THE REORDERING TRANSITION IN LAYER DISORDERED SOLIDS: RARE EARTH - TRANSITION METAL INTERMETALLIC ALLOYS

TRANSICIÓN DE REORDENAMIENTO EN SÓLIDOS DE CAPAS DESORDENADOS: ALEACIONES INTERMETÁLICAS DE TIERRAS RARAS - METALES DE TRANSICIÓN

Arbelio Penton-Madrigal[a,b†], Ernesto Estevez-Rams[a,b], Cristy Azanza-Ricardo[c] y Raymundo Lora Serrano[d]

a) Facultad de Física, Universidad de la Habana, 10400 La Habana, Cuba; arbelio@fisica.uh.cu†
b) Instituto de Ciencia y Tecnología de Materiales(IMRE), Universidad de la Habana, 10400 La Habana, Cuba
c) University of Trento, Dipartimento di Ingegneria dei Materiali e delle Tecnologie Industriali, via Mesiano 77, 38050 Trento, Italia
d) Instituto de Fisica, Universidade Federal de Uberlandia, 38400-902 Uberlandia-MG, Brazil
† corresponding author

Recibido 20/9/2015; Aceptado 20/10/2015

Planar faulting in in rare earth – cobalt alloys with type structures Th_2Ni_{17} and Th_2Zn_{17} are studied. The structure changes from hexagonal for heavy rare earth to rhombohedral for light rare earth, all exhibiting different degrees of planar disorder. Faulting is quantitatively studied beyond the model of independent faulting events showing the strength of direct solutions to extract defects information from the diffraction patterns. It is showed that the analysis of the decaying term of the probability correlation function, does not only allow to quantify the loss of memory in the system through the correlation length but also, the strength of interaction between faults. The behavior of the decaying terms turns not to be of universal character when scaled against the correlation length and instead depends on the interaction of faulting. The reconstructive phase transition in this system seems to follow a path where the new phase appears within the disordered phase and grows without homogeneous reordering of the disordered arrangement.

Se estudia la ocurrencia de defectos planares en aleaciones de tierras raras – cobalto con estructuras tipos Th2Ni17y Th2Zn17. La estructura cambia desde hexagonal para tierras raras pesadas hasta romboédrica para tierras raras ligeras. La ocurrencia de defectos se estudia cuantitativamente más allá del modelo de ocurrencia de defectos independientes mostrando la robustez de las soluciones directas para extraer información sobre defectos a partir de los patrones de difracción. Se demuestra que el análisis del término de decaimiento de la función de correlación de probabilidades, no solo permite cuantificar la pérdida de memoria en el sistema a través de la longitud de correlación, sino también el grado de interacción entre defectos. El comportamiento del término de decaimiento muestra no ser de carácter universal cuando este es escalado respecto a la longitud de correlación y en su lugar depende de la interacción entre defectos. La transición de fase reconstructiva en este sistema parece seguir un recorrido donde la nueva fase emerge dentro de la fase desordenada y crece sin un reordenamiento homogéneo del arreglo desordenado.

PACS: planar faulting 61.72.Bb, intermetallic 61.72.Dd, diffraction 61.72.Nn

I. INTRODUCTION

Planar faults are frequent crystal defects. The disruption of the periodicity in the stacking order leads to measurable effects in the profiles of the maxima of the diffraction pattern of a crystal [1].

Random faulting model (RFM) with independent occurrence of defects is the oldest and simplest model that can be considered, and there is an extensive literature on this approach specially for the so called deformation and growth faults. The RFM considers non interacting defects, this assumptions allows to make mathematical simplifications that results in analytical expressions for the faulting probability [1–6]. Yet, by its very nature, the strong assumption of non-interaction makes the RFM valid in the range of low density of defects.

More recently, there has been an attempt to extract useful information on the stacking order from the diffraction pattern without considering any underlying order, or any particular model for disorder. Yet, it has been argued that methods that do not depend on specific faulting models [7–9] have little to non practical utility [10]. In this article we will show that this is not the case, and the information obtained from faulting models can be reproduced by non-faulting-model approaches without the strong assumptions of non-interacting defects.

Furthermore, even in the case where it is clear the presence of large density of defects, and therefore independent faulting does not hold, direct methods still applies. In this sense direct approaches are of broader scope than ad hoc defect models, besides from being, from a theoretical point of view, a more consistent framework from which mathematical treatment of faulting can be based [6–8].

