta_{25f}\nabla \cdot \overleftrightarrow{\tau} + \epsilon_2'\overleftrightarrow{\tau} \cdot \nabla\delta_{25f} \\
& + \epsilon_4'\delta_{25f}\overleftrightarrow{\tau} \cdot (\mathbf{E} + \mathbf{v} \times \mathbf{B}) + \delta_{17f}(\mathbf{i} \times \mathbf{B}) + \delta_{18f}(\nabla\mathbf{v})^s \cdot \mathbf{i} \\
& + \delta_{19f}(\nabla\mathbf{v})^a \cdot \mathbf{i} + \delta_{23f}(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \cdot \overleftrightarrow{\tau} + T^{-1}(\mathbf{E} + \mathbf{v} \times \mathbf{B}).
\end{aligned} \tag{A9c}$$

Eqs. ($A9b$) and ($A9c$) are easily decoupled to yield Eq. (5), where the γ_{ij} are given in terms of the δ_{ij}. For instance, $\gamma_1 = (\delta_{7f}\delta_{5f} - \delta_{4f}\delta_{8f})/\delta_{12f}$ and similarly for the other coefficients.

We now indicate the process to derive Eqs. (6) using the variational approach. Let

$$\int \left(\rho \frac{d\eta}{dt} + \nabla \cdot J - \sigma \right) dV, \tag{$A10$}$$

which with the aid of Eqs. (3), (*A*1–2) and (*A*4) may be written as

$$\begin{aligned} \delta I = \delta \int \big(& -\beta_1 \nabla \cdot \mathbf{q} - \beta_1 \rho \nabla \cdot \mathbf{v} - \beta_1 \overleftrightarrow{\tau} : \nabla \mathbf{v} + \beta_1 \mathbf{i} \cdot (\mathbf{E} + \mathbf{v} \times \mathbf{B}) - \beta_1 \tau \nabla \cdot \mathbf{v} + \beta_2 \nabla \cdot \mathbf{v} \\ & - \beta_3 \nabla \cdot \mathbf{i} - \beta_4 \cdot \frac{d\mathbf{q}}{dt} + \overleftrightarrow{\beta}_5 : \frac{d\overleftrightarrow{\tau}}{dt} + \beta_6 \cdot \frac{d\mathbf{i}}{dt} \beta_7 : \frac{d\tau}{dt} + \alpha_1 \nabla \cdot \mathbf{q} + \mathbf{q} \cdot \nabla \alpha_1 \\ & + \alpha_2 \nabla \cdot \mathbf{i} + \mathbf{i} \cdot \nabla \alpha_2 + \alpha_3 \nabla \cdot (\overleftrightarrow{\tau} \cdot \mathbf{q}) + (\overleftrightarrow{\tau} \cdot \mathbf{q}) \cdot \nabla \alpha_3 + \alpha_4 \nabla \cdot (\overleftrightarrow{\tau} \cdot \mathbf{i}) \\ & + (\overleftrightarrow{\tau} \cdot \mathbf{i}) \cdot \nabla \alpha_4 - \sigma \big) \, dV. \end{aligned} \tag{$A11$}$$

Performing now the variation of the right hand side of Eq. (*A*11) (keeping as stated the tangent extended thermodynamic space fixed during the variation) yields

