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Anelastic (dielectric) relaxation of point defects at any concentration, with blocking effects and formation of complexes

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A derivation of the relaxation strength for anelastic and dielectric relaxation of point defects is proposed, and the calculation is extended to cases not yet treated; the formulas reported in the literature can be obtained as particular cases. The relaxation strength is expressed as the sum of the contributions of all the pairs of configurations that the defect can assume. The case of arbitrarily high concentrations with blocking, short-range interactions, and formation of defect complexes is also treated, and the formulas of the partial concentrations of the various defect configurations are provided. The proposed approach is useful if the formation of complexes and the short-range interactions occur within independent cells or subsystems into which the crystal can be divided. Two specific cases are discussed as applications: the anelastic relaxation of a four-level tunnel system and of interstitial hydrogen in the hcp rare earths with the formation of H pairs.

I. INTRODUCTION

The theory of anelastic and dielectric relaxation of a crystal containing point defects, i.e., of the linear response of the crystal to the application of a stress or electric field, has been systematized by Nowick and Heller in a series of papers.[1-4] They considered defects reorienting among configurations that are made nonequivalent by the application of stress or an electric field and calculated both the relaxation rates and strengths. They provided expressions valid in the low-concentration limit for all the possible symmetries of the applied stress, defects, and host crystals by using the results of group theory.

The case of relaxation among configurations that are nonequivalent even in the absence of stress or which involve defect complexes appears more complicated. Nowick and Heller extended the analysis also to such cases in Ref. 1 and 4, calling them "reaction modes" as opposed to the "reorientation modes." That analysis is based on a thermodynamic approach and is restricted to low concentrations, without blocking effects; no prescriptions are given for the calculation of the relative concentrations in the general case where several nonequivalent configurations are possible.

In the present paper, a very simple derivation of the expressions of the relaxation strength is provided, which is based on a statistical rather than thermodynamic approach and which covers in a unified manner the reorientation and reaction cases or any mixed situation. The relaxation strength is also expressed as the sum of the contributions of all the pairs of configurations between which relaxation occurs. The calculation scheme may include a method recently proposed[5] for evaluating the probabilities of the configurations of point defects with arbitrarily high concentration, taking into account short-range interactions, such as blocking effects or the formation of defect complexes. Such a method is valid when the crystal can be divided into independent cells or subsystems within which the short-range interactions and the formation of complexes take place; the simplest case is that of independent defects.

The great majority of the experimental work avoids the analysis of aspects related to the relaxation among nonequivalent configurations. Nevertheless, in recent times much attention is being devoted to systems containing nonequivalent configurations of defects and where the concentrations of the relaxing interstitials or vacancies may be so high that blocking effects come into play. We mention here the high-T_c superconducting oxides of the $YBa_2Cu_3O_{6+x}$ family, whose CuO_x planes $(0<x<1)$ contain highly mobile O atoms, giving rise to a variety of effects that have been only partly analyzed.[6] Furthermore, the hcp RH_x systems ($R=$Y, Sc, Lu) are being extensively studied also by anelastic relaxation with H contents up to tens of percent or near the stoichiometry of the dihydride RH_{2+x}.[7-11] Here H can relax between tetrahedral and octahedral sites and tends to form pairs in tetrahedral sites separated by an R atom along the c axis. Several anelastic relaxation measurements of RH_x exist, but no analysis of the possible involved relaxations has been made; in Sec. IV B, formulas appropriate for such cases will be provided as an application of the presently proposed calculation scheme. Another example will be provided in Sec. IV A by calculating the different relaxation modes of a four-site tunnel system. Hydrogen trapped by substitutional Ti in Nb is supposed to tunnel among four sites, giving rise to a four-level tunnel system; recent experiments may only be explained by discriminating the possible relaxations between the four levels.[12]

II. ANELASTIC AND DIELECTRIC RELAXATION

Anelastic relaxation is the phenomenon that occurs when a solid contains defects that produce a local elastic distortion, which may exist in at least two configurations differing in magnitude or orientation of the associated local strain. The anelastic contribution to the macroscopic strain may be written as

$$\varepsilon_{ij}^{\mathrm{an}}=\sum_{\alpha}\lambda_{ij}^{(\alpha)}c_{\alpha}\ , \tag{1}$$

where c_α is the molar concentration of the defects of type α (or in configuration α) and $\lambda_{ij}^{(\alpha)}$ is the ij component of the so-called elastic dipole of defect α; by definition $\lambda_{ij}^{(\alpha)}$ is the contribution to ε_{ij} of one mole of defects of type α $(i,j=x,y,z)$.[1,13]

This is completely analogous to the case of paraelectric relaxation, and in fact it is also called paraelastic relaxation when only a reorientation of the elastic dipoles is involved. In the case of defects with an associated electric dipole, their contribution to the ith component of the electric polarization P_i can be written as

$$P_i=\sum_{\alpha}\mu_i^{(\alpha)}c_\alpha\ , \tag{2}$$

where $\mu_i^{(\alpha)}$ is the electric dipole moment associated with 1 mol of defects of type α. The only difference between the electric and elastic cases is that stress, strain, and the elastic dipole are second-rank tensors, while the electric field, polarization, and dipole moment are vectors. In what follows we will explicitly refer to the elastic case, but without taking into account the tensor character of the physical quantities, so that the electric case is obtained simply by changing σ into E, ε into P, and λ into μ. As explained in Ref. 2, one can always choose the representation of the normal coordinates of σ and ε, where they become vectors related to each other by a diagonal matrix: $\sigma_i=M_{ii}\varepsilon_i$. In what follows we will refer to a particular normal mode, for which σ, ε, and M are scalar quantities, and therefore the subscript i will be dropped.

On application of an external stress σ (electric field E), the energies of the various configurations will be perturbed and their concentrations will change to reach a new thermal equilibrium, changing in turn the value of the anelastic strain $\varepsilon^{\mathrm{an}}$ (polarization P). Each relaxation process reaches the equilibrium with a relaxation time τ, which is related to the rate of conversion of the defect among its possible configurations.

After the application of a constant stress, each relaxation process will contribute to the strain with

$$\Delta(1-e^{-t/\tau})\ , \tag{3}$$

giving rise to the so-called aftereffect.[13,14] The quantity Δ is the relaxation strength, defined as

$$\Delta=\frac{\varepsilon^{\mathrm{an}}}{\varepsilon}=\frac{\delta M^{\mathrm{an}}}{M}=\frac{1}{M}\frac{\partial\varepsilon^{\mathrm{an}}}{\partial\sigma}\ , \tag{4}$$

where $\varepsilon=M\sigma$ is the elastic strain, M being the appropriate unrelaxed modulus.

Instead, on application of a periodic stress with angular frequency ω, the resulting strain will follow the stress with a delay; this can be described in terms of a complex contribution δM to the dynamic modulus $M(\omega)$:[13,14]

$$\mathrm{Im}\left[\frac{\delta M}{M}\right]=\Delta\frac{\omega\tau}{1+(\omega\tau)^2}\ ,\quad \mathrm{Re}\left[\frac{\delta M}{M}\right]=\frac{-\Delta}{1+(\omega\tau)^2}\ . \tag{5}$$

The imaginary part is the elastic energy-loss coefficient (the inverse of the mechanical Q), and the real part is called the modulus defect.