In order to develop this ideas, RE_2Co_{17}(RE: rare earth) alloys will be studied. This compounds have a rhombohedral structure for light rare earth, while the alloys with heavy rare earth exhibit a hexagonal symmetry stacking. In all cases the structures shows different degree of planar disorder [11, 12].

The main result of this analysis, is to show how the correlation length can be used to compare degree of disorder between faulted structures without regard to the actual type of defect happening. The scaling of the decaying term in the

correlation function has no universal character and instead depends on the interaction between defects.

The remainder of this contribution is organized as follows. In section II the probability correlation function and the associated correlation length will be introduced and their relation to the diffraction pattern of the layer structure will be explained. In section III the disordered nature of the RE_2Co_{17} alloys will be described as inferred from the X-ray diffraction patterns of the studied samples, this results will be used in section IV to discuss reordering phase transition in the studied intermetallic compounds. The correlation length will be used as a parameter that allows to quantitatively measure disorder without regard of the actual type of faulting. Finally, in section V, it will be shown the scaling behavior of the decaying term in the probability correlation function of the RE_2Co_{17} structures. Conclusions will then be given.

II. THE PROBABILITY CORRELATION FUNCTION AND THE CORRELATION LENGTH

If faults are considered to be independent (non interacting) then, due to the stochastic nature of the process, a probability can be associated with the event of occurrence of each type of defect [3]. This approach lacks validity when planar faults starts interacting and the assigned fixed probability looses physical meaning.

In any case, as defects by definition need to show some random behavior, the occurrence of planar disorder results in the loss of correlation in the stacking sequence. Loss of correlation means that knowing the stacking sequence at a finite number of consecutive sites in the crystal does not allow, unambiguously, to predict the complete stacking sequence of the infinite crystal.

To characterize correlations in the stacking sequence of close packed structures, the probability correlation function $P_i(\Delta)$ was first introduced by Wilson [1] and Warren [3] and since then, has been central, directly or indirectly, to the treatment of faulting [4, 13–15]. $P_0(\Delta)$ is the probability of finding two layers, Δ layers apart, in the same position ($A-A$, $B-B$, $C-C$). Similarly, $P_f(\Delta)$ is defined for pair of layers of the type $A-B$, $B-C$ or $C-A$ and $P_b(\Delta)$ for the remaining choices. Normalization condition for the probabilities at each Δ value holds.

In terms of the correlation function, the loss of long range order means that the $P_i(\Delta)$ (i=0, f, b) tends to 1/3 for large enough Δ values. This behavior is interpreted as loss of memory of the system: knowing the layer position up to a particular site, for a sufficiently large Δ value, one can only make an unbiased guess as to which layer, A, B or C can be found.

For an Ising model of faulting, it has been found that the loss of correlation can be described by an exponential decaying behavior [13], which in turn allows to introduce a correlation length as the characteristic Δ_c value for which the decaying part of $P_i(\Delta)$ falls to $1/e$. Even if the type of Ising model used for simulating stacking disorder has been strongly criticized [16], the exponential decaying nature of the$P_i(\Delta)$ for the disordered crystal holds in a more general context [17,18] as found in experimental cases [4].

Recently Tiwary and Pandey [10] have shown that within the deformation and growth random faulting model, the decaying behavior of the correlation functions collapse to a master curve when scaled with respect to Δ_c. This result should come as no surprise, as it can be derived from the analytical functions describing the correlation functions as readily demonstrated by the same authors [19].

If layer structures are considered, where the arrangement is built by different displacement (but not rotation or reflection of the layers) of a basic two dimensional periodic layer, the interference function for a powder sample can be written as [8, 9]

$$Q(l) = 1 + 2\sum_{\Delta=1}^{N_c-1} A_\Delta \cos(2\pi\Delta l), \tag{1}$$

where l is the coordinate associated with the reciprocal base vector c^* taken as the stacking direction, N_c is the number of layers, and A_Δ is the Fourier coefficient, which can be expressed as a linear function of $P_s(\Delta)$. Equation (1) gives the possibility of directly obtaining the Fourier coefficient from the diffraction pattern.

