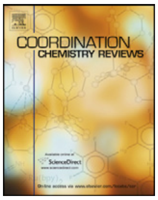
Coordination Chemistry Reviews 254 (2010) 3026–3029

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

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



Letters to the Editor

Luminescent lanthanide complexes: Selection rules and design

In this letter we address and resolve in a wider sense some of the points in a recent article (Armelao et al., Coord. Chem. Rev. 254 (2010) 487) which may be unclear to Coordination Chemists. The major focus is upon the qualitative description of the selection rules for the electronic transitions of lanthanide ions in complexes. Attention is also given to a major factor which determines the non-radiative decay rate from a given energy level.

1. Selection rules for transitions of lanthanide ions

Selection rules foretell whether or not a spectral transition will be observed. In fact, this depends upon the approximation entertained. Although a transition may be forbidden to first order, it can be allowed (albeit, much weaker) under higher-order selection rules. This will become apparent in the following discussion.

As mentioned by Armelao et al. [1], under the Russell–Saunders coupling scheme, the multiplet terms of lanthanide ions are represented by the notation $^{2S+1}L_J$, where the quantum numbers refer to total electron spin (S), total orbital angular momentum (L) and total momentum (J). It was stated in [1] that the selection rules for intraconfigurational optical transitions of lanthanide ions between $^{2S+1}L_J$ levels are $\Delta L = \pm 1$ or $\Delta J = \pm 1$. This is incorrect and is actually an incomplete statement of the selection rules for interconfigurational electric dipole (ED) allowed transitions. Notice that these quantum numbers given just refer to the orbital characteristics (and not the spin) of the electrons. ED allowed transitions must involve a change in parity for the initial and terminal states, which is indeed obeyed for the types of interconfigurational transition such as from $4f^1$ to $5d^1$: i.e. from odd parity to even parity. The S, L, J selection rules for these transitions are listed in Table 1 and are exemplified, for example, in the emission spectra of Ce^{3+}, which can be in the ultraviolet to yellow spectral regions, depending upon the particular host. There is a further restriction for ED electronic transitions that the single electron transition selection rule makes $(nl)^N \leftrightarrow (nl)^{N-1} n'l'$ only allowed when $l = l' \pm 1$.

The types of intraconfigurational $4f^N$–$4f^N$ electronic transitions that are allowed to first order are magnetic dipole (MD) or electric quadrupole (EQ) transitions. In MD intraconfigurational electronic transitions, it is not the oscillating electric vector of radiation that interacts with the 4f electrons of Ln^{3+}, but the oscillating magnetic vector of the radiation. Although the oscillator strengths of these MD transitions are roughly about 10^{-6} times that of a fully allowed ED transition, they can be very important for some lanthanide ions [2]. The S, L, J selection rules for MD transitions are collected in Table 1. For example, the $^4I_{13/2}$–$^4I_{15/2}$ transition of Er^{3+} is employed in fiber optics communications and this transition obeys the selection rules for MD transitions. The very weak EQ transitions (oscillator strength $\sim 10^{-10}$ of an ED allowed transition) are mostly uncharacterized for Ln^{3+}, except for the infrared absorption of Sm^{3+} near 6000 cm^{-1} [3]. The S, L, J selection rules are collected in Table 1.

The $4f^N$–$4f^N$ electronic transitions are thus ED forbidden to first order because the initial and final states belong to the same parity. The most important type of pure electronic transition for lanthanide ions is the forced (induced) ED transition. This arises because in noncentrosymmetric Ln^{3+} systems, as for many complexes, parity no longer exists (i.e. there is no centre of symmetry, and no "even" or "odd" orbitals) so that some d-orbital character can mix with f-orbitals. The transition between initial (i) and final (f) states then becomes $x[4f^N(i)] + y[4f^{N-1}5d(i)] \rightarrow t[4f^N(f)] + u[4f^{N-1}5d(f)]$, where although $x \gg y$ and $t \gg u$, there is now a pathway to make the transition become ED allowed. This mixing is brought about by the odd terms in the crystal field. The oscillator strength of such $4f^N$–$4f^N$ forced ED transitions is roughly about 10^{-4} times that of a fully allowed ED transition. Formally, the ED selection rules can be applied to the transition, because of the interconfigurational state admixture, if we know which states are mixed into the initial and terminal levels of the transition. However, Judd [4] and Ofelt [5] introduced a simplification of the selection rules for forced ED transitions (Table 1) so that for example, for Eu^{3+} as in Figs. 13, 14 of [1], although $^5D_0 \rightarrow {}^7F_2$ is enabled by the forced ED transition mechanism, $^5D_0 \rightarrow {}^7F_0$, $^7F_3$, $^7F_5$ are not, and are much weaker. The S, L, J selection rules for forced ED transitions are collected in Table 1.