III. CALCULATION OF THE RELAXATION STRENGTH

According to Eq. (4), the relaxation strength is proportional to the stress derivative of the anelastic strain (1). In the case of paraelastic response, the elastic dipole is independent of stress, and all the stress dependence comes from the defect concentrations through the defect energies:[15]

$$\frac{d\varepsilon^{\mathrm{an}}}{d\sigma}=\sum_{\alpha}\lambda_\alpha\frac{dc_\alpha}{d\sigma}=\sum_{\alpha}\sum_{\beta}\lambda_\alpha\frac{dc_\alpha}{dE_\beta}\frac{dE_\beta}{d\sigma}\ . \tag{6}$$

The stress derivative of the energy E_α of a defect α is simply related to the component λ_α of its elastic dipole, because they are the same second derivative of the Gibbs free energy. In fact, the differential of the free energy per unit volume is

$$dg=-s\,dT-\varepsilon\,d\sigma+\frac{1}{v_0}\sum_{\alpha}E_\alpha dc_\alpha\ , \tag{7}$$

where v_0 is the unit-cell volume and s is the entropy per unit volume, disregarding the configurational entropy due to the distribution of the defects in the possible sites.[16] From Eq. (7) one obtains the desired relation:

$$\lambda_\alpha=\frac{\partial\varepsilon^{\mathrm{an}}}{\partial c_\alpha}=-\frac{\partial^2 g}{\partial\sigma\,\partial c_\alpha}=-\frac{1}{v_0}\frac{\partial E_\alpha}{\partial\sigma}\ . \tag{8}$$

Equation (6) can then be written as

$$\frac{d\varepsilon^{\mathrm{an}}}{d\sigma}=-\frac{1}{v_0}\sum_{\alpha}\sum_{\beta}\lambda_\alpha\lambda_\beta\frac{dc_\alpha}{dE_\beta}\ . \tag{9}$$

We will see later that the derivatives of the concentrations of independent configurations with respect to the energies are of the form

$$\frac{dc_\alpha}{dE_\beta}=\beta c'_\alpha\left[\frac{c'_\beta}{c'}-\delta_{\alpha\beta}\right]\ ,\quad c'=\sum_{\alpha}c'_\alpha\ , \tag{10}$$

where $\beta=1/kT$, $\delta_{\alpha\beta}$ is the Kronecker symbol, and c'_α tend to c_α for small concentrations and unpaired defects (there should not be confusion between the index β and $\beta=1/kT$, which instead appears as a factor).

If the configurations exclude each other within the same cell, instead of being independent, an additional term appears, which, however, is of the same form and allows the same manipulations to be done. Equation (10) allows us to write

$$\frac{v_0}{\beta}\frac{\partial\varepsilon^{\mathrm{an}}}{\partial\sigma}=\sum_{\alpha}\sum_{\beta}\lambda_\alpha\lambda_\beta c'_\alpha\left[\delta_{\alpha\beta}-\frac{c'_\beta}{c'}\right]$$

$$=\sum_{\alpha}\left[\lambda_\alpha^2 c'_\alpha\left[1-\frac{c'_\alpha}{c'}\right]-\lambda_\alpha c'_\alpha\left[\sum_{\beta\neq\alpha}\lambda_\beta\frac{c'_\beta}{c'}\right]\right]=\sum_{\alpha}\left[\lambda_\alpha^2 c'_\alpha\left[\sum_{\beta\neq\alpha}\frac{c'_\beta}{c'}\right]-\lambda_\alpha c'_\alpha\left[\sum_{\beta\neq\alpha}\lambda_\beta\frac{c'_\beta}{c'}\right]\right]$$

$$=\sum_{\alpha}\sum_{\beta<\alpha}(\lambda_\alpha^2-\lambda_\alpha\lambda_\beta+\lambda_\beta^2-\lambda_\beta\lambda_\alpha)\frac{c'_\alpha c'_\beta}{c'}=\sum_{\alpha}\sum_{\beta<\alpha}\frac{c'_\alpha c'_\beta}{c'}(\lambda_\alpha-\lambda_\beta)^2\ . \tag{11}$$

This means that the relaxation strength can simply be decomposed into the contributions from all the pairs of configurations between which relaxation occurs:

$$\Delta=\sum_{\alpha}\sum_{\beta<\alpha}\Delta_{\alpha\beta}\ . \tag{12}$$

Moreover, all the terms have the same simple expression for any number and type of the configurations; in fact, no hypotheses have been made about the elastic dipoles and energies. The formulas generally adopted appear to not satisfy Eq. (12), but they can always be put in that form after appropriate changes of notation and manipulations.

It may also be instructive to rewrite the above expressions in terms of the averages of the elastic dipoles over the concentrations (for simplicity in the low-concentration limit):

$$\bar{\lambda}=\frac{1}{c}\sum_{\alpha}c_\alpha\lambda_\alpha=\frac{\varepsilon^{\mathrm{an}}(\sigma=0)}{c}\ ,\quad \overline{\lambda^2}=\frac{1}{c}\sum_{\alpha}c_\alpha\lambda_\alpha^2\ . \tag{13}$$

The change of the population of the αth configuration can be written as

$$\frac{dc_\alpha}{d\sigma}=\sum_{\beta}\frac{dc_\alpha}{dE_\beta}\frac{dE_\beta}{d\sigma}=\beta v_0\sum_{\beta}\lambda_\beta c_\alpha\left[\delta_{\alpha\beta}-\frac{c_\beta}{c}\right]$$

$$=\beta c_\alpha v_0(\lambda_\alpha-\bar{\lambda})\ ; \tag{14}$$

i.e., on application of a stress, the relative variation of c_α is equal to the deviation of λ_α with respect to the mean elastic dipole or mean anelastic strain divided by temperature. Similarly, the specific total relaxation strength is equal to the mean-squared deviation of the elastic dipoles, divided by temperature:

$$\frac{d\varepsilon^{\mathrm{an}}}{d\sigma}=\sum_{\alpha}\lambda_\alpha\frac{dc_\alpha}{d\sigma}=\beta c v_0(\overline{\lambda^2}-\bar{\lambda}^2)\ . \tag{15}$$

A. Noninteracting defects obeying Boltzmann statistics (low-concentration limit)

In the present paragraph, we will deal with noninteracting defects whose mean occupation numbers follow Boltzmann statistics. This is the usual case already treated by Nowick and most of the other authors. The use of Boltzmann statistics is justified when the defect concentrations are so small that the occurrence of double occupation of a defect site is negligible.

In contrast with the previous treatments, all the defect configurations will be considered on the same level, whether they are equivalent by energy and symmetry or not. The summations are intended over all the possible configurations α (types of sites) of the atomic species representing the defect, whose total concentration c is conserved. Each configuration must be constituted by only one defect atom in order to avoid the complications due to the change in the configurational entropy with the formation of defect complexes. At most, all the configurations may contain the same number of defects; for example, they may consist of different orientations of pairs of atoms, but cannot include the dissociated atoms. The case of the formation of defect complexes will be treated in Secs. III C and III D with a different statistics. We will use the terms "site" and "configuration" in an interchangeable way.

The statistical weight of a particular configuration α with energy E_α is

$$w_\alpha=e^{-\beta E_\alpha}\ . \tag{16}$$

If the configuration has multiplicity m_α; i.e., it can be realized in m_α modes (or there are m_α sites of type α per unit cell); then, according to Boltzmann statistics, its weight is $m_\alpha w_\alpha$ and its molar concentration is

$$c_\alpha=c\frac{m_\alpha w_\alpha}{z}\ ,\quad z=\sum_{\alpha}m_\alpha w_\alpha\ , \tag{17}$$

where c is the total molar concentration of the defect, i.e., the number of defects per unit cell. The derivative of c_α with respect to the defect energies can be easily put in the form of Eq. (10):

$$\frac{dc_\alpha}{dE_\beta}=c\left[\frac{m_\alpha}{z}\frac{dw_\alpha}{dE_\beta}-\frac{m_\alpha w_\alpha}{z^2}\frac{dz}{dE_\beta}\right]=\beta c_\alpha\left[\frac{c_\beta}{c}-\delta_{\alpha\beta}\right]\ . \tag{18}$$

Then, proceeding as in Eq. (11), one finds that the relaxation strength is

$$\Delta=\frac{\beta}{Mv_0}\sum_{\alpha}\sum_{\beta<\alpha}\frac{c_\alpha c_\beta}{c}(\lambda_\alpha-\lambda_\beta)^2=\sum_{\alpha}\sum_{\beta<\alpha}\Delta_{\alpha\beta}\ , \tag{19}$$

where the relaxation between α and β contributes with

$$\Delta_{\alpha\beta}=\frac{\beta}{Mv_0}\frac{c_\alpha c_\beta}{c}(\lambda_\alpha-\lambda_\beta)^2\ . \tag{20}$$

Such an expression of $\Delta_{\alpha\beta}$ was already derived by Nowick[4] following a thermodynamic method, although for the case of only one pair of configurations. With that approach a major complication is connected with the calculation of the configurational entropy of the defects. The mixed case of a reaction between two types of dipoles, each having different orientations, was also considered in Ref. 1, and Eq. (4.23) of that paper can be put in the form of Eq. (20).

