Chemical Physics Letters 521 (2012) 138–141

Contents lists available at SciVerse ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

The J-mixing effect in Ln^{3+} ions crystal field levels

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ARTICLE INFO

Article history:
Received 26 July 2011
In final form 26 October 2011
Available online 4 November 2011

ABSTRACT

The J-mixing effect in the $^{2S+1}L_J$ level barycentre energy and splitting of trivalent lanthanide ions is analysed. The main predictions are that the maximum $^{2S+1}L_J$ level splitting (ΔE) is reduced and the barycentre energy can become lower with increasing ΔE. This effect is particularly important in low symmetries. Satisfactory agreement between the predictions and experimental data was obtained to all analysed systems, namely, the maximum $^7F_1$ level splitting of the Eu^{3+} ion and its barycentre energy in crystals and glasses.

1. Introduction

The crystal field effect on tripositive lanthanide ions (Ln^{3+}) is still an attractive theme of study in theoretical physics and chemistry. The recent interest for this study is stimulated by necessity of the luminescent materials with Ln^{3+} used in telecommunication, lighting, electroluminescent devices, (bio-) analytical sensors and bio-imaging set-ups [1,2]. The Eu^{3+} ions in several structures have been analysed by various techniques, and has been often used as a luminescent structural probe [3,4]. However, the splitting of levels and its barycentre energy position are very important and some aspects are still in study [4–6]. In a crystal field (CF) the states may be completely defined by a $|JM\rangle$ basis, J being the total angular momentum and M its projection [7]. However, states with deferent J can be mixed due to the CF; this effect is known as J-mixing effect and can leads to change in the energy level positions. This Letter aims to discuss how the J-mixing effect affects the barycentre position and the nonlinear behaviour of the maximum splitting of the $^7F_1$ energy level of the Eu^{3+} ion as a function of the crystal field parameters.

The CF Hamiltonian can be obtained by phenomenological simulation, but the CF parameters (B^k_q) depend on the base functions used to describe the 4f electronic configuration [8]. However if J-mixing is considered the problem of finding the B^k_q becomes more complex due to the nonlinear terms in B^k_q. In the case of a strong CF, the J-mixing contribution cannot be neglected in predicting the energy level scheme [9]. Two effects are frequently attributed to the J-mixing: the change in the barycentre energy position and the nonlinear maximum splitting of the ^{2S+1}LJ manifold versus CF strength parameters [10,11].

The standard form of the Hamiltonian acting within the $4f^N$ configuration of trivalent lanthanides in any host is commonly written with 19 free ion parameters [3,7]. When a lanthanide ion is incorporated into a crystal host, the Slater parameter, F^k, and the spin–orbit parameter, ζ, change with respect to their free-ion value. This changing is usually attributed to the nephelauxetic effect and cause a change in the barycentre of the $^{2S+1}L_J$ energy level. However, this shift depends only on the type and distance of the nearest neighbour and not on the angular part of the CF.

For each $^{2S+1}L_J$ manifold, the J-splitting depends on the B^k_q, only for $k \leqslant 2J$. Neglecting J-mixing, the relation between the maximum Stark splitting of the $^{2S+1}L_J$ manifold and B^k_q is found in Ref. [10]. In the case that the degeneracy of the $^5D_1$ and $^7F_1$ level is removed the $B^2_{|q|=1,2}$ values are nonzero. For the $^7F_1$ level splitting, ΔE, there is an expression for the maximum splitting as a function of the B^2_q. This has been discussed for some crystals in Refs. [11,12]. The discrepancy in the predictions of ΔE is attributed to the J-mixing effect. However, the calculations have not yet been discussed without approximations.