If $\Delta S = 0$ for these forced ED transitions (Table 1), then one can ask, why is the spin-forbidden $^5D_0 \rightarrow {}^7F_2$ transition the strongest one from $^5D_0$? Actually, L and S are not good quantum numbers, but J is (to a certain extent: see below) good. Thus spin-orbit coupling leads to mixing of values of L and S that differ by 1 unit, to give the same J value, to describe a multiplet term: e.g. $S = 1$, $L = 1$, $J = 2$: $^3P_2$ can mix with $S = 0$, $L = 2$, $J = 2$: $^1D_2$, depending upon how far apart their energies are. This type of state description is termed intermediate coupling. The multiplet is normally identified by the dominant $^{2S+1}L_J$, and the complete intermediate coupling wavefunction is written as $[^{2S+1}L_J]$. Hence the spin selection rule for $^5D_0 \rightarrow {}^7F_2$ can be satisfied by the mixing of $^5D_0$ with $^7F_0$ and $^7F_2$ with $^5D_2$. Although spin-orbit coupling is not important for light elements (e.g. in carbon compounds), the ΔS and ΔL restrictions for forced ED and for MD transitions $^{2S+1}L_J \rightarrow {}^{2S'+1}L'_{J'}$ of Ln^{3+} are often greatly lifted due to spin-orbit coupling.

There is a further complication in the solid state spectra of lanthanide ions, since each multiplet term comprises crystal field levels, and mixing of these states from different multiplet terms can also occur if the crystal field levels correspond to the same symmetry representation. This is called J-mixing and it is therefore more important for low site symmetry systems where many crystal field levels have the same symmetry labels. Each state is therefore described by a linear combination of different multiplet terms, some of which have different J-values, but with the same symmetry representation. Again, the particular state is identified by the dominant multiplet term: e.g. the lowest $[^1D_2]$ state of Pr^{3+}

0010-8545/$ – see front matter

Table 1
SLJ selection rules for various types of transition of lanthanide ions.

Type of transition	*SLJ* selection rules	Approximate order of magnitude of oscillator strength
Electric dipole (ED)	$\Delta S = 0$; $\lvert\Delta L\rvert \le 1$; $\lvert\Delta J\rvert \le 1$; $J = 0 \leftrightarrow J' = 0$ and $L = 0 \leftrightarrow L' = 0$ are forbidden	~0.01–1
Forced (induced) ED	$\Delta S = 0$; $\lvert\Delta L\rvert \le 6$; if $L = 0$ or $L' = 0$, $\lvert\Delta L\rvert = 2,4,6$; $\lvert\Delta J\rvert \le 6$; if $J = 0$ or $J' = 0$, $\lvert\Delta J\rvert = 2,4,6$. This implies that $J = 0 \leftrightarrow J' = 0$ and $L = 0 \leftrightarrow L' = 0$ are forbidden	~10^{-4} of ED
Magnetic dipole (MD)	$\Delta S = 0$; $\Delta L = 0$; $\lvert\Delta J\rvert \le 1$; $J = 0 \leftrightarrow J' = 0$ is forbidden	~10^{-6} of ED
Electric quadrupole (EQ)	$\Delta S = 0$; $\lvert\Delta L\rvert \le 2$; $\lvert\Delta J\rvert \le 2$; $J = 0 \leftrightarrow J' = 0,1$ and $L = 0 \leftrightarrow L' = 0,1$ are forbidden	~10^{-10} of ED
One phonon ED vibronic	The same as forced (induced) ED	~10^{-7}–10^{-10} of ED

is made up of 86.5% $^1D_2$ + 10.9% $^3P_2$ + 2% $^3F_2$ + 0.5% $^1I_6$ +... even in $Cs_2NaPrCl_6$ [6], which has Pr^{3+} at a site of octahedral symmetry. The reader is referred to a text on Group Theory, such as [7], for a description of site symmetry selection rules for transitions between crystal field levels and the changes when using polarized radiation.