Equation (20) asserts that the magnitude of the relaxation between configurations α and β is proportional to the concentration of both. In the case of a reorientation among m configurations with the same energy, one has $c_\alpha = c_\beta = c/m$ and the temperature dependence of the relaxation strength becomes the well-known $1/T$ law. Instead, if $E_\alpha - E_\beta = E$, the product $c_\alpha c_\beta$ will be maximum at $kT \sim E$; in the frequent case of relaxation between only two levels differing in energy of E, the temperature dependence of the relaxation strength is given by

$$\Delta \sim c\beta \operatorname{sech}^2(\beta E/2) , \tag{21}$$

which is maximum at $kT = 0.65E$, tends to c/kT for $kT \gg E$, and tends to zero as $\beta e^{-\beta E}$ for small T. Such a temperature dependence of Δ is well known for two-level tunnel systems,[17,18] where it may dominate the shape of the relaxation curves. One should take into account the falling off of Δ whenever relaxation occurs between states whose energy separation is $E > kT$.

B. Noninteracting defects obeying Fermi-Dirac statistics (any concentration)

When the probability of multiple occupation of a same defect state (site) becomes appreciable, one should use Fermi-Dirac statistics instead of that of Boltzmann. This may happen because of the high concentration of the defects or because at low temperature they tend to stay in a restricted number of low-energy sites. In Fermi-Dirac statistics, the occupation number n_α of site α may only assume the value 0 or 1, and the expression of its mean value may be easily evaluated in the framework of the grand-canonical ensemble,[19] as briefly shown in the Appendix.

Again, we will suppose that the occupation of a configuration (site) is independent of the others; i.e., there are no interactions between the defects. Also, all the configurations consist of a single defect atom (or of the same number of atoms).

In the absence of interactions between different cells, we can consider the grand-partition function z of a single elementary cell; this is, in turn, the product of the grand-partition functions of its sites, which are independently filled (in the present context, it looks more natural to consider sites to be filled with at most one defect rather than configurations to be assumed by the defect):

$$z = \prod_\alpha z_\alpha^{m_\alpha} ,$$
$$z_\alpha = 1 + e^{\beta(\mu - E_\alpha)} = 1 + w_\alpha . \tag{22}$$

Here m_α is the multiplicity of site α; i.e., there are m_α identical sites per cell, and w_α is the statistical weight for the occupation of a particular site α. The chemical potential μ must be chosen in order to satisfy the condition of defect conservation [Eq. (A4)]:

$$c = \frac{1}{\beta}\frac{\partial \ln z}{\partial \mu} = \sum_\alpha \frac{m_\alpha}{\beta}\frac{\partial \ln z_\alpha}{\partial \mu} = \sum_\alpha m_\alpha \frac{w_\alpha}{z_\alpha} = \sum_\alpha c_\alpha , \tag{23}$$

which is a polynomial equation for $e^{\beta\mu}$ with degree equal to $\sum_\alpha m_\alpha$ and defines the partial concentrations c_α as

$$c_\alpha = m_\alpha \frac{w_\alpha}{z_\alpha} . \tag{24}$$

As before, c is the molar defect concentration, which can have the maximum value of $\sum_\alpha m_\alpha$ when μ is infinite.

We now repeat the steps followed to obtain Eqs. (19)–(21), starting with the derivative of c_α with respect to E_β and keeping in mind that c_α depends on E_β also through μ:

$$\begin{aligned} \frac{dc_\alpha}{dE_\beta} &= m_\alpha \left[\frac{1}{z_\alpha}\frac{dw_\alpha}{dE_\beta} - \frac{w_\alpha}{z_\alpha^2}\frac{dz_\alpha}{dE_\beta} \right] \\ &= \beta c_\alpha \left[1 - \frac{c_\alpha}{m_\alpha} \right] \left[\frac{\partial \mu}{\partial E_\beta} - \delta_{\alpha\beta} \right] . \end{aligned} \tag{25}$$

We would like to express $d\mu/dE_\beta$ in terms of the concentrations in order to have an expression analogous to Eq. (10) or (18). This can be obtained by deriving Eq. (23) with respect to E_β:

$$0 = \frac{dc}{dE_\beta} = \sum_\alpha \frac{dc_\alpha}{dE_\beta} . \tag{26}$$

If we define new quantities c',

$$c'_\alpha = c_\alpha \left[1 - \frac{c_\alpha}{m_\alpha} \right] , \quad c' = \sum_\alpha c'_\alpha , \tag{27}$$

then Eq. (26) becomes

$$\frac{\partial \mu}{\partial E_\beta} = \frac{c'_\beta}{c'} \tag{28}$$

and Eq. (25) becomes

$$\frac{dc_\alpha}{dE_\beta} = \beta c'_\alpha \left[\frac{c'_\beta}{c'} - \delta_{\alpha\beta} \right] , \tag{29}$$

which is exactly of the form of Eq. (10). Therefore, following Eq. (11), we write the final expression

$$\Delta = \frac{\beta}{M v_0} \sum_\alpha \sum_{\beta<\alpha} \frac{c'_\alpha c'_\beta}{c'} (\lambda_\alpha - \lambda_\beta)^2 . \tag{30}$$

This expression is the same as Eq. (20) obtained with Boltzmann statistics, though with the concentrations substituted by the primed concentrations defined in Eq. (27).

In order to understand the meaning of the primed concentrations, we note that the probability that a particular site α is occupied is $p_\alpha = c_\alpha / m_\alpha$; in fact, c_α is the mean number of the m_α sites of a cell which are occupied. Then the factor in parentheses in Eq. (27) is the probability that a particular site α is empty, $q_\alpha = 1 - p_\alpha$, i.e., an availability factor that ensures that there are empty sites where the defect can go for relaxation to occur. At low concentrations this factor is close to 1, and the above formulas tend to the previous Boltzmann case. We can also write

$$c'_\alpha = m_\alpha p_\alpha q_\alpha \ ,$$

symmetrical in the probabilities of the sites being vacant and filled. In this way we recognize that also the relaxation strength is symmetrical in the concentrations of the filled and vacant sites; at low c, it is proportional to the concentration of filled sites and vice versa at high c to the concentrations of the vacant sites.

C. Short-range interactions and defect complexes

The calculations of the two preceding paragraphs were limited to the case of configurations consisting of only one defect atom (or at least all of them consisting of the same number of atoms) and independent of each other. We consider now the case with blocking effects and with the formation and dissolution of complexes. The calculation of the concentrations in the framework of the grand-canonical ensemble can include such effects, as shown in Ref. 5 and briefly in the Appendix. The method consists in constructing the grand-partition function z of a cell by summing the statistical weights of all the possible mutually exclusive configurations that the defects can assume in that cell. The general form of these terms is

$$m_\alpha w_\alpha = m_\alpha e^{\beta n_\alpha (\mu - E_\alpha)} \ , \tag{31}$$

where n_α is the number of atoms forming that complex (and therefore of occupied sites), m_α is the multiplicity, i.e., the number of ways in which the complex can exist in the cell, and E_α is its mean energy per defect atom.[20] The grand-partition function of the cell is

$$z = 1 + \sum_\alpha m_\alpha w_\alpha \ . \tag{32}$$

The difference with respect to the case of the preceding paragraph is that here the configurations are incompatible, while in the former case [Eq. (22)] all the configurations are independent of each other and therefore can be simultaneously occupied. In fact, Eq. (22) also contains terms such as $w_\alpha w_\beta \cdots w_\gamma$ due to sites $\alpha, \beta, \ldots, \gamma$ simultaneously occupied with energy $E_\alpha + E_\beta + \cdots + E_\gamma$. The advantage of expressing z as in Eq. (32) is that one may include only the desired configurations, each with its own energy. One can easily include blocking effects; for example, if a cell cannot contain more than one defect atom, then all the configurations will have $n_\alpha = 1$. It is also possible to impose that certain complexes are favored or unfavored by giving them an appropriate energy, which is not necessarily the sum of the energies of their sites, when independently filled. An example where these possibilities are exploited will be given in Sec. IV B. Of course, one can also cover the case of the independent occupation of two sites α and β by summing the probabilities of only the first one being filled, w_α, or only the second one, w_β, or both, $w_\alpha w_\beta$.