$$\begin{aligned} \delta I = \int \big\{ & -\nabla \cdot \mathbf{q} \mathcal{O}_1 \beta_{10} - \rho \nabla \cdot \mathbf{v} \mathcal{O}_1 \beta_{10} - \overleftrightarrow{\tau} : \nabla \mathbf{v} \mathcal{O}_1 \beta_{10} \\ & + \mathbf{i} \cdot (\mathbf{E} + \mathbf{v} \times \mathbf{B}) \mathcal{O}_1 \beta_{10} + \nabla \cdot \mathbf{v} \mathcal{O}_1 \beta_{20} - \nabla \cdot \mathbf{i} \mathcal{O}_1 \beta_{30} \\ & + \frac{d\mathbf{q}}{dt} \otimes (\beta_{41} + \mathbf{q} \mathcal{O}_1 \beta_{41} + \mathbf{i} \mathcal{O}_1 \beta_{42} \\ & + \beta_{43} \overleftrightarrow{\tau} + \mathbf{q} \cdot \overleftrightarrow{\tau} \mathcal{O}_1 \beta_{43} + \mathbf{i} \cdot \overleftrightarrow{\tau} \mathcal{O}_1 \beta_{44}) \\ & + \frac{d\overleftrightarrow{\tau}}{dt} \otimes (\overleftrightarrow{\tau} \mathcal{O}_1 \beta_{51} + 2\beta_{52} \mathbf{q} + \mathbf{q}\mathbf{q} \mathcal{O}_1 \beta_{52} \\ & + \mathbf{i}\mathbf{i} \mathcal{O}_1 \beta_{53} + \beta_{54} \mathbf{i} + \mathbf{q}\mathbf{i} \mathcal{O}_1 \beta_{54} \\ & + \overleftrightarrow{\tau} \cdot \overleftrightarrow{\tau} \mathcal{O}_1 \beta_{55} + \mathbf{i} \overleftrightarrow{\tau} \cdot \mathbf{i} \mathcal{O}_1 \beta_{56} + 2\beta_{57} \mathbf{q} \cdot \overleftrightarrow{\tau} \\ & + \mathbf{q} \overleftrightarrow{\tau} \cdot \mathbf{q} \mathcal{O}_1 \beta_{57} + \beta_{58} \overleftrightarrow{\tau} \cdot \mathbf{i} + \mathbf{q} \overleftrightarrow{\tau} \cdot \mathbf{i} \mathcal{O}_1 \beta_{58} \\ & + \frac{d\mathbf{i}}{dt} \otimes (\beta_{61} + \mathbf{q} \mathcal{O}_1 \beta_{61} + \mathbf{i} \mathcal{O}_1 \beta_{62} \\ & + \beta_{63} \overleftrightarrow{\tau} + \mathbf{q} \cdot \overleftrightarrow{\tau} \mathcal{O}_1 \beta_{63} + \mathbf{i} \cdot \overleftrightarrow{\tau} \mathcal{O}_1 \beta_{64}) \\ & + \nabla \cdot \mathbf{q} \mathcal{O}_1 \alpha_1 + \nabla \alpha_1 + \nabla \cdot \mathbf{i} \mathcal{O}_1 \alpha_2 \\ & + \nabla \cdot (\overleftrightarrow{\tau} \cdot \mathbf{q}) \mathcal{O}_1 \alpha_3 + \alpha_3 \nabla \cdot \overleftrightarrow{\tau} + \overleftrightarrow{\tau} \cdot \nabla \alpha_3 \\ & + \nabla \cdot (\overleftrightarrow{\tau} \cdot \mathbf{i}) \mathcal{O}_1 \alpha_4 - (\delta \sigma)_q \big\} \cdot \delta \mathbf{q} \end{aligned}$$