In the case of close packed structures

$$A_\Delta = P_0(\Delta) + (1 - P_0(\Delta))\cos\left[2/3\pi(h-k)\right] \tag{2}$$

the use of eqs. (1) and (2) allows to calculate from the diffraction pattern, the pair correlation function $P_0(\Delta)$.

Instead of using directly equation (1) to adjust the diffraction profile as done in Ref. [8], where dozens of Fourier coefficients are directly extracted from the data and instability in the solution can result, a less numerically unstable approach can be designed if it is assumed that the correlation function can be in general described by two terms [15]

$$P_0(\Delta) = \textit{Decay term} \times \textit{Oscillating term} = D(\Delta) \times O(\Delta),$$

where, the decaying term $D(\Delta)$ has an exponential behavior of the form $\exp(-\Delta/\Delta_c)^k$. Such functional dependence is a simple generalization of previous approaches [13, 19]. Different from those models, here the value of k is not predefined according to some criteria about the nature of the disorder but instead, is left to be adjusted from the actual experimental data.

Under the above assumptions, the following analytical profile function can be deduced [15]

$$\nu_\Delta(l) = \nu_0\{G^c_\Delta(l) + S\, G^s_\Delta(l)\} \tag{3}$$

where G^c_Δ and G^s_Δ are the symmetrical and the anti-symmetrical component of the peak profile, respectively.

$$G^c_\Delta(l) = \frac{1}{2}\sum_{\Delta=1}^{\infty} \exp[-(\frac{\Delta}{\Delta_c})^k]\cos[2\pi\Delta(l_0 - l)] \tag{4}$$

$$G^s_\Delta(l) = \frac{1}{2}\sum_{\Delta=1}^{\infty} \exp[-(\frac{\Delta}{\Delta_c})^k]\sin[2\pi\Delta(l_0 - l)] \tag{5}$$

the parameters to be fitted are the peak position l_0, the correlation length Δ_c, the exponent k and the coefficient S which governs the weight of the asymmetry in the peak profile, together with an intensity scale factor ν_0. In this way, the number of refined parameters drops from a large number (as much as Fourier coefficients are needed to reproduce the profiles) to only five.

Contrary to the use of empirical analytical expressions for describing peak profiles, equations (4) and (5) are not arbitrary mathematical convenient functional forms which allows to introduce fitting parameters as needed. We should expect that when the physical system departs significantly from planar faulting dominant role, the obtained equations are incapable of describing the peak profile.

The correlation length introduced in such a way is more general in the sense that it does not directly depends on a particular faulting model or Ising dynamical calculations.

III. RE_2CO_{17} INTERMETALLIC COMPOUNDS

RE_2Co_{17} alloys can be described as close packed layer structure with one type of layer. They can be found in two crystallographic modifications, one described as a rhombohedral crystal system (Th_2Zn_{17} - type structure, $R\bar{3}m$ - space group), which occurs for the lighter rare earth, and the other a hexagonal crystal system (Th_2Ni_{17} - type structure, $P6_3/mmc$ - space group) corresponding to heavier rare earth [11]. Both crystallographic modifications can be considered as a result of the ordered substitution of RE atoms by Co pairs in the $RECo_5$ structure ($CaCu_5$ - type structure) [12].

One single layer, no matter which of both crystals structure is considered, is formed by two planes of atoms; a Co_9 atomic plane and a mixed RE_2Co_8 plane. However, the stacking order can be followed taking only into account the mixed planes. The 3R (The symbol is in the Ramsdel notation composed by the number of layers in the periodic unit followed by the symmetry of the 3D lattice for the perfect crystal) rhombohedral stacking corresponds to a sequence $ABCABCABC\ldots$, while the 2H hexagonal one corresponds to a $ABABAB\ldots$ stacking order.

The planar disorder in RE_2Co_{17} alloys is studied as we go from the rhombohedral stacking sequence to the hexagonal stacking sequence while changing the rare earth elements. The analysis can be taken as effectively freezing the reconstructive phase transformation at different stages of development.

III.1. EXPERIMENTAL DETAILS

The samples were obtained from starting materials of 99.9 % purity, melted several times to achieve homogeneity, and further annealed at 1273 K for two weeks and then slowly cooled. The studied alloys were prepared with rare earth Pr, Nd, Sm, Gd, Tb, Dy, Ho and Lu.