2. The $^{2S+1}L_J$ levels barycentre energy position shift

The shift in barycentre of the level J through of the non spherical part occurs due to the J-mixing effect and depends on the symmetry of the CF. The CF states are written as $|J\Gamma\rangle = \sum_M |JM\rangle\langle JM|J\Gamma\rangle$. $|JM\rangle$ are states of the free ion and all others quantum number are implicit. The perturbation that removes the degeneracy in J also causes mixing of states with different J. By using perturbation theory as found in text books [14], to describe the corrections due to the J-mixing, the energy level is given by:

$$E_{J\Gamma} = \langle J\Gamma|H_{cf}|J\Gamma\rangle + \sum_{\substack{J'\neq J\\ \Gamma'}} \frac{|\langle J\Gamma|H_{cf}|J'\Gamma'\rangle|^2}{E(J)-E(J')} \qquad (1)$$

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doi:10.1016/j.cplett.2011.10.060

H_{cf} is the non-spherical part of the crystal field Hamiltonian, $H_{cf} = \sum_{kq} B^k_q C^k_q, k = 2, 4, 6$ and $|q| \leqslant k$ [2,7]. The CF states and energy level are $|J'\Gamma'\rangle$ and E(J′) respectively and $\sum_\Gamma g_\Gamma \langle J\Gamma|H_{cf}|J\Gamma\rangle = 0$. Therefore, the shift in barycentre due J-mixing effect is given by:

$$\Delta E_B[J] = (2J+1)^{-1} \sum_{\Gamma J'\Gamma'} \frac{|\langle J\Gamma|H_{cf}|J'\Gamma'\rangle|^2}{E(J) - E(J')} \tag{2}$$

The summation over the Γ and Γ quantum numbers can be converted to a sum in M and M′ through the projection operator $P_0 = \sum_M |JM\rangle\langle JM|$ onto the subspace of the free-ion state acts in $|J\Gamma\rangle$ and $|J'\Gamma'\rangle$ one gets:

$$\Delta E_B[J] = (2J+1)^{-1} \sum_{J' \neq J} \frac{1}{E(J) - E(J')} \sum_{\substack{M=-J\ldots J \\ M'=-J'\ldots J'}} |\langle JM|H_{cf}|J'M'\rangle|^2 \tag{3}$$

By using the Wigner–Eckart theorem and the 3-j symbol orthogonal proprieties, the sum over M and M′ can be readily performed [10,13]. Therefore, an exact analytical formula for the change of the barycentre of the CF levels is:

$$\Delta E_B[J] = (2J+1)^{-1} \sum_{J'k} \frac{|\langle J|C^k|J'\rangle|^2}{E(J) - E(J')} S^k \tag{4}$$

$S^k = (2k+1)^{-1} \sum_q |B^k_q|^2$ is the CF strength parameter [10] and $\langle J|C^k|J'\rangle$ is the reduced matrix elements, which can be rewriting in terms of the unit tensor U^k [7,15]. Eq. (4) has been already obtained through an effective Hamiltonian that includes J-mixing [9]. In weak CF or high symmetry $\Delta E_B[J]$ is negligible because the S^k parameters are small.The composition of the wave functions now contains different J values. The appropriate wave functions can be obtained through perturbation theory [14].

3. The maximum splitting of the $^{2S+1}L_J$ manifold

The relation between the maximum splitting squared of the $^{2S+1}L_J$ manifold, $(\Delta E[J])^2$, is linear with the root-mean-square $(\Delta\varepsilon)^2$ [10]:

$$(\Delta\varepsilon)^2 = \frac{1}{g} \sum_i g_i (E_i)^2 \propto (\Delta E[J])^2 \tag{5}$$

E_i is the energy of the i^{th} level with respect to the free ion position and g_i is its degeneracy. The $(\Delta\varepsilon)^2$ of the $E_{J\Gamma}$ levels of a 2J+1 degenerate level after the CF perturbation is given by [14]:

$$\begin{aligned}(\Delta\varepsilon)^2 &= (2J+1)^{-1} \mathrm{Tr} P_0 (V - \Delta E_B[J]) P_0 (V - \Delta E_B[J]) \\ &= (2J+1)^{-1} \mathrm{Tr} P_0 V P_0 V - 2(2J+1)^{-1} \Delta E_B[J] \mathrm{Tr} P_0(V) + (\Delta E_B[J])^2\end{aligned} \tag{6}$$

In related literature it is assumed that $\Delta E_B[J] = 0$ [6,10,11]. However, because of the J-mixing effect, the term in $\Delta E_B[J]$ in Eq. (6) can be no more neglected. Therefore, in order to consider the J-mixing effect, the CF potential is now expressed by [16]: V = H_{cf} + H_{corr}, and

$$H_{corr} = \sum_{\substack{J' \neq J \\ M=-J'\ldots J'}} \frac{H_{cf}|J'M'\rangle\langle J'M'|H_{cf}}{E(J) - E(J')} \tag{7}$$