$$\begin{aligned}
&+\bigl\{-\nabla\cdot\mathbf{q}\mathcal{O}_2\beta_{10}-\rho\nabla\cdot\mathbf{v}\mathcal{O}_2\beta_{10}-\overleftrightarrow{\tau}:\nabla\mathbf{v}\mathcal{O}_2\beta_{10}\\
&+\beta_{10}(\mathbf{E}+\mathbf{v}\times\mathbf{B})+\mathbf{i}\cdot(\mathbf{E}+\mathbf{v}\times\mathbf{B})\mathcal{O}_2\beta_{10}-\nabla\cdot\mathbf{v}\mathcal{O}_2\beta_{20}\\
&-\nabla\cdot\mathbf{i}\mathcal{O}_2\beta_{30}+\frac{d\mathbf{q}}{dt}\otimes(\mathbf{q}\mathcal{O}_2\beta_{41}+\beta_{42}\\
&+\mathbf{i}\mathcal{O}_2\beta_{42}+\mathbf{q}\cdot\overleftrightarrow{\tau}\mathcal{O}_2\beta_{43}+\beta_{44}\overleftrightarrow{\tau}\\
&+\mathbf{i}\cdot\overleftrightarrow{\tau}\mathcal{O}_2\beta_{44})+\frac{d\overleftrightarrow{\tau}}{dt}\otimes(\overleftrightarrow{\tau}\mathcal{O}_2\beta_{51}+\mathbf{q}\mathbf{q}\mathcal{O}_2\beta_{52}\\
&+2\beta_{53}\mathbf{i}+\mathbf{i}\mathbf{i}\mathcal{O}_2\beta_{53}+\beta_{54}\mathbf{q}\\
&+\mathbf{q}\mathbf{i}\mathcal{O}_2\beta_{54}+\overleftrightarrow{\tau}\cdot\overleftrightarrow{\tau}\mathcal{O}_2\beta_{55}+2\beta_{56}\mathbf{i}\cdot\overleftrightarrow{\tau}\\
&+\mathbf{i}\overleftrightarrow{\tau}\cdot\mathbf{i}\mathcal{O}_2\beta_{56}+\mathbf{q}\overleftrightarrow{\tau}\cdot\mathbf{q}\mathcal{O}_2\beta_{57}+\beta_{58}\mathbf{q}\cdot\overleftrightarrow{\tau}\\
&+\mathbf{q}\overleftrightarrow{\tau}\cdot\mathbf{i}\mathcal{O}_2\beta_{58})+\frac{d\mathbf{i}}{dt}\otimes(\mathbf{q}\mathcal{O}_2\beta_{61}+\beta_{62}\\
&+\mathbf{i}\mathcal{O}_2\beta_{62}+\mathbf{q}\cdot\overleftrightarrow{\tau}\mathcal{O}_2\beta_{63}+\beta_{64}\overleftrightarrow{\tau}\\
&+\mathbf{i}\cdot\overleftrightarrow{\tau}\mathcal{O}_2\beta_{64})+\nabla\cdot\mathbf{q}\mathcal{O}_2\alpha_1+\nabla\cdot\mathbf{i}\mathcal{O}_2\alpha_2\\
&+\nabla\alpha_2+\nabla\cdot(\overleftrightarrow{\tau}\cdot\mathbf{q})\mathcal{O}_2\alpha_3+\nabla\cdot(\overleftrightarrow{\tau}\cdot\mathbf{i})\mathcal{O}_2\alpha_4\\
&+\alpha_4\nabla\cdot\overleftrightarrow{\tau}+\overleftrightarrow{\tau}\cdot\nabla\alpha_4-(\delta\sigma)_{\mathbf{i}}\bigr\}\cdot\delta\mathbf{i}\\
&+\bigl\{-\nabla\cdot\mathbf{q}\mathcal{O}_3\beta_{10}-\rho\nabla\cdot\mathbf{v}\mathcal{O}_3\beta_{10}-\beta_1\nabla\mathbf{v}-\tau:\nabla\mathbf{v}\mathcal{O}_3\beta_{10}\\
&+\mathbf{i}\cdot(\mathbf{E}+\mathbf{v}\times\mathbf{B})\mathcal{O}_3\beta_{10}-\tau\nabla\cdot\mathbf{v}\mathcal{O}_3\beta_{10}-\nabla\cdot\mathbf{v}\mathcal{O}_3\beta_{20}\\
&-\nabla\cdot\mathbf{i}\mathcal{O}_3\beta_{30}+\frac{d\mathbf{q}}{dt}\otimes(\mathbf{q}\mathcal{O}_3\beta_{41}+\mathbf{i}\mathcal{O}_3\beta_{42}+\beta_{43}\mathbf{q}\\
&+\mathbf{q}\cdot\overleftrightarrow{\tau}\mathcal{O}_3\beta_{43}+\beta_{44}\mathbf{i}+\mathbf{i}\cdot\overleftrightarrow{\tau}\mathcal{O}_3\beta_{44})\\
&+\frac{d\overleftrightarrow{\tau}}{dt}\otimes(\beta_{51}+\overleftrightarrow{\tau}\mathcal{O}_3\beta_{51}+\mathbf{q}\mathbf{q}\mathcal{O}_3\beta_{52}\\
&+\mathbf{i}\mathbf{i}\mathcal{O}_3\beta_{53}+\mathbf{q}\mathbf{i}\mathcal{O}_3\beta_{54}+2\beta_{55}\overleftrightarrow{\tau}\\
&+\overleftrightarrow{\tau}\cdot\overleftrightarrow{\tau}\mathcal{O}_3\beta_{55}+\beta_{56}\mathbf{i}\mathbf{i}+\mathbf{i}\overleftrightarrow{\tau}\cdot\mathbf{i}\mathcal{O}_3\beta_{56}\\
&+\beta_{57}\mathbf{q}\mathbf{q}+\mathbf{q}\overleftrightarrow{\tau}\cdot\mathbf{q}\mathcal{O}_3\beta_{57}+\beta_{58}\mathbf{q}\mathbf{i}\\
&+\mathbf{q}\overleftrightarrow{\tau}\cdot\mathbf{i}\mathcal{O}_3\beta_{58})+\frac{d\mathbf{i}}{dt}\otimes(\mathbf{q}\mathcal{O}_3\beta_{61}+\mathbf{i}\mathcal{O}_3\beta_{62}+\beta_{63}\mathbf{q}\\
&+\mathbf{q}\cdot\overleftrightarrow{\tau}\mathcal{O}_3\beta_{63}+\beta_{64}\mathbf{i}+\mathbf{i}\cdot\overleftrightarrow{\tau}\mathcal{O}_3\beta_{64})
\end{aligned}$$