The X-ray diffraction experiments were conducted on the beam line XRD1 at the LNLS synchrotron facility in Campinas, Brazil. The Hubber diffractometer with a Bragg-Brentano optical system consisted of a bending magnet light source, a double - crystal Si (111) monochromator and a Ge (111) crystal analyzer. The specimen was mounted in a 10 mm diameter rotating sample holder; the radiation energy was 7098.6 eV. The diffraction data were collected at room temperature, with fixed count number and a step of 0.005^o. A LaB_6 sample was used as an external standard reference material (SRM).

The lattice parameters were calculated from those reflections which are not affected by planar disorder using a least square fit with an external SRM [20]. The diffraction pattern were then converted from 2θ to l values, using the corresponding lattice parameter for each alloy. Profiles were fitted by the function (3) using equations (4) and (5). Figure 1 shows the agreement between data and fitted function for two reflections. The solid curve represents the result of the refinement procedure. It can be noted that the calculated profiles does not overfit the experimental data as it does not follow the rapidly varying background noise of the recorded signal.

III.2. THE DIFFRACTION PATTERNS

As expected, the diffraction patterns of the RE_2Co_{17} compounds for light rare earth atoms (RE= Pr, Nd, Sm, Gd) shows a rhombohedral crystal structure, while those corresponding to heavy rare earth elements (RE= Ho, Lu) exhibit a hexagonal crystal structure. In the middle range (RE= Tb, Dy) mixed reflections are observed, which can be indexed assuming either a rhombohedral or a hexagonal stacking arrangement. The mixed reflections suggest the possibility of a mixture of both phases as the absence of additional reflections excludes the existence of higher order polytypes. In all cases, the reflections fulfilling the condition $h - k \neq 3p$, where p is an integer are clearly broadened. This selective broadening effect is typical for a system with stacking faulting [3].

The refined line positions shows very small deviation from the Bragg position of the rhombohedral ($l_0 = 1/3$) and the hexagonal ($l_0 = 3/2$) perfect sequence.

Figures 1a and 1b shows the (211) and the (203) reflections for the studied compounds RE_2Co_{17}. On the top left side of the figure, the low intensity reflection (203) for Tb_2Co_{17} has been magnified. The points represent the experimental data, the solid curve the fitted peak. The shape of the peaks reveals different degree of planar disorder. The correlation length for the Lu compound was fitted to $\Delta_c = 174$ layers which decreases to $\Delta_c = 48$ layers for the Ho sample (figure 1a), indicating a drastic increase of disorder. The same figure shows the evolution of the (211) reflection of the rhombohedral compounds RE_2Co_{17} with RE=Pr, Nd and Gd. The three alloys have a similar correlation length around 20-25 layers.

As already described, for the middle range of rare earth elements mixed reflections from rhombohedral and hexagonal arrangements, are found (figure 1b). From the

hexagonal reflection (203), a correlation length for the hexagonal polytype can be calculated while the same calculation, can be performed for the rhombohedral phase using the (211) reflection.

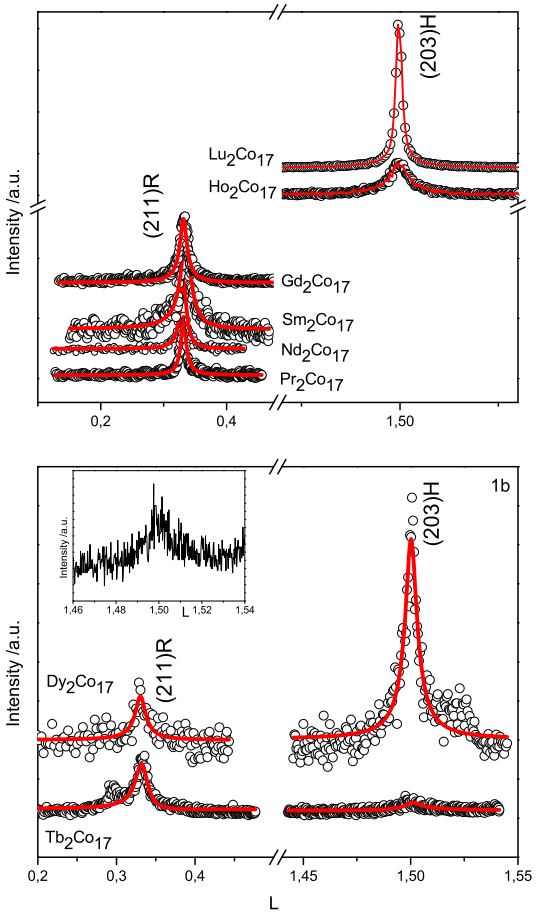

Figure 1. Fragment of a periodic interval of L with diffuse diffraction peaks at the position $l_0 = 1/3$ corresponding to the reflection (211) associated to a rhombohedral stacking sequence and at the position $l_0 = 3/2$, reflection (203) of a hexagonal stacking sequence. The inset shows the magnified (203) reflection for the Tb_2Co_{17} sample.