The condition of the conservation of the number of defect atoms is

$$c = \frac{1}{\beta} \frac{\partial \ln z}{\partial \mu} = \sum_\alpha \frac{n_\alpha m_\alpha w_\alpha}{z} = \sum_\alpha c_\alpha \ , \tag{33}$$

which is a polynomial equation for $e^{\beta\mu}$ with degree equal to the maximum n_α and which allows the partial concentrations c_α to be written as

$$c_\alpha = \frac{n_\alpha m_\alpha w_\alpha}{z} \ . \tag{34}$$

It has been chosen to include the number of atoms of a complex into the concentrations. If we used the concentrations of the complexes instead of the atoms forming the complexes, we would later obtain expressions containing some more n_α and n_β. We proceed now to calculate the derivatives of the concentrations with respect to the energies, as in Eqs. (25)–(29). As in the preceding paragraph, we need the derivative of μ with respect to E_β, which can be calculated starting from Eq. (33). It is convenient to rewrite it as

$$c \left[1 + \sum_\alpha m_\alpha w_\alpha \right] = \sum_\alpha n_\alpha m_\alpha w_\alpha \rightarrow c = \sum_\alpha m_\alpha w_\alpha (n_\alpha - c) \ ;$$

deriving both sides with respect to E_β, we obtain

$$0 = \beta z \sum_\alpha c_\alpha (n_\alpha - c) \left[\frac{\partial \mu}{\partial E_\beta} - \delta_{\alpha\beta} \right] \ ,$$

which, defining the primed concentrations as

$$c'_\alpha = c_\alpha (n_\alpha - c) \ , \quad c' = \sum_\alpha c'_\alpha \ , \tag{35}$$

becomes

$$\frac{\partial \mu}{\partial E_\beta} = \frac{c'_\beta}{c'} \ . \tag{36}$$

By using Eq. (36) and the relations

$$\begin{aligned} m_\alpha \frac{dw_\alpha}{dE_\beta} &= \beta z c_\alpha \left[\frac{\partial \mu}{\partial E_\beta} - \delta_{\alpha\beta} \right] \ , \\ \frac{dz}{dE_\beta} &= \sum_\alpha m_\alpha \frac{dw_\alpha}{dE_\beta} = \beta z \left[c \frac{\partial \mu}{\partial E_\beta} - c_\beta \right] \ , \end{aligned} \tag{37}$$

we can write

$$\frac{dc_\alpha}{dE_\beta}=n_\alpha m_\alpha \frac{d}{dE_\beta}\left[\frac{w_\alpha}{z}\right]$$
$$=\beta\left[n_\alpha c_\alpha\left[\frac{c'_\beta}{c'}-\delta_{\alpha\beta}\right]-c_\alpha\left[c\frac{c'_\beta}{c'}-c_\beta\right]\right]$$
$$=\beta\left[\frac{c'_\alpha c'_\beta}{c'}+c_\alpha c_\beta-n_\alpha c_\alpha\delta_{\alpha\beta}\right]$$
$$=\beta\left[c'_\alpha\left[\frac{c'_\beta}{c'}-\delta_{\alpha\beta}\right]+c_\alpha(c_\beta-c\delta_{\alpha\beta})\right] , \qquad (38)$$

where in the last step $cc_\alpha\delta_{\alpha\beta}$ has been added and subtracted. This expression is the same as the case of independent configurations [Eq. (29)] plus a term of second order in the concentrations having the same form of the main term. We can therefore proceed exactly as in Eq. (11) to obtain

$$\Delta=\frac{\beta}{Mv_0}\sum_\alpha\sum_{\beta<\alpha}(\lambda_\alpha-\lambda_\beta)^2\left[\frac{c'_\alpha c'_\beta}{c'}+c_\alpha c_\beta\right] . \qquad (39)$$

This formula is very similar to those obtained previously [Eqs. (19) and (30)], although the new corrections may not be interpreted in the same straightforward manner. In fact, the factor $(1-c/n_\alpha)$ in the primed concentrations [Eq. (35)] is not exactly the probability that the configuration α is empty, as in the preceding paragraph; moreover, the second-order term $c_\alpha c_\beta$ is not obviously explained.[21]

To first order in the concentration, Eq. (39) corresponds to Eq. (19), obtained following Boltzmann statistics. This can be seen when $n_\alpha=n_\beta=1$, by noting that in the limit of small c the primed concentrations tend to the unprimed ones and the second term becomes negligible. The coincidence of the cases of independent and incompatible configurations is expected at low concentrations, when the occurrences of incompatible states become more and more unlikely.

When treating cases with complexes, it may be useful to rewrite Eq. (39) as

$$\Delta=\frac{\beta}{Mv_0}\sum_\alpha\sum_{\beta<\alpha}(\lambda_\alpha-\lambda_\beta)^2 c_\alpha c_\beta\left[\frac{(n_\alpha-c)(n_\beta-c)}{\sum_\gamma n_\gamma c_\gamma-c^2}+1\right] , \qquad (40)$$

with the n_α put in evidence. We remind the reader that when $n_\alpha>1$, λ_α is the elastic dipole per atom, as is clear from the definition (33) of c_α and from that of the elastic dipole [Eq. (1)]. In the discussion it will be shown that in specific cases the low-concentration limit of Eq. (40) coincides with the formulas provided by Nowick in Ref. 4.

D. General case of coexisting incompatible and independent configurations

We will now discuss the case of incompatible configurations coexisting with independent configurations. This is the combination of the two last paragraphs, and it is worth being discussed both for the sake of completeness and for the simplicity of the result.

We will index the M incompatible configurations (as in Sec. III C) by α,β, with $1\le\alpha,\beta\le M$, and the N independent ones (as in Sec. III B) by σ,τ, with $M+1\le\sigma,\tau\le M+N$; indexes μ and ν will be used for the complete range of the configurations. Recalling Eqs. (22) and (32), we write the total grand-partition function as

$$\mathcal{Z}=z\prod_\sigma z_\sigma^{m_\sigma}=\left[1+\sum_\alpha m_\alpha w_\alpha\right]\prod_\sigma(1+w_\sigma)^{m_\sigma} , \qquad (41)$$

where the configuration ν has multiplicity m_ν (it can be realized in m_ν ways) and statistical weight

$$w_\nu=e^{\beta n_\nu(\mu-E_\nu)} , \quad \nu=\alpha,\sigma . \qquad (42)$$

Note that the number n_ν of atoms constituting the configuration ν is written explicitly also for $\nu=\sigma$ in order to have a better compatibility with the case $\nu=\alpha$. In Sec. III B the configurations were considered as sites to be filled with no more than one atom, and therefore n_ν was always equal to 1; however, it is possible that some of the independent configurations may contain more than one atom.[22]