The $\mathrm{Tr}P_0(V)$ in Eq. (6) is obtained using both Eq. (4) and $\mathrm{Tr}P_0(H_{cf}) = 0$ [3]. This leads to $\mathrm{Tr}P_0(V) = (2J+1)\Delta E_B[J]$. Eq. (6) then becomes

$$(\Delta\varepsilon)^2 = (2J+1)^{-1} \mathrm{Tr} P_0 V P_0 V - (\Delta E_B[J])^2 \tag{8}$$

For the phenomenological $\bar{B}^k_q$ values obtained through the base functions without J-mixing it is assumed that the effective CF can be written as $V = \sum_{kq} \bar{B}^k_q C^k_q$ and that $\Delta E_B[J]$ = 0. Considering the corrected Eq. (7), the first term in Eq. (8) can be clearly explained by the following expression:

$$\begin{aligned}\mathrm{Tr}P_0VP_0V = {} & \mathrm{Tr}P_0H_{cf}P_0H_{cf} + \mathrm{Tr}P_0H_{cf}P_0H_{corr} + \mathrm{Tr}P_0H_{cf}P_0H_{corr} \\ & + \mathrm{Tr}P_0H_{corr}P_0H_{corr}\end{aligned} \tag{9}$$

The last term in Eq. (9) can be obtained from Eq. (8) by entering $V = H_{corr}$ and using that $(\Delta\varepsilon_{mix})^2 = (2J+1)^{-1} \sum_\Gamma g_\Gamma (\Delta E_\Gamma)^2$, which is the root-mean-square of the H_{corr} correction. Then,

$$\mathrm{Tr}P_0H_{corr}P_0H_{corr} = \sum_\Gamma g_\Gamma (\Delta E_\Gamma)^2 + (2J+1)(\Delta E_B[J])^2 \tag{10}$$

ΔE_Γ is the corrections due J-mixing and g_Γ it is the degeneracy.

The second and three terms can be obtain through of the project operator and the proprieties that the H_{cf} is orthogonal in relations to functions $|J\Gamma\rangle = \sum_M |JM\rangle\langle JM|J\Gamma\rangle$ thus the trace is give as:

$$\begin{aligned}\mathrm{Tr}P_0H_{cf}P_0H_{corr} &= \sum_{\Gamma\Gamma'} \langle J\Gamma|H_{cf}|J\Gamma'\rangle\langle J\Gamma'|H_{corr}|J\Gamma\rangle \\ &= \sum_\Gamma g_\Gamma E^0_\Gamma \Delta E_\Gamma\end{aligned} \tag{11}$$

E^0_Γ is the energy level of the CF without J-mixing. $\mathrm{Tr}P_0H_{corr}P_0H_{cf}$ have the same results. Therefore the $(\Delta\varepsilon)^2$ is found using the Eqs. (11) and (10) in the Eq. (9) and substitute in Eq. (8). Thus as has

$$\begin{aligned}(\Delta\varepsilon)^2 = {} & \frac{1}{2J+1} \sum_k \left|\langle J|C^k|J\rangle\right|^2 S^k + \frac{2}{2J+1} \sum_\Gamma g_\Gamma E^0_\Gamma \Delta E_\Gamma + \frac{1}{2J+1} \\ & \times \sum_\Gamma g_\Gamma (\Delta E_\Gamma)^2\end{aligned} \tag{12}$$

From Eq. (1) ΔE_Γ have the same signal for all Γ if the mixing is only with one J. Using the propriety of the energy level without J-mixing $\sum_\Gamma g_\Gamma E^0_\Gamma = 0$ and the approximation $E^0_\Gamma = \Delta E_B/(2J+1)$, one has

$$(\Delta\varepsilon)^2 \cong \frac{1}{2J+1} \sum_k \left|\langle J|C^k|J\rangle\right|^2 S^k + \left(\frac{\Delta E_B[J]}{2J+1}\right)^2 \tag{13}$$

In this case the J-mixing effect can lead to a decrease or increase in $(\Delta\varepsilon)^2$, and then in $\Delta E[J]^2$, depending on if J-mixing decreases or increases the magnitude of $\Delta E_B[J]$.