$$
\begin{aligned}
&+\nabla\cdot\mathbf{q}\mathcal{O}_3\alpha_1+\nabla\cdot\mathbf{i}\mathcal{O}_3\alpha_2+\nabla\cdot(\overleftrightarrow{\tau}\cdot\mathbf{q})\mathcal{O}_3\alpha_3\\
&+\alpha_3\nabla\mathbf{q}+\mathbf{q}\cdot\nabla\alpha_3+\nabla\cdot(\overleftrightarrow{\tau}\cdot\mathbf{i})\mathcal{O}_3\alpha_4\\
&+\mathbf{i}\cdot\nabla\alpha_4-(\delta\sigma)\overleftrightarrow{\tau}\Big\}:\delta\overleftrightarrow{\tau}
\end{aligned}
$$

Setting finally $\delta_i = 0$ and taking the variation $\delta\mathbf{i}, \delta\mathbf{q}$ and $\delta\overleftrightarrow{\tau}$ as independent leads directly to Eq. (6).

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The pseudopotential method and the Z_1 band in KCl:KBr mixed crystals

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ABSTRACT. By taking into account that experimentally the X-ray spectrum of mixed crystals gives a lattice constant a_M which is different from the lattice constant of the two crystals which form the mixed crystal, the optical absorption of the Z_1-center was calculated in KCl:KBr mixed crystals with Ca^{++} impurities. The pseudopotential method was used. Good agreement with the experimental results is found for pure KCl and KBr.

RESUMEN. Usando el hecho experimental según el cual el espectro de rayos X de cristales mixtos da una constante de la red a_M, la cual es diferente de las dos constantes de la red de los cristales que constituyen el cristal mixto, se calculó la absorción óptica del centro Z_1 en cristales de KCl:KBr con impurezas de Ca^{++}. El método usado fue el de corrección de tamaño. Se encontró buen acuerdo con los resultados experimentales para KCl y KBr puros.