The derivation of the relaxation strength goes parallel to that made in the two preceding paragraphs. The intermediate formulas are longer, because the sums must be split in a sum over the first M configurations and one over the other N; in fact, the terms with index α are in general different from those with index σ. Moreover, one cannot write $\sum_\alpha c_\alpha=c$ any more, because now

$$c=\frac{1}{\beta}\frac{\partial\ln\mathcal{Z}}{\partial\mu}=\sum_\alpha\frac{m_\alpha n_\alpha w_\alpha}{z}+\sum_\sigma\frac{m_\sigma n_\sigma w_\sigma}{z_\sigma}$$
$$=\sum_\alpha c_\alpha+\sum_\sigma c_\sigma \qquad (43)$$

and neither $\sum_\alpha c_\alpha$ nor $\sum_\sigma c_\sigma$ are constants. By deriving Eq. (43) with respect to E_ν, we obtain

$$\frac{\partial\mu}{\partial E_\nu}\left[\sum_\alpha c_\alpha\left[n_\alpha-\sum_\beta c_\beta\right]+\sum_\sigma c_\sigma\left[n_\sigma-\frac{c_\sigma}{m_\sigma}\right]\right]$$
$$=\begin{cases} c_\nu\left[n_\nu-\sum_\alpha c_\alpha\right] , & \nu=\alpha,\beta,\dots, \\ c_\nu(n_\nu-c_\nu/m_\nu) , & \nu=\sigma,\tau,\dots . \end{cases} \qquad (44)$$

If we define the primed concentrations exactly as in the last two paragraphs,

$$c'_\alpha=c_\alpha\left[n_\alpha-\sum_\beta c_\beta\right], \qquad c'=\sum_\alpha c'_\alpha+\sum_\sigma c'_\sigma , \qquad (45)$$
$$c'_\sigma=c_\sigma(n_\sigma-c_\sigma/m_\sigma),$$

we can write Eq. (44) as

$$\frac{\partial\mu}{\partial E_\nu}=\frac{c'_\nu}{c'} , \quad \nu=\alpha,\sigma . \qquad (46)$$

After a straightforward calculation completely analogous to those carried out in the two preceding paragraphs, we can express the derivatives of the concentrations with respect to the energies as

$$\frac{dc_\mu}{dE_\nu}=\beta\left\{c'_\mu\left[\frac{c'_\nu}{c'}-\delta_{\mu\nu}\right]+c_\mu\left[c_\nu-\delta_{\mu\nu}\left[\sum_\alpha c_\alpha\right]\right]\left[\sum_\alpha\delta_{\alpha\mu}\right]\left[\sum_\alpha\delta_{\alpha\nu}\right]\right\}, \tag{47}$$

where the second term exists only if both μ and ν refer to the first M incompatible configurations. Introducing Eq. (47) into Eq. (9) and proceeding as usual, we finally find

$$\Delta=\frac{\beta}{Mv_0}\left\{\sum_\mu\sum_{\nu<\mu}\frac{c'_\mu c'_\nu}{c'}(\lambda_\mu-\lambda_\nu)^2+\sum_\alpha\sum_{\beta<\alpha}c_\alpha c_\beta(\lambda_\alpha-\lambda_\beta)^2\right\}. \tag{48}$$

This result is the plain combination of the formulas valid for either cases of the independent and incompatible configurations [Eqs. (30) and (39)]. The last term appears only for pairs of configurations which are both incompatible.

IV. DISCUSSION

A major advantage of the present approach is that of considering all the defect configurations in the same way without distinguishing between defect reorientations or reactions. This simplifies the derivation of the relaxation strength and its final form. The expression derived by adopting the Boltzmann distribution function coincides with those already reported in the literature, though it is expressed as the sum of the contributions from all the pairs of configurations. This is useful when one wants to separate the various contributions to relaxation; an example will be given in Sec. V A.

When calculating the partial defect concentrations within the grand-canonical ensemble, one can adopt Fermi-Dirac statistics and obtain formulas valid for arbitrarily high concentrations. As long as the configurations are independent, the relaxation strength is simply proportional to the product of the concentrations of the filled and vacant sites involved in the relaxation. In Secs. III C and III D, it has been shown how to introduce short-range interactions into the computation, such as blocking effects and the formation of complexes. The proposed method may be used in complicated cases where other approaches would be too difficult or useless.

Some of the formulas available in the literature may be obtained as particular cases of the present approach. We will demonstrate it by comparing the low-concentration limit of Eq. (40), valid for relaxation among defect complexes, with the expressions provided by Nowick in Ref. 4. This can be done only case by case, because Nowick's formulas refer to particular reactions, for instance, $\alpha+\beta\leftrightarrows\eta$, without conversion between α and β, whereas here it is assumed that all the configurations are accessible through any path. We consider the case of sites of type α, which may be divided in pairs, each cell containing a pair; when both sites of a pair are filled, we obtain a complex β with $n_\beta=2$, $E_\alpha\neq E_\beta$, and $\lambda_\beta\neq\lambda_\alpha$. We therefore have, from Eq. (40),

$$\lim_{c\to0}\Delta_{\alpha\beta}=\frac{\beta}{Mv_0}(\lambda_\alpha-\lambda_\beta)^2\frac{2c_\alpha c_\beta}{c}, \tag{49}$$

where we recognized that $c_\beta \ll c_\alpha$ and $c_\alpha \sim c$. This result corresponds to that provided by Nowick in Eqs. (31)–(34) of Ref. 4, if we consider the reaction $\alpha+\alpha\leftrightarrows\beta$ and take into account that in Nowick's paper c_β and λ_β are the concentration and elastic dipole of the pairs and not of the paired atoms.

It is worthwhile to evaluate the concentrations c_α and c_β in both cases to see the differences between the thermodynamic and statistical methods. According to Eqs. (31) and (32), we have

$$z=1+2e^{\beta(\mu-E_\alpha)}+e^{2\beta(\mu-E_\beta)}=1+2x+bx^2, \tag{50}$$

where $x=\exp(\beta\mu)$, $b=\exp(-2\beta E_b)$, $2E_b=2(E_\alpha-E_\beta)$ is the binding energy of the pair, and E_α was chosen as the zero of energy. Correspondingly, we write

$$c_\alpha=2x/z, \quad c_\beta=2bx^2/z. \tag{51}$$

Equation (33) becomes a second-degree equation for x, whose solutions are

$$x=\frac{1-c}{b(2-c)}\left[\pm\left[1+\frac{bc(2-c)}{(1-c)^2}\right]^{1/2}+1\right], \tag{52}$$

where the minus sign has to be chosen in order to have the correct limit of μ to minus infinity when c goes to zero. In this limit we have, to first order in c, $x=c/2$, $z=1$, and therefore

$$\lim_{c\to0}c_\alpha=c, \quad \lim_{c\to0}c_\beta=bc^2/2. \tag{53}$$

On the other hand, according to the thermodynamic method,[4] we solve the system of equations constituted by the condition of constant number of defect atoms and by the mass action law

$$\begin{aligned}&c_\alpha+c_\beta=c,\\&c_\alpha^2/c_\beta=ke^{2\beta(E_\beta-E_\alpha)}=k/b,\end{aligned} \tag{54}$$

where the constant k comes from the configurational entropy of the particular system. The evaluation of the latter may be difficult, and in this case we will let k as a parameter to be adjusted in order to obtain the correct low-concentration limit of c_β [Eq. (53)]. The solution of Eq. (54) is

$$c_\beta=\frac{k}{4b}\left[\left[1+\frac{4bc}{k}\right]^{1/2}-1\right]^2, \tag{55}$$

whose low-c limit is $c_\beta\sim bc^2/k$; by comparison with the previous case, we put $k=2$. The main difference between

Eqs. (51) and (55) is that in the former case c_β correctly tends to c as c approaches 2, whereas in Eq. (55) it is always lower, approaching 2 only in the limit of infinite binding energy of the pair. The failure of Eq. (55) is due to the fact that the mass action law (54) is only valid in the low-c limit. The formula corresponding to the mass action law becomes more complicated when using the configurational entropy of the defects without the approximation of small c; moreover, the evaluation of the configurational entropy may be a very difficult task.

Another approach for obtaining the relative concentrations of defect complexes consists in writing the rate equations of the possible reactions and imposing the equilibrium condition; one obtains a system of equations for c_α (in general nonlinear) without the need of evaluating the configurational entropy. In the general case, however, the solution of the system of equations may be not trivial; moreover, at arbitrarily high concentrations one should include into the equations the probability that the site where the atom is jumping is empty, and this further complicates the problem.