4. Applications to the Eu^{3+} ion

The Eq. (8) predicts that the theoretical value of the $(\Delta\varepsilon)^2$ from B^k_q without J-mixing $(\bar{B}^k_q)$ is smaller than the experimental value due the value $\Delta E_B[J]$. This prediction is confirmed in Figure 1 for the $^7F_2$ of the Eu^{3+} ion for different crystals.

One has just shown that the shift in the barycentre of the energy of the $^7F_1$ level in a CF is due to two effects: J-mixing and changing in the spin–orbit interaction parameter. Considering these effects, the correction in the energy of the $^7F_0$ and $^7F_1$ levels are given by the Eq. (4). Thus, the position of the $^7F_1$ level in relation the $^7F_0$ level can be written as:

$$E_B[^7F_1] = E[^7F_1] + \delta(S^2) + \delta(S^{k \geqslant 4}) \tag{14}$$

$E[^7F_1]$ is the free ion energy position. $\delta(S^2)$ and $\delta(S^{k \geqslant 4})$ are obtained by expanding the right side of Eq. (4). This leads to:

$$\delta(S^2) = \frac{1}{3}\left(\frac{|\langle ^7F_1|C^2|^7F_2\rangle|^2}{E[^7F_1] - E[^7F_2]} + \frac{|\langle ^7F_1|C^2|^7F_3\rangle|^2}{E[^7F_1] - E[^7F_3]} + \frac{3|\langle ^7F_0|C^2|^7F_2\rangle|^2}{E[^7F_2]}\right) S^2 \tag{15}$$

Then, $\delta(S^2) > 0$ and $\delta(S^{k \geqslant 4}) < 0$, this latter because the denominator in Eq. (4) is negative. Therefore, three cases in Eq. (14) can be analysed: firstly, for $\delta(S^{k \geqslant 4})$ small in comparison to $\delta(S^2)$. This can be found in sites with high symmetry, due to the fact that several B^k_q components are zero, or for high values of $E[^7F_1]$.

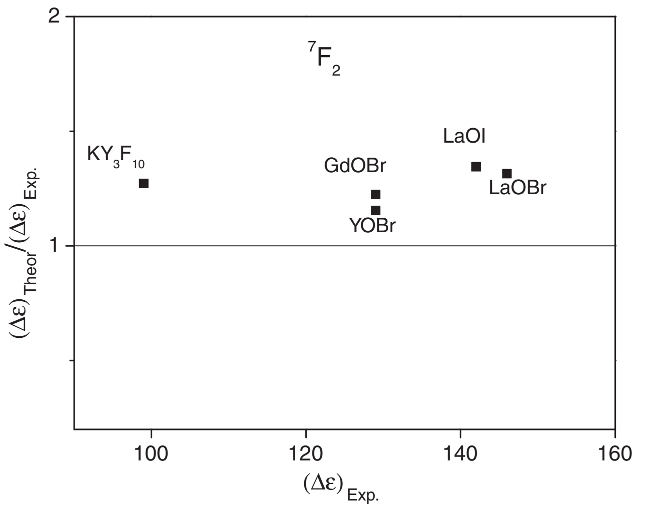

Figure 1. The $(\Delta\varepsilon)_{\text{theor}}/(\Delta\varepsilon)_{\text{Exp}}$ ratio for the $^7F_2$ level of the Eu^{3+} ion. The horizontal line shows the ideal theoretical prediction. The points show that, without J-mixing, the experimental values are lower than the theoretical prediction, according to Eq. (8). KY$_3$F$_{10}$ in Ref. [17], YOBr LaOI LaOBr and GdOBr in Ref. [20].

The degeneracy lifting of the $^7F_1$ level is due to non-vanishing crystal field parameters of rank 2, namely, B^2_q. The value $(\Delta\varepsilon)^2$ of the $^7F_1$ is given by: [10]

$$(\Delta\varepsilon)^2 = \frac{1}{(2J+1)}\left(\frac{\Delta E}{2}\right)^2(2+\alpha^2) \tag{16}$$

By using Eqs. (13) and (16) the maximum splitting of the $^7F_1$, ΔE, is given by:

$$\Delta E = \left[4\frac{|\langle {}^7F_1|C^2|{}^7F_1\rangle|^2}{(2+\alpha^2)}S^2 + 4\frac{(\Delta E_B)^2}{3(2+\alpha^2)}\right]^{1/2} \tag{17}$$