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1. INTRODUCTION

Recently we have studied the behavior of the F an F_A optical absorption in mixed crystals [1-4]. Rodríguez and Ruiz-Mejía [1] conducted a theoretical study of the shift with concentration variation on the optical-absorption F band in KCl:RbCl and KCl:KBr mixed crystals using an F-center semicontinuum model [1]. Logatorov *et al.* [5,6] performed a theoretical calculation employing the ion-point model for a mixed crystal $K_{0.5}Cl:Na_{0.5}Cl$; they consider a statistical distribution of different types of positive ions around the F-center, and assume that the substitution of ions at a lattice place has a perturbative effect on the F-center electron and also produce F_A, F_B and F_C centers, with increased mixed concentration in the colored crystals. The calculations can be done in a systematic way when the concentration of components are the same, such as those by Logatorov *et al.* [6], but for unbalanced concentrations the calculations are more difficult. We have proposed a new point of view [2-4] in order to calculate the optical absorption in mixed crystals. By taking into account that experimentally the X-ray spectrum of mixed crystals [7] gives a lattice constant a_M which is different from the lattice constant of the two crystals which form the mixed crystal. We have performed calculations for the mixed crystals considering [2-4] that these crystals have an specific physical properties and intrinsic constants, derived from Vegard's rule [8]. For the F and $\mathrm{F_A}$-band in mixed crystals there are good agreement with the Asami and Ishiguro [9] experimental values. The interest in mixed crystals is due [9] to the possibility of using them in IR (infrared regions) laser operation. Also the Z_1-center can be used in laser operation [10], that is why our interest in the study of Z_1-band in mixed crystals. The Z_1 center consists of an F center with a $[00\bar{1}]$ cation vacancy and a $[11\bar{1}]$ divalent ion near to it [10]. The calculations for the optical absorption of the Z_1 center were made for mixed KCl:KBr mixed crystals with divalent impurities of $\mathrm{Ca^{++}}$.

2. THEORY

The variational method to obtain the energy levels of the F-center in the point-ion approximation [11] consist of the minimization of the energy functional E_{lm}. That is

$$E_{lm} = \int \psi^* \left[-\tfrac{1}{2}\nabla^2 + V_{\mathrm{PI}}(r)\right] \psi \, d\tau, \tag{1}$$

where $V_{\mathrm{PI}}(r)$ is the point-ion potential and ψ is the trial wave function. For the ground state Gaussian wave function we have

$$\psi_{\mathrm{g}}(r, \lambda_{\mathrm{g}}) = \left[\frac{2\lambda_{\mathrm{g}}^2}{\pi}\right]^{3/4} \exp(-\lambda_{\mathrm{g}}^2 r^2), \tag{2}$$

$$\psi_{\mathrm{e}}(r, \theta\lambda_{\mathrm{e}}) = \left[\frac{2^7\lambda_{\mathrm{e}}^{10}}{\pi^3}\right]^{1/4} r\cos\theta \exp(-\lambda_{\mathrm{e}}^2 r^2), \tag{3}$$

for the excited state. The λ_{g} and λ_{e} are the corresponding variational parameters. For the F-center the point-ion functional energies are given by

$$E_{1s}^{\mathrm{F}} = \frac{3}{2}\lambda_{\mathrm{g}}^2 + \left(\frac{\pi}{2}\right)^{3/2} \left[\frac{2}{\pi}\lambda_{\mathrm{g}}^2\right]^{3/2} \sum_i \frac{q_i n_i}{r_i \lambda_{\mathrm{g}}^2} \operatorname{erf}(\sqrt{2}\lambda_{\mathrm{g}} r_i) \tag{4}$$

for the ground state, where n_i is the number of ions with charge q_i.