Finally, vibronic transitions not only involve electronic excitations but also the (de)excitation of vibrational quanta. This type of ED transition involving the excitation of one quantum of an odd vibration of a metal–ligand system is important for centrosymmetric environments of Ln^{3+} (selection rules in Table 1) and typical oscillator strengths are in the range of 10^{-7}–10^{-10}. The selection rules for simultaneous excitation of electronic transitions together with internal ligand modes are given, for example, in [8] and these two-centre transitions generally have oscillator strengths ~10^{-10} or less.

Note that although ED transitions may be allowed under *S*, *L*, *J* selection rules, a crystal field transition may not be observed if it is forbidden by site symmetry selection rules (for example, for the $5d^14f^1 \rightarrow 4f^2$ emission of Pr^{3+} to the electronic ground state [9]).

In summary, room temperature emission spectra of lanthanide complexes mainly show partially or unresolved structure due to crystal field transitions between initial and terminal states. Most luminescent complexes of interest to chemists have lanthanide ions in noncentrosymmetric low symmetry environments so for $4f^N$–$4f^N$ transitions, forced ED selection rules for quantum numbers *S*, *L*, *J* of the multiplet $^{2S+1}L_J$ give a qualitative indication of spectral intensities for multiplet–multiplet transitions, whereas the original selection rules given in [1] are incomplete/irrelevant to the transitions concerned. For the interested reader, more detailed theoretical discussions of transition selection rules are given in [10,11].

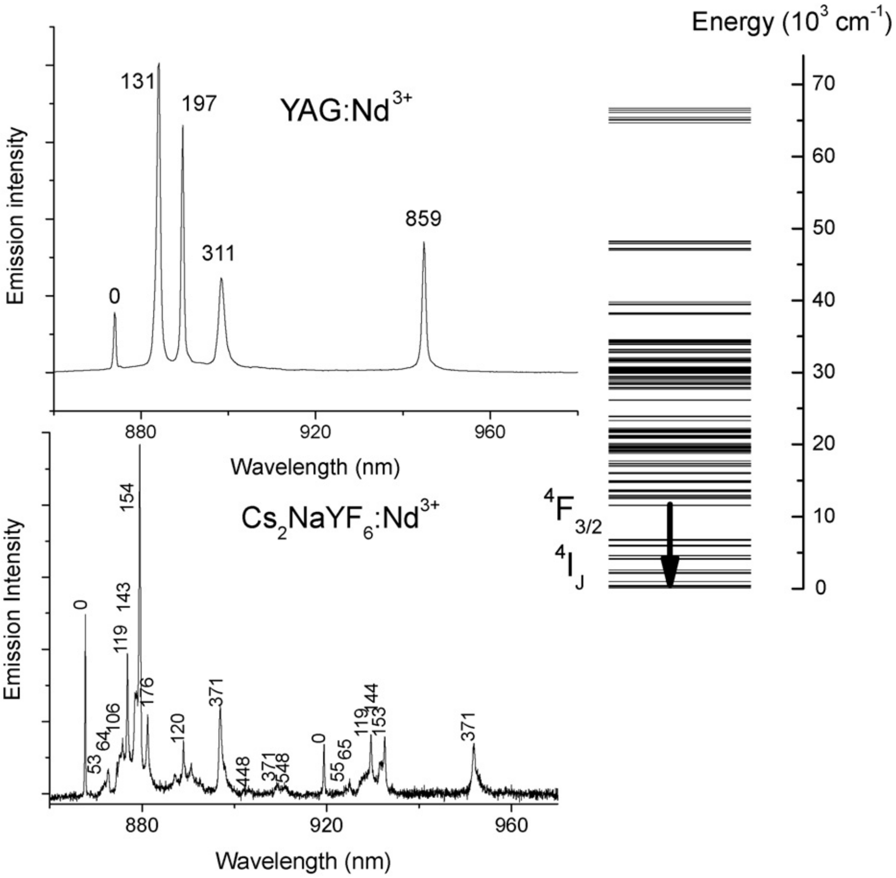


Fig. 1. Comparison of $^4F_{3/2} \rightarrow {}^4I_{9/2}$ emission spectra of YAG:Nd^{3+} and Cs_2NaYF_6:Nd^{3+} at 10 K. (YAG = yttrium aluminium garnet, $Y_3Al_5O_{12}$). The energy level scheme of Nd^{3+} is indicated with the infrared emission transition as marked. The derived $^4I_{9/2}$ ground state energy levels are marked for Nd^{3+} in YAG:Nd^{3+}, and the derived vibrational energies are marked for Cs_2NaYF_6:Nd^{3+}.