From the above comparison, we see that the advantages of using the grand-canonical ensemble are that (i) it is valid at arbitrarily high concentrations; (ii) the construction of the grand-partition functions of the cells and the evaluation of the concentrations are straightforward, whatever the complexity of the configurations; and (iii) the only possible time-consuming step is the evaluation of the chemical potential μ, which, however, reduces to the solution of a polynomial equation in $e^{\beta\mu}$. This approach is therefore simpler than the others, but it cannot be used always. In fact, it relies on the possibility of dividing the system in noninteracting subsystems or cells whose grand-partition function can be evaluated; the trivial case is that of each site constituting a subsystem. A situation that does not satisfy the above requirement is that of interstitial atoms that can form a complex in all the possible pairs of nearest-neighboring sites. In this case, whatever partition one chooses between the sites, there is always a pair that crosses the partition, which therefore cannot be properly taken into account.

A final point regards the type of interactions modeled in the present paper, which are only of the short-range type. The adopted formalism is well suited to the description of such interactions, such as the blocking of neighboring sites or the formation of defect complexes, up to the maximum possible concentration. Instead, no attempt has been made here to incorporate long-range interactions or critical ordering of the dipoles, as, for instance, in Refs. 1, 14, and 23.

V. APPLICATIONS

A. Four-level tunnel system

A simple application of the result of Sec. III A is the calculation of the relaxation magnitude between the four levels of a four-level tunnel system (FLS). Hydrogen trapped by substitutional Ti in Nb is thought to tunnel among four equivalent tetrahedral sites in squared coordination, giving rise to a FLS;[12] a variety of anelastic relaxation effects below 50 K seems explainable only by separately taking into account the possible different types of relaxation between the four levels of the tunnel system. Indeed, Granato, Hultman, and Huang[18] calculated the relaxation strength of a FLS with the approach of Sec. III, although they did not separate the contributions of the different relaxation modes.

The response of a tunnel system to stress cannot be simply described by elastic dipoles, because the energy levels have a finite curvature as a function of stress. It is generally supposed that the effect of shear strain ε on a symmetric tunnel system mainly consists in changing the energies of the otherwise identical sites of a quantity $\delta=\gamma\varepsilon$, where the deformation potential γ is the parameter characterizing the influence of stress on the tunnel system. Instead, the tunneling energy Δ_0 is supposed to depend on ε much less than the asymmetry energy δ.[17] The energy levels of a symmetric FLS subjected to a homogeneous stress are

$$E_{1,4}=\pm(4\Delta_0^2+\delta^2)^{1/2}\ , \quad E_{2,3}=\pm\delta\ , \tag{56}$$

where $\delta=\gamma(\varepsilon_0+\varepsilon)$ contains a constant contribution $\gamma\varepsilon_0$ due to random elastic interactions with other defects. The elastic response of such a FLS to a small applied elastic strain $\varepsilon=\sigma/M$ can be described by four strain-dependent elastic dipoles λ_i:

$$\begin{aligned} Mv_0\lambda_{1,4}&=-\frac{\partial E_{1,4}}{\partial\varepsilon}=\pm\frac{\delta}{(4\Delta_0^2+\delta^2)^{1/2}}\ ,\\ Mv_0\lambda_{2,3}&=-\frac{\partial E_{2,3}}{\partial\varepsilon}=\pm\gamma\ . \end{aligned} \tag{57}$$

Therefore the relaxation of the FLS is described by Eqs. (6) and (57), and the populations of its four levels obey the Boltzmann distribution function, i.e., Eq. (17), with $m_\alpha=1$; in fact, for each FLS there is only one atom that can occupy four levels, and therefore there are no multiple occupations or blocking effects to take into account. Therefore the relaxation strengths for the transitions between the various pairs of levels are described by Eqs. (17) and (20) with the elastic dipoles given by Eq. (57).[24] A comparison with the experimental data on NbTi$_x$H$_y$ will be provided in a future publication.[25]

B. Hydrogen in the hcp rare earths

As an application of the analysis made in Sec. III C, we consider the case of interstitial hydrogen in the hcp rare earths, which has been under investigation for many years.[7–11,26] There are two types of sites available for H in these metals: two tetrahedral (T) and one octahedral (O) per each metal atom. All the T sites remain equivalent under the application of any stress, and the same holds for the O sites; therefore, the relaxation of isolated hydrogens may only consist of a change of the relative concentrations of the T and O sites. Povolo and Bisogni[27] recognized this fact and analyzed the symmetry and relaxation kinetics of some point-defect pairs in a hcp lattice, but not the corresponding relaxation magnitudes. It has also been experimentally established that the H atoms occupy mainly the T sites and tend to form pairs along the c axis.[26]

Several anelastic relaxation measurements have been made on such systems. The main relaxation process has an activation energy of about 0.6 eV, coincident with that for the H long-range diffusion, and an intensity roughly proportional to the H molar concentration c_H, for c_H between 0.01 and 0.2.[7] Besides, many other processes of lower intensity have been found at low values of c_H and in the presence of O impurities,[9] but they have not yet been analyzed.

Although it has been recognized that the main relaxation process should be connected with the H pairs,[7] an analysis has never been attempted. Moreover, the fact that the dependence of its intensity on c_H is linear rather than quadratic seems puzzling at first, so that some authors doubt whether the process actually consists of a redistribution of H between T and O sites.[11]

The main phenomenon which we want to describe here is the pairing of hydrogen in the T sites and its distribution between T and O sites. We will divide the system into independent cells, each containing one metal atom, one O site, and the two T sites that can contain the H pair, as schematically shown in Fig. 1. In the real case, the occupation of two nearest-neighboring T sites belonging to different cells is forbidden. Such a condition cannot be easily imposed within the present approach, because different cells are considered as independent; it will be neglected here. We will proceed as in Sec. III C.

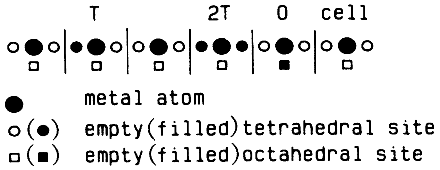

FIG. 1. Partition of a hcp lattice into cells, used for calculating the partial concentrations of the singly occupied tetrahedral (T) and octahedral (O) sites and pairs of occupied tetrahedral ($2T$) sites.

The grand-partition function of each cell may be written as

$$z=1+2e^{\beta(\mu-E_T)}+e^{\beta(\mu-E_O)}+e^{2\beta(\mu-E_{2T})}$$
$$=1+(2+a)x+bx^2\ , \tag{58}$$

where we put $x=\exp(\beta\mu)$, $a=\exp(-\beta E_O)$, $b=\exp(-2\beta E_{2T})$, $-E_{2T}$ being the pair-binding energy per atom, and we chose E_T as the zero of the energy. We have supposed that the T and O sites are mutually blocked within the same cell, and therefore the possible configurations of a cell are empty, with one H in either T site, with one H in the O site, or with an H pair in the T sites. The condition (33) for the chemical potential is a second-degree equation in x, whose solution is

$$x=\frac{(2+a)(1-c)}{2b(2-c)}\left[\pm\left[1+\frac{4bc(2-c)}{(2+a)^2(1-c)^2}\right]^{1/2}-1\right]\begin{cases}+ & \text{for } 0\le c\le 1\ ,\\ - & \text{for } 1\le c\le 2\ ,\end{cases} \tag{59}$$

where the sign has to be chosen in order to make μ an increasing function of c. According to Eq. (34), the partial concentrations are

$$c_T=\frac{2x}{z}\ ,\quad c_{2T}=\frac{2bx^2}{z}\ ,\quad c_O=\frac{ax}{z}\ . \tag{60}$$

We could have added the simultaneous occupation of one T and O site with an energy $E_{OT}=E_T+E_O$, without complicating the problem: We would just have an additional term in x^2 which does not increase the degree of the equation for x, and an additional concentration c_{OT}. Instead, if we imposed that the O sites are filled independently of the T sites, the grand-partition function of a cell would be, according to Sec. III D,

$$z=(1+2e^{\beta(\mu-E_T)}+e^{2\beta(\mu-E_{2T})})(1+e^{\beta(\mu-E_O)})$$
$$=(1+2x+bx^2)(1+ax)\ ,$$

and the equation for x would be of the third degree.