ΔE_B is the change in the position of the barycentre of the $^7F_1$ level. Here is performance a new relation between S^2 and the maximum $\Delta\varepsilon$ splitting, however in Eq. (17) have relation also with $(\Delta E_B)^2$ due the J-mixing effect.The value of S^2 can be obtained through of the Eq. (17). Using a symmetric repartition, $\alpha = 0$, one obtains

$$S^2 = \frac{1}{2}\frac{\Delta E^2 - (2/3)(\Delta E_B)^2}{|\langle {}^7F_1|C^2|{}^7F_1\rangle|^2} \tag{18}$$

Therefore, in the case of $\delta(S^{k\geqslant 4})$ negligible, and using the Eq. (18) in Eq. (15), and then in Eq. (14), one has

$$\Delta E_b = \frac{1}{6}\left(\frac{|\langle {}^7F_1|U^2|{}^7F_2\rangle|^2}{E[{}^7F_1] - E[{}^7F_2]} + \frac{|\langle {}^7F_1|U^2|{}^7F_3\rangle|^2}{E[{}^7F_1] - E[{}^7F_3]} + \frac{3|\langle {}^7F_0|U^2|{}^7F_2\rangle|^2}{E[{}^7F_2]}\right) \times \frac{\Delta E^2 - (2/3)(\Delta E_B)^2}{|\langle {}^7F_1|C^2|{}^7F_1\rangle|^2} \tag{19}$$

$\Delta E_b = E_{cf}[{}^7F_1] - E[{}^7F_1]$. ΔE_b is also equal to the difference $\Delta E_B - \Delta E_B[{}^7F_0]$. From Eq. (4) only in the first term (k = 2) ΔE_B is proportional to $\Delta E_B[{}^7F_0]$. Thus ΔE_B can be written in terms of ΔE_b as follows:

$$\Delta E_B = \left(1 - \frac{|\langle {}^7F_1|U^2|{}^7F_2\rangle|^2(E[{}^7F_0] - E[{}^7F_2])}{|\langle {}^7F_0|U^2|{}^7F_2\rangle|^2(E[{}^7F_1] - E[{}^7F_2])}\right)^{-1}\Delta E_b \tag{20}$$

Using the value of $|\langle {}^7F_1|U^2|{}^7F_J\rangle|^2$, $E[{}^7F_2] = 1024\ \text{cm}^{-1}$, and $E[{}^7F_3] = 1800\ \text{cm}^{-1}$ given in Ref. [15], as the barycentre energy positions of each respective manifold, the Eq. (20) leads to $\Delta E_B = 2.4\Delta E_b$ and the Eq. (19) can be written as:

$$\Delta E_b = 2.0 \times 10^{-4}\left[\Delta E^2 + (2.4 \times (2/3)(\Delta E_b)^2\right] \tag{21}$$

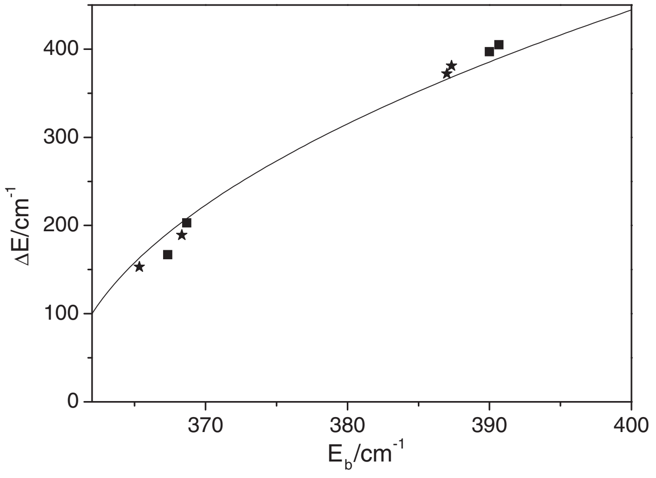

Figure 2. The increasing in the maximum splitting of the $^7F_1$ level due to the increase in barycentre position. The experimental data are from the KYF$_4$ (stars) and KLuF$_4$ (squares) crystals [17]. The solid line is the theoretical prediction.