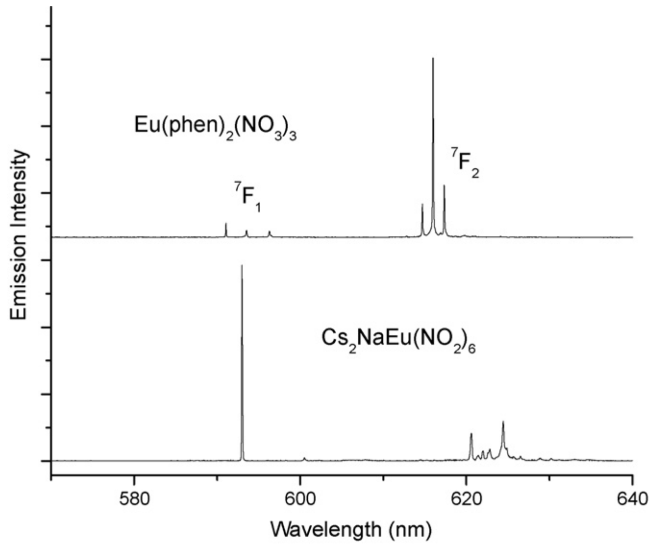


Fig. 2. Comparison of 10 K emission spectra of Eu^{3+} in Cs$_2$NaEu(NO$_2$)$_6$ and Eu(phen)$_2$(NO$_3$)$_3$. The initial state is ^{5}D$_0$ and terminal multiplets are marked. The relative intensities are arbitrary.

Illustrations are given in Figs. 1 and 2 of the completely different types of transition that may be observed in the emission spectra of Ln^{3+}. These examples serve to show that if a transition is forbidden by one mechanism, it can be enabled by another, weaker mechanism. The infrared emission transition $^4F_{3/2} \rightarrow {}^4I_{9/2}$ of 4f^3 Nd^{3+} in Y$_3$Al$_5$O$_{12}$ (YAG) and Cs$_2$NaYF$_6$ is shown in Fig. 1. In the former noncentrosymmetric case, the forced ED transitions to the five terminal crystal field levels of the ^{4}I$_{9/2}$ electronic ground state are observed, and the derived ground state energies are marked. This type of transition is forbidden for the latter centrosymmetric environment of Nd^{3+} so that all features correspond to MD (marked as 0) or ED vibronic (marked in some cases with the derived vibrational energy) transitions to three terminal states. The spectra of Eu^{3+} are more familiar to coordination chemists. In Fig. 2, the 10 K emission spectra of this ion at the C_2 symmetry site of Eu(phen)$_2$(NO$_3$)$_3$ (phen = 1,10-phenanthroline) and at the T_h symmetry site of the hexanitrito ion Eu(NO$_2$)$_6{}^{3-}$ are displayed. The features are sharp in both cases. Major differences occur, however, in the multiplet band splittings and relative intensities of the $^5D_0 \rightarrow {}^7F_{1,2}$ transitions. One band is observed for Eu^{3+} at the T_h site for the $^5D_0 \rightarrow {}^7F_1$ transition whereas three bands are observed in the case of the C_2 site.

2. Design of luminescent lanthanide complexes

Armelao et al. have noted that the emission from long-lived excited states of lanthanide ions may be quenched when the ion is in the proximity of high frequency vibrational oscillations, such as for OH, NH groups. These authors employed the term “deactivation by vibronic coupling”. Whilst this term is correct, we prefer to say nonradiative deactivation and reserve the words “vibronic coupling” for radiative transitions. Actually, vibronic coupling has many facets, in radiative and nonradiative transitions and affects spectral intensities and line widths [12].

It is incorrect, however, to state that “the lower is the excited state energy of the Ln^{3+} ion, the more efficient will be the deactivation by vibronic coupling”, so that with Ln^{3+} emitting in the near infrared the emission is strongly reduced. In fact it is the energy gap, not the absolute energy, which plays a major role of quenching Ln^{3+} emission [13]. As a rule of thumb, if the energy gap between two levels exceeds four quanta of the highest vibration energy then the upper level is potentially luminescent. Thus Ho^{3+} and Er^{3+} emit strongly in the mid-infrared at ~5000 and ~6000 cm^{-1}, respectively, in addition to the Yb^{3+} emission in the near infrared at ~10,000 cm^{-1}. In addition to the importance of vibrational frequency, the luminescence intensity can also be quenched by various other factors, including migration of the excitation energy to “killer” sites in concentrated materials, photoionization [14] or intervalence charge transfer mechanisms [15].