Table 1. Refined Δ_c and k parameters obtained from the experimental diffraction pattern using equation (3). The fourth column is the Δ_c value obtained using the method described by [10] for those samples where the random faulting model holds. (*Calculated according to [10])

RE_2Co_{17}	Δ_c R/H	k R/H	Δ_c^*
Pr	25/-	1.01/-	26
Nd	24/-	0.97/-	22
Sm	15/-	1.00/-	17
Gd	20/-	1.01/-	15
Tb	19/6	0.99/0.71	-
Dy	8/36	0.85/0.87	-
Ho	-/48	-/1.00	49
Lu	-/174	-/1.08	152

For the Tb sample the rhombohedral arrangement shows a Δ_c value of 19, three times that for the hexagonal phase with a value of 6. The Dy sample, on the other hand, shows an reverse relation of the correlation length values with 8 and 36 layers for the rhombohedral and hexagonal stacking, respectively.

Table 1 summarizes the obtained Δ_c and k values from the fitted profiles.

IV. REORDERING PHASE TRANSITION AND THE DEPARTURE FROM THE RANDOM FAULTING MODEL

Figure 2 now shows the behavior of the correlation length for all the studied samples. The Δ_c value for the hexagonal phase decrease as we go from the heavy rare earth alloy Lu_2Co_{17}, to the lighter one Tb_2Co_{17}. The reverse behavior is shown by the rhombohedral phase, which increases the correlation length as we go from Dy_2Co_{17} to the even lighter alloy Pr_2Co_{17}. The smallest Δ_c value (largest density of defects) occurs for the Tb sample.

The correlation lengths were also calculated following the procedure described in [10] for those alloys for which the RFM holds, and compared to the values obtained from the fitted diffraction patterns. Results are shown in Table 1. A good agreement between the values reported from both approaches is found, confirming the robustness of the procedure followed in this work. More importantly, this agreement points to validity of the Δ_c value calculated from the direct approach, for the region where RFM is no longer a valid approximation.

For the mixed phase alloys, the difference in correlation length between both stacking arrangement for the same alloy can be understood as follows.

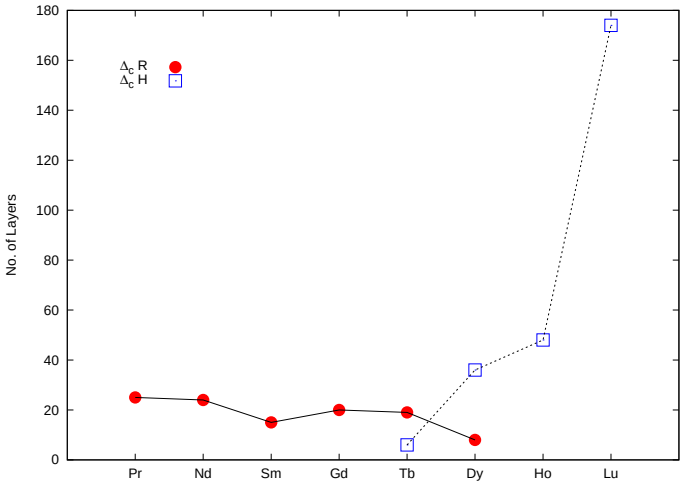

Figure 2. The correlation length Δ_c for the rhombohedral and hexagonal phase for the studied rare earth alloys. The rare earth are organized in increasing atomic number.

The absence of additional reflections in the diffraction pattern shows that higher order polytypes do not occur. There is a unique stacking direction in both symmetries and the 3R stacking sequence of the rhombohedral phase has a full match with the 2H stacking of the hexagonal one, leading to the absence of arrested ordering near the boundary between both phases.