For the excited state

$$E_{2p}^{\mathrm{F}} = \sum_i \frac{[2^7\lambda^{10}/\pi^3]^{1/2} q_i n_i}{(\sqrt{2}\lambda_{\mathrm{e}})^2} \exp(-2\lambda_{\mathrm{e}}^2 r_i^2) + \frac{5}{32}\sqrt{2}\frac{\pi^{3/2}}{\lambda_{\mathrm{e}}^3} \left[\frac{2^7\lambda_{\mathrm{e}}^{10}}{\pi^3}\right]^{1/2}. \tag{5}$$

The energy functional E_{1S}^{Z} of the Z_1-center corresponding to the ground state is

$$E_{\mathrm{1S}}^{Z} = E_{\mathrm{1S}}^{\mathrm{F}} + Y_{\mathrm{1S}}(\sqrt{3}a) - Y_{\mathrm{1S}}(a), \tag{6}$$

where a is the interatomic distance and

$$Y_{1S}(r) = -A_{\mathrm{g}}^2 \frac{(\pi/2)^{3/2}}{r\lambda_{\mathrm{g}}^3} \operatorname{erf}(\sqrt{2}\lambda_{\mathrm{g}} r); \tag{7}$$

A_{g} is the wave function normalization constant.

The energy functional E_{2p}^{Z} corresponding to the excited state is

$$E_{2p}^{Z} = E_{2p}^{\mathrm{F}} + Y_{2p}(\sqrt{3}a) - Y_{2p}(a), \tag{8}$$

where

$$\begin{aligned} Y_{2p}(\hat{r}) = {} & \frac{\pi A_{\mathrm{e}}^2 Q}{3(\sqrt{2}\lambda_{\mathrm{e}})^4} \exp(-2\lambda_{\mathrm{e}}^2 r^2) - \frac{\pi A_e^2 Q}{r(\sqrt{2}\,\lambda_{\mathrm{e}})^5} \frac{\sqrt{\pi}}{2} \operatorname{erf}(\sqrt{2}\,\lambda_{\mathrm{e}} r) \\ & + \frac{8\pi Q P_2(\cos\theta) A_{\mathrm{e}}^2}{15 r^2 (\sqrt{2}\lambda_{\mathrm{e}})^7} \left[\frac{(\sqrt{2}\lambda_{\mathrm{e}} r)^5}{2} + \frac{5}{4}(2\lambda_{\mathrm{e}} r)^3 \right. \\ & \left. + \frac{15}{8}(\sqrt{2}\,\lambda_{\mathrm{e}} r) \exp(-2\lambda_{\mathrm{e}}^2 r^2) + \frac{15}{8}\frac{\sqrt{\pi}}{2} \operatorname{erf}(\sqrt{2}\lambda_{\mathrm{e}} r) \right] \\ & + \frac{8\pi}{15} A_{\mathrm{e}}^2 \frac{P_2(\cos\theta)}{\left(\sqrt{2}\lambda_{\mathrm{e}}\right)^2} r^2 \frac{1}{2} \exp(-2\lambda_{\mathrm{e}}^2 r^2); \end{aligned} \tag{9}$$

A_{e} is the excited wave function normalization constant, Q is the charge distribution at a point r. $P_2(\cos\theta)$ is the Legendre polynomial of order two, where θ is the angle between the vector at the point r and the axis of the p-function.

For the ground state of the Z_1-center we can choose the wave function for the F-center $\psi_{\mathrm{g}}(r, \lambda_{\mathrm{g}})$. In the case of the excited state is necessary to choose the direction for the p-function axes according to the symmetry of the impurity and the vacancy which together with the F-center form the Z_1-center. A suitable choice of the three mutually perpendicular axis will be the three principal axes of the field gradient tensor set up by the Z_1-center. Dick [12] calculated the directions of those axes. The direction cosines of the principal axes are approximately $(0,0,1)$, $\left(\frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}}, 0\right)$ and $\left(\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0\right)$. That is

$$\psi_{\mathbf{e}xy} = \frac{1}{\sqrt{2}}(\psi_{\mathbf{e}x} + \psi_{\mathbf{e}y}) \tag{10}$$

and

$$\psi_{\mathbf{e}x\bar{y}} = \frac{1}{\sqrt{2}}(\psi_{\mathbf{e}x} + \psi_{\mathbf{e}y}), \tag{11}$$

where $\psi_{\mathbf{e}x}$ and $\psi_{\mathbf{e}y}$ are the wave functions for the F-center. Equation (3) gives the $\psi_{\mathbf{e}z}$ for the F-center.