We now pass to the evaluation of the relaxation magnitudes for the formation and dissolution of pairs and for the change between O and T sites. These are readily obtained from Eq. (39) in terms of the primed concentrations

$$\begin{aligned}c'_T&=c_T(1-c)\ ,\\ c'_{2T}&=c_{2T}(2-c)\ ,\\ c'_O&=c_O(1-c)\ ,\\ c'&=c'_T+c'_{2T}+c'_O\ ,\end{aligned} \tag{61}$$

and are

$$\begin{aligned}\Delta_{T\text{-}2T}&=\frac{(\lambda_T-\lambda_{2T})^2}{Mv_0}\beta\left[\frac{c'_Tc'_{2T}}{c'}+c_Tc_{2T}\right]\ ,\\ \Delta_{O\text{-}2T}&=\frac{(\lambda_O-\lambda_{2T})^2}{Mv_0}\beta\left[\frac{c'_Oc'_{2T}}{c'}+c_Oc_{2T}\right]\ ,\\ \Delta_{T\text{-}O}&=\frac{(\lambda_T-\lambda_O)^2}{Mv_0}\beta\left[\frac{c'_Tc'_O}{c'}+c_Tc_O\right]\ .\end{aligned} \tag{62}$$

We remind the reader that c_{2T} is the concentration of the paired atoms and that the distortion of a pair is $2\lambda_{2T}$. A set of the above equations will correspond to each component of the elastic modulus. Note that the relaxation due to the dissolution of a pair $2T$ in two isolated T sites is observable only if the elastic dipole of a pair, $2\lambda_{2T}$, is different from that of the unpaired atoms, $2\lambda_T$, for at least one type of deformation; this is expected to be true in view of the strong tendency to pair formation. Anelastic relaxation experiments have only been performed on polycrystals, and we cannot have information on the magnitudes of the various components of the elastic dipoles, at the moment.

Rather than attempting a fit of some of the experimental data, we will show the general behavior predicted by the above equations, assuming reasonable values of the pair-binding energy $-2E_{2T}$ and O-site energy E_O ($E_T=0$). The estimates of c_{2T} and c_O available in the literature (in particular for $YH_{0.15}$ from Ref. 8 and $YH_{0.2}$ from Ref. 10) can be reasonably accounted for by Eqs. (58)–(60) with $E_O/k \sim 1000$ K and $E_{2T}/k \sim -500$ K, and we will use these values. The choice of a value of 1000 K for the difference between the energies of the octahedral and tetrahedral sites relies especially on estimates that the O occupancy is of only a few percent in Y, even at 700 K.[10]

Figure 2 shows the relaxation strengths as a function of the H concentration for the three types of relaxation T-$2T$, T-O, and O-$2T$. It has been put as $(\Delta\lambda)^2/(Mv_0)=1$ for all three cases. At 200 K the intensities of the relaxations involving the O sites are at least two orders of magnitude smaller than that involving the T sites only, as a result of the low octahedral occupancy. The decrease of Δ when c approaches its maximum value is due to the disappearance of empty sites into which H can jump; in this condition, Δ becomes proportional to the concentration of vacant sites, as noted in Sec. III B. The curves of Fig. 2 do not describe the real RH_x systems (R = rare earth) at $x=c_H$ close to 2, because at that stoichiometry one has hydrides with different site energies and symmetries; moreover, the occupation of two nearest-neighboring T sites (belonging to two adjacent cells) seems unlikely, but the model allows it.

A relevant feature appearing in Fig. 2 is that $\Delta_{T\text{-}2T}$ is no longer proportional to c^2 already for c as low as 0.01, which is about the lowest concentration used in the experiments. The curve that is closest to the actual conditions of the reported anelastic relaxation experiments is that of $T=200$ K, which is about proportional to the first power of c for $c>0.01$. This means that the large dissipation peak observed around 250 K may well be due to the formation and dissolution of the H pairs, even if its intensity is roughly proportional to the H content. This assignment becomes the only reasonable one if the population of the octahedral sites is confirmed to be as low as supposed here, because of the already mentioned depression of the relaxation strengths associated with such sites.

The fact that the pair concentration and therefore the strength associated with their relaxation are less than proportional to c^2 results also when using the approximation of low concentrations. The dotted lines of Fig. 2 are obtained from Nowick's analysis[4] by using Eqs. (49), (54), and (55) and neglecting the octahedral occupancy. Although $\Delta_{T\text{-}2T}$ is definitely higher than in the preceding case, it exhibits exactly the same trend up to very high concentrations. The curves merge at concentrations that become lower with decreasing temperature. This is due to the fact that c is multiplied by $\exp(2E_b/kT)$ in the expressions of c_{2T}; that factor drastically increases for T below E_b/k, and therefore the first-order expansions of c_{2T} in a series of powers of c is valid at lower and lower values of c.

The temperature dependence of $\Delta_{T\text{-}2T}$ is shown in Fig. 3 for two concentrations. Both the present calculation and the approximated one (dotted line) have a maximum at a temperature that is about half of the energy

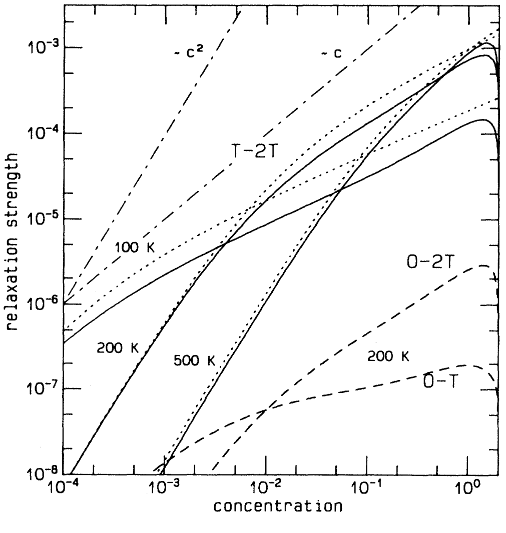

FIG. 2. Normalized intensities of the relaxations between paired ($2T$) and isolated T and O occupations of an interstitial atom in a hcp lattice, according to Eq. (62). The pair-binding energy and O-site energy are given in the text. The dotted lines are calculated with the approximation of low concentration; the dashed-dotted lines are the slopes of curves proportional to c and c^2.

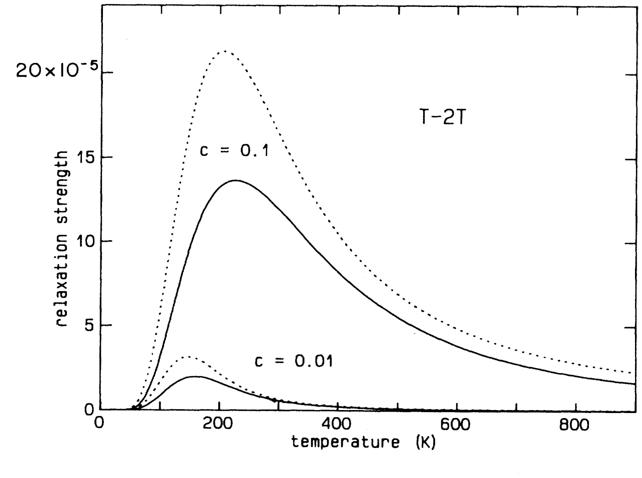

FIG. 3. Normalized relaxation strength between the paired and unpaired occupations of an intersititial atom in a hcp lattice. The parameters are the same as in Fig. 1 and are given in the text. The dotted lines are calculated with the approximation of low concentration.

difference between the paired and unpaired hydrogen atoms, as explained at the end of Sec. III A.