Solving for ΔE with ΔE_b the solution with physical meaningful is

$$\Delta E = (2/5)\left[31250(\Delta E_b) - 10(\Delta E_b)^2\right] \tag{22}$$

In order to test this prediction, one enters the hypothetical values $E[{}^7F_1] = 360\ \text{cm}^{-1}$ (in the case of the Eu^{3+}: KYF$_4$ and Eu^{3+}: KLuF$_4$ crystals and $E[{}^7F_1] = 356\ \text{cm}^{-1}$ (in the case of Eu^{3+} doped calcium diborate glass) lead to very satisfactory predictions (Figures 2 and 3).

The second case is for $\delta(S^2)$ small compared to $\delta(S^{k\geqslant 4})$. This occurs when $E[{}^7F_1]$, S^4 and S^6 are large. Therefore, the change in ΔE_B [Eq. (12)] due to S^2 is small. So, the J-mixing contributes to a decrease in the barycentre energy position. For instance, in Figure 3 it is shown that $E[{}^7F_1] = 447\ \text{cm}^{-1}$ while $\Delta\varepsilon\,({}^7F_1) = 0$ for Eu^{3+} in zinc oxyfluorotellurite glass [19]. This is being predicted for the first time. In Ref. [19], as a function of excitation energy, it is observed *repulsion* between neighbouring levels J. Figure 3 shows both cases: $\delta(S^2) > \delta(S^{k\geqslant 4})$ calculated via Eq. (21) and $\delta(S^2) < \delta(S^{k\geqslant 4})$. In Ref. [21], now as a function of an external magnetic field, it is observed

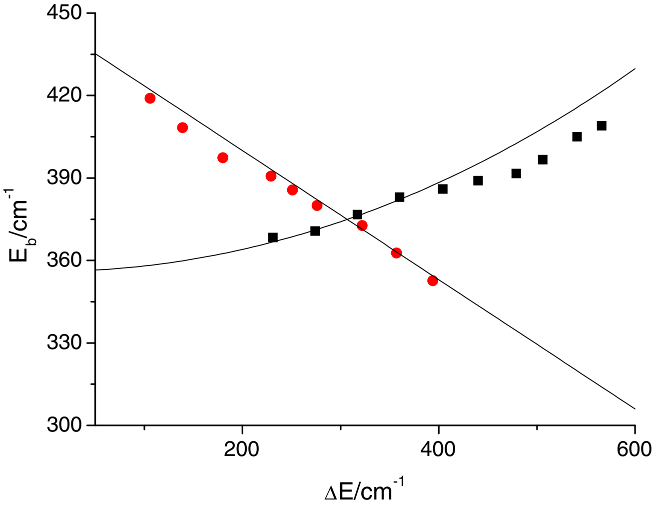

Figure 3. Increase and decrease in the barycentre energy with increasing maximum $^7F_1$ level splitting. The circles are the experimental data of the Eu^{3+} ions in calcium diborate glasses [18]. The squares are experimental data the Eu^{3+} in the zinc oxyfluorotellurite glass [19]. The solid line is the theoretical prediction [Eq. (22)].

and simulated *repulsion* between neighbouring levels with the same irreps. In very low site symmetries all Stark sublevels are described by similar irreducible representations (irreps) [3].

For the case when S^4 and S^6 are comparable to S^2, as S^4 and S^6 have opposite sign in comparison to S^2, the barycentre may not change appreciably and the maximum splitting will remain linear with S^2.

5. Conclusions

The levels of the Eu^{3+} ion have been revisited by considering the J-mixing effect using first order perturbation theory without approximations. A reduction in the ^7F_J level splitting is predicted and the barycentre energy position can become lower. This latter is in the opposite sense when compared to the shift due to the spin–orbit coupling. The relation between the $^7F_1$ level splitting and the S^2 strength parameter shows that the J-mixing contributes to reduce the splitting. In sites with high symmetry the J-mixing can be negligible depending on the energy separation between neighbouring Stark levels. The prediction of lowering the barycentre energy position with increasing ΔE is being made for the first time. Very satisfactory predictions is found between theory and experiment to all analysed systems.

Acknowledgments

The authors deeply acknowledge the CAPES, CNPq and INAMI (Brazilian agencies) and FAPITEC (state agency) for financial support.

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