Then for the Z_1-center we have three wave functions: $\psi_{exy}, \psi_{ex\bar{y}}$ and ψ_{ez}.

The point-ion interaction potential is given by

$$\left\langle \psi_\mathrm{e} \left| \frac{Q}{|\hat{r} - \hat{r}_i|} \right| \psi_a \right\rangle = A^2 \int \left(\tfrac{4}{3}\delta_0 + \tfrac{8}{15}\delta_2 P_2(\cos\theta) \right) \pi f(r) r^2 \, dr, \tag{12}$$

where $f(r)$ is the part of the wave function ψ_a which depends only on r, and δ_0 and δ_2 are given by

$$\delta_0 = \begin{cases} \dfrac{1}{r_i}, & r < r_i \\[2ex] \dfrac{1}{r}, & r > r_i \end{cases} \tag{13}$$

and

$$\delta_2 = \begin{cases} \dfrac{r^2}{r_i^3}, & r < r \\[2ex] \dfrac{r_i^2}{r^3}, & r > r_i. \end{cases} \tag{14}$$

In order to obtain Eq. (12) we have used the result given by Coulson [12]:

$$I = \sum_{n,k} \int P_n(\cos\theta_a) P_k(\cos\theta_b) \, dw = \sum_k \frac{2\pi}{2k+1} P_k(\cos\gamma), \tag{15}$$

where $\theta_a = \gamma - \theta_b$.

The ground-state energy for the Z_1-center is obtained minimizing an energy functional of the form

$$E_\mathrm{g}^z = E_\mathrm{g}^\mathrm{F} + \sum_s \langle \psi_\mathrm{g}(\hat{r}_s) | V_p^z | \psi_\mathrm{g}(\hat{r}_s) \rangle. \tag{16}$$

For the first-excited-state the energy is obtained minimizing the energy functional

$$E_\mathrm{C}^z = E_\mathrm{C}^\mathrm{F} + \sum_s \langle \psi_\mathrm{e}(\hat{r}_s) | V_\mathrm{p}^Z | \psi_\mathrm{e}(\hat{r}_s) \rangle, \tag{17}$$

where

$$\begin{aligned} V_\mathrm{p}^Z = V_\mathrm{p}^\mathrm{F} &- V_\mathrm{pI} \left[A_\mathrm{C} + (\bar{V}_\mathrm{p}^\mathrm{F} - U_1) B_\mathrm{C} \right] \delta(\hat{r} - \hat{r}_\mathrm{c}) \\ &+ \left[A_\mathrm{d} - A_\mathrm{c} + (\bar{V}_\mathrm{p} - U_3)(B_\mathrm{d} - B_\mathrm{c}) \right] \delta(\hat{r} - \hat{r}_\mathrm{d}) \end{aligned} \tag{18}$$

and

$$V_\mathrm{p}^\mathrm{F} = V_\mathrm{pI} + \sum_s \left[A_s + (\bar{V}_\mathrm{p} - U_s) B_s \right] \delta(\hat{r} - \hat{r}_s); \tag{19}$$

TABLE I. Energy values in atomic units for the ground (E_g) and the excited (E_e) states of the Z, center in KCl:Br:Ca$^+$ for several concentrations c_x.