VI. CONCLUSIONS

General expressions of the relaxation strength for anelastic (dielectric) relaxation have been provided in terms of the concentrations of the various defect configurations together with the expressions of the concentrations. Cases of increasing complexity have been treated: (i) defects relaxing according to Boltzmann statistics among configurations that are independent of each other, which contain the same number of defect atoms; (ii) as before, but within the formalism of the grand-canonical ensemble, according to Fermi-Dirac statistics in order to prevent the multiple occupation of sites; (iii) configurations that are excluded from each other, but which can contain any number of defect atoms, according to Fermi-Dirac statistics (formation and dissolution of complexes, blocking and trapping effects); and (iv) cases (ii) and (iii) mixed together. The formulas previously reported in literature may be obtained as particular cases.

In all the situations, the relaxation strength Δ assumes the simple form of a sum over all pairs of configurations, each term being the relaxation magnitude $\Delta_{\alpha\beta}$ between configurations α and β. The calculation and final expression of $\Delta_{\alpha\beta}$ are simple and do not depend on the type of relaxation (reorientation, relaxation between sites of different energy, formation and/or dissolution of complexes). When using Boltzmann statistics, $\Delta_{\alpha\beta}$ is proportional to the product of the concentrations $c_\alpha c_\beta$ divided by the total concentration. When using Fermi-Dirac statistics, the concentration of each site (configuration) is multiplied by the probability that the site to which relaxation occurs is empty. When imposing that the configurations are mutually incompatible, an additional term arises, which is of the second order in the concentrations.

The advantage of the grand-canonical ensemble over the thermodynamic method for calculating the partial concentrations is that there is no need of calculating the configurational entropy of the defects. One has only to construct the grand-partition function appropriate for the particular system, which can be done in a straightforward manner, however complex the system. The expressions of the partial concentrations can also be written in a straightforward way in terms of the chemical potential. The latter is computed as the root of a polynomial equation whose degree depends on the number of the independent configurations and of the atoms that they are composed of.

The results provided here are particularly useful when dealing with high concentrations of defects and short-range interactions (long-range interactions have not been included). Arbitrarily complex situations with several types of defect configurations can be treated in the same simple way, provided that the crystal can be divided in independent subsystems or cells within which relaxation occurs.

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APPENDIX

We will give a brief description of the method of calculating the mean occupation numbers n_α (partial concentrations, not to be confused with the number n_α of atoms forming the complex α used in Sec. III) of single sites or complexes of sites within the grand-canonical ensemble, including short-range interactions. The method, proposed in Ref. 5, is an extension of the textbook calculation.[19]

By definition, the mean occupation number of a site α with energy E_α is

$$\begin{aligned} \bar{n}_\alpha &= \frac{1}{Z} \sum_{\{n\}} n_\alpha e^{-\beta(n_\alpha E_\alpha + n_\beta E_\beta + \cdots)} , \\ Z &= \sum_{\{n\}} e^{-\beta(n_\alpha E_\alpha + n_\beta E_\beta + \cdots)} , \end{aligned} \tag{A1}$$

where the sums are over all the possible configurations $\{n\} = n_\alpha, n_\beta, \ldots$; each configuration has energy $E_{\{n\}} = \sum_\alpha n_\alpha E_\alpha$, statistical weight $\exp(-\beta E_{\{n\}})$, and fixed total number N of defect atoms, $\sum_\alpha n_\alpha = N$. In Fermi-Dirac statistics, one does not allow for multiple occupation of a site: $n_\alpha = 0, 1$. The set of all possible configurations, $\{n\}$, is called the canonical ensemble, and generally the sums with the restriction of a fixed total number of atoms cannot be performed. Therefore one introduces the grand-canonical ensemble, where the sum is extended to all the sets of possible configurations, $\{n\}$, without a condition on the total number $N_{\{n\}} = \sum_\alpha n_\alpha$. The statistical weights become $\exp(-\beta E_{\{n\}} + \beta\mu N_{\{n\}})$, where the parameter μ (chemical potential) has to be chosen in order to peak the probability distribution at the desired total number of atoms, $N_{\{n\}} = N$. We then have

$$\begin{aligned} \bar{n}_\alpha &= \frac{1}{\mathcal{Z}} \sum_{\{n\}} n_\alpha e^{\beta[n_\alpha(\mu - E_\alpha) + n_\beta(\mu - E_\beta) + \cdots]} , \\ \mathcal{Z} &= \sum_{\{n\}} e^{\beta[n_\alpha(\mu - E_\alpha) + n_\beta(\mu - E_\beta) + \cdots]} . \end{aligned} \tag{A2}$$

The grand-partition function $\mathcal{Z}$ can be written as the product of the grand-partition functions of all the independent sites:[19]

$$\mathcal{Z} = \prod_\alpha z_\alpha = \prod_\alpha (1 + w_\alpha) , \quad w_\alpha = e^{\beta(\mu - E_\alpha)} , \tag{A3}$$

where w_α is the statistical weight for site α being filled (the statistical weight of any site to be empty is 1) and Fermi-Dirac statistics was assumed. The condition for the total number of atoms is

$$N=\sum_\alpha \bar{n}_\alpha=\frac{1}{\beta}\frac{\partial \ln Z}{\partial\mu}=\sum_\alpha \frac{1}{e^{\beta(E_\alpha-\mu)}+1} . \quad \text{(A4)}$$

Equation (A4) expresses the mean occupation numbers in terms of the site energies, and it must be solved with respect to μ.

In the above formulas, the sites are considered as independent of each other, because $E_{\{n\}}=\sum_\alpha n_\alpha E_\alpha$, with E_α independent of the occupation. In this case Z can be written as in Eq. (A3). The method proposed in Ref. 5 consists of grouping together the sites within which the short-range interactions or the formation of complexes takes place and of writing and manipulating the corresponding grand-partition functions. For example, the grand-partition function of sites A, B, and C is

$$\begin{aligned} Z(ABC)&=(1+w_A)(1+w_B)(1+w_C)\\ &=1+w_A+w_B+w_C+w_Aw_B+w_Aw_C\\ &\quad +w_Bw_C+w_Aw_Bw_C , \end{aligned} \quad \text{(A5)}$$

where one can easily recognize the contributions of one, two, or all three sites occupied. In order to introduce interactions between these sites, it is sufficient to change properly the energies of the various types of occupation. If no more than one site can be filled as a result of blocking effects, then the terms with two or three atoms are suppressed (their energy is infinity). The formation of a stable pair in sites A and B with binding energy E_b is described by $w_Aw_B=\exp(2\beta\mu-\beta E_{AB})$ with $E_{AB}=E_A+E_B-E_b$.

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[15] Such an approach was followed by Granato, Hultman, and Huang in Ref. 18 in order to calculate the elastic response of a four-site tunnel system, although they did not separate the contributions of the different pairs of levels.

[16] For an extensive discussion, see Ref. 13.

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[20] The single atoms forming the complex do not need to have the same energy E_α, because only the total energy of the complex $n_\alpha E_\alpha$ is relevant.

[21] That term increases the relaxation magnitude with respect to the case of independent configurations, and this can be qualitatively explained as follows. With independent configurations the relaxation magnitude is reduced by the fact that there are cases in which an atom cannot relax to a site, because the latter is already occupied. Part of these situations does not occur in the presence of blocking effects (incompatible configurations), and the relaxation strength is accordingly increased.

[22] One must be careful when using $n_\sigma>1$; for example, it would be wrong to introduce a concentration with $n_\sigma=2$ in order to compute the probability of a pair of independent sites to be filled. In fact, the occurrences of either site filled and both sites filled are incompatible instead of independent, and they fall within the description of Sec. III C. It would be appropriate to put $n_\sigma=2$ only for pairs of sites that are always filled together, so that no one of them appears in the grand-partition function as filled alone.

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