Going from Pr to Lu, already for the Tb sample, large enough domains (to coherently diffract) of hexagonal stacking appear, the number and size of such domains increases as heavier rare earth are considered. This behavior follows from the increase of the coherent length for the hexagonal phase for Dy, Ho and Lu, in this order.

The fact that Δ_c value for the rhombohedral phase does not decrease significantly, shows that the emergence of the hexagonal phase is a result of reordering within the $R\bar{3}m$ phase without increase of disorder (or decrease, for that matter). This mechanism of reconstructive phase transformation is at odds with the RFM, where phase transformation is driven by the twinning faults (assisted by the deformation errors), and the emergence of hexagonal phase is at the expense of gradual disappearance of the cubic local environments. For independent growth and twinning faulting, the coexistence of both phases is excluded and the line dividing both phases as a function of defect probabilities is well defined [6]. The behavior shown in figure 2 is more consistent with nucleation and growth of hexagonal domains within the $R\bar{3}m$ crystal structure.

V. SCALING OF THE DECAYING TERM IN THE CORRELATION FUNCTION

Tiwary and Pandey reported the collapse of the decaying part of $P_0(\Delta)$ to a master curve when scaled with normalized Δ/Δ_c values [10]. The collapse is verified by simulation, within the tight constrains of the RFM.

From the experimental data, the decaying contribution to the $P_0(\Delta)$ was extracted and scaled according to the fitted Δ_c value for each sample. The results is shown in figure 3. As can be seen, the curves do not merge into a single master curve but instead a more rich behavior is observed: Master curves can be seen for weak faulting, one for the rhombohedral alloys and one for the hexagonal alloys.

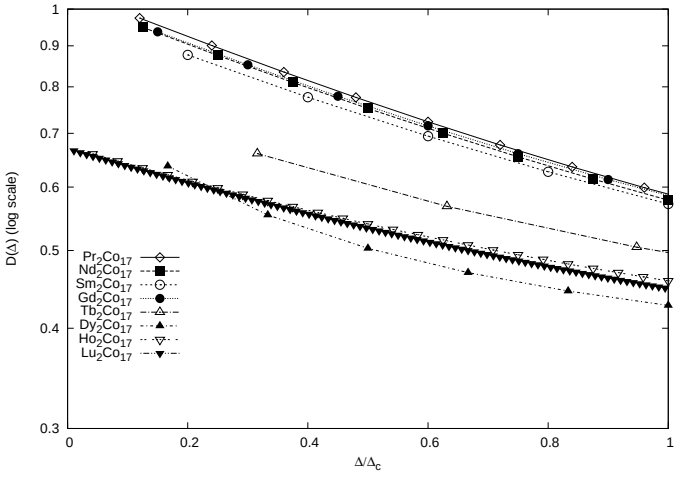

Figure 3. The decaying term of the P_0 correlation function scaled according to the correlation length Δ_c calculated for each sample. Curves fall into three master curves corresponding to the rhombohedral, mixed and hexagonal stacking order.

For strong faulted samples there is no master curve. This behavior is consistent with the analysis already done.

VI. CONCLUSION

It has been shown that the correlation length can be extracted from the diffraction data without need to assume the random faulting model by directly fitting the diffraction data.

The developed procedure was used to analyze the layer disorder in RE_2Co_{17} alloys which undergoes a reordering transition from rhombohedral to hexagonal arrangement when going from the light rare earth elements to the heavy rare earths. The increasing ordered character of the hexagonal phase was quantified as well as the evolution of the rhombohedral stacking through the value of the correlation length. Scaling behavior was proved to be of non-universal character.

The analysis shows the strength of the direct approach to the analysis of the diffraction pattern of planar disordered structures. The used approach allows to recognize more complex defect behavior than independent occurrence of disorder. This is specially relevant in the case at hand, as the samples considered are, at room temperature, between two polytypes belonging to the same polytypic family.

VII. ACKNOWLEDGMENT

The authors would like to thank LNLS, in Campinas, Brazil for the synchrotron experiments and the financial assistance in the framework of the project D12A-XRD1-1830. The program CAPES/MES-CUBA (310/2012) Cooperation Brazil Cuba is also acknowledge for partial financial support. This work was also supported by CLAF.

This work was partially financed by FAPEMIG under the project BPV-00047-13. EER which to thank PVE/CAPES for financial support under the grant 1149-14-8. Infrastructure support was given under project FAPEMIG APQ-02256-12.

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