KCl:BrCa^{++}	λ_g	$-V_g$	$-E_g$	λ_e	$-V_e$	$-E_e$
$c_x = 0$	1.18	0.096	0.1081	0.95	0.130	0.0272
$c_x = .25$	1.17	0.095	0.1088	0.94	0.132	0.0330
$c_x = .50$	1.15	0.094	0.1095	0.93	0.135	0.0390
$c_x = .75$	1.13	0.092	0.1100	0.92	0.136	0.0442
$c_x = 1.00$	1.12	0.092	0.1108	0.92	0.141	0.0505

the U_s is the potential of the 5th ion due to all the all the other ions and A_s and B_s are the characteristic parameters of the ions alone, V_{PI} is the point-ion potential and $V_{\mathrm{P}}^{\mathrm{F}}$ the pseudopotential corresponding to the F-center. The indices D and C mean divalent impurity and cation respectively.

E_{g}^{z} (or E_{e}^{z}) is minimized with respect to λ_{g} (or λ_{e}) for a fixed value of $\bar{V}_{\mathrm{P}}$, then $\langle\psi|V_{\mathrm{P}}^{Z}|\psi\rangle$ is recomputed from Eq. (18) and the procedure is continued to self-consistency [13].

In order to solve the problem for mixed crystals [2] we take A_γ and B_γ as

$$A_\gamma = A_\gamma^1(1-x) + A_\gamma^2 x$$

and

$$B_\gamma = B_\gamma^1(1-x) + B_\gamma^2 x,$$

where A_γ^1 and A_γ^2 correspond to one type of crystal and A_γ^2 and B_γ^2 to the other type (which are the components of the mixed crystal), and

$$a_{\mathrm{M}} = a_1(1-x) + a_2 x,$$

where a_{M} is the lattice constant of the mixed crystal; a_1 and a_2 are the lattice constant of the pure crystal, and x the concentration.

3. RESULTS AND CONCLUSIONS

Recently we have found good agreement between theoretical and experimental results for the F [2] and the F$_{\mathrm{A}}$ [3,4] band in mixed crystals. The same idea is used in the study of the Z_1-band in mixed crystals of KCl:KBr with Ca^{++} impurities. The results are given in Table I and the behavior of the optical absorption of Z_1-band in Fig. 1. There is not experimental results for these mixed crystals, but the behavior of the Z_1-band as function of the concentration is similar to that of the F-band.

The calculations were carried on using Gaussian wave functions for the semiempirical parameter $\alpha = 1$. There are other methods in order to calculate the optical absorption of the F-band [14-24] but the Bartram *et al.* method [13] have been [25-30] applied to wide variety of color centers with good results.

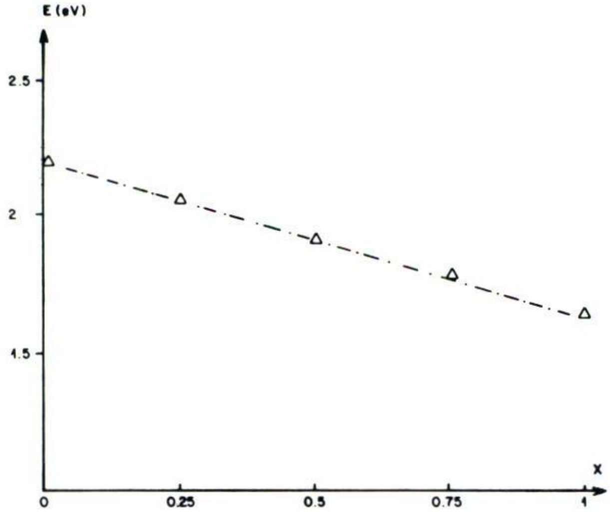

FIGURE 1. Dashed line joints the theoretical values of the absorption energy *vs.* concentration for Z_1 center. Then for energy the following Vegard law type is possible: $\Delta E = \Delta E_1(1-x) + \Delta E_2 X$, and where ΔE is the absorption energy of the mixed crystal; ΔE_1 and ΔE_2 are the absorption energies of the pure crystals, and x the concentration.

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