3. Electronic properties and coordination number of lanthanide complexes

Armelao et al. [1] have stated that Ce^{4+} is the only rare-earth element for which molecular precursors are in the +4 state. Note that the molecular precursor route has also employed divalent complexes of Nd, Dy, Eu, Sm, Tm and Yb [16–21]. Strzelecki et al. [16] prepared the derivatives Ln(QR)$_2$(solv)$_x$ (Ln = Eu, Sm, Yb; Q = Se, Te; R – mesityl, supermesityl) by transmetalation of LnX$_2$(THF)$_3$ (X = Br, I) with the potassium salt of the arylselenolate or -tellurolate anions. Zhao and Gao [17] discussed the precursors to generate Eu(II) and sulphide ions. Evans et al. showed that DyI$_2$ is a powerful reducing agent in organic synthesis [19]. Thermally stable lanthanide(II) complexes with ability to cleave the C–O bond of dimethoxyethane were synthesized by Cassani et al. [20].

The simplest interpretation of the lanthanide contraction for Ln^{3+} states that the decrease from Ce^{3+}(VI) to Yb^{3+}(VI) (101–86.8 pm [22]) is due to the poor shielding by 4f electrons of the nuclear charge experienced by outer 5p electrons, although about 10% of the contraction has been attributed by Pykko to relativistic effects [23].

It is not always common that Ln^{3+} complexes of the same ligand are isostructural. Even for simple complexes such as complex rare earth halides there are changes in crystal structure on crossing the lanthanide series [24]. Otherwise, there may be a change in coordination number on crossing the series [25], or even from the ground to excited state of Ce^{3+} [26].

References

[1] L. Armelao, S. Quici, F. Barigelletti, G. Accorsi, G. Bottaro, M. Cavazzini, E. Tondello, Coord. Chem. Rev. 254 (2010) 487.
[2] P.A. Tanner, Top. Curr. Chem. 241 (2004) 167.
[3] M.D. Faucher, P.A. Tanner, J. Phys.: Condens. Matter 18 (2006) 8503.
[4] B.R. Judd, Phys. Rev. 127 (1962) 750.
[5] G.S. Ofelt, J. Chem. Phys. 37 (1962) 511.
[6] P.A. Tanner, C.S.K. Mak, M.D. Faucher, J. Chem. Phys. 114 (2001) 10860.
[7] B.S. Tsukerblat, Group Theory in Chemistry and Spectroscopy, Academic Press, New York, 1994.
[8] M. Stavola, L. Isganitis, M.G. Sceats, J. Chem. Phys. 74 (1981) 4228.
[9] P.A. Tanner, C.S.K. Mak, M.D. Faucher, W.M. Kwok, D.L. Phillips, V. Mikhailik, Phys. Rev. B 67 (2003) 115102.
[10] M.F. Reid, in: G.K. Liu, B. Jacquier (Eds.), Spectroscopic Properties of Rare Earths in Optical Materials, Tsinghua University Press and Springer-Verlag, Berlin, Heidelberg, 2005 (Chap. 2, Section 2.3.4).
[11] C. Görller-Walrand, K. Binnemans, in: K.A. Gschneidner Jr., L. Eyring, Handbook on the Physics and Chemistry of Rare Earths, vol. 25, Elsevier Science B.V., Amsterdam, 1998 (Chap. 167) (MD selection rules: page 123; induced ED selection rules: pp. 145–146. For the context of this letter, In Table 2, p. 146, right hand side: $\Delta l = \pm 1$ should be replaced by ‘lacking of center of inversion’, and $\Delta\tau = 0$ should be deleted. We have not discussed ΔM herein).
[12] B. Henderson, G.F. Imbusch, Optical Spectroscopy of Inorganic Solids, Clarendon Press, Oxford, 1989.
[13] M.F.H. Schuurmans, J.M.F. van Dijk, Physica 123B (1984) 131.
[14] W.M. Yen, Opt. Mater. 27 (2005) 1647.
[15] P. Boutinaud, P. Putaj, R. Mahiou, E. Cavalli, A. Speghini, M. Bettinelli, Spectrosc. Lett. 40 (2007) 209.
[16] A.R. Strzelecki, C.L. Likar, B.A. Helsel, T. Utz, M.C. Lin, P.A. Bianconi, Inorg. Chem. 33 (1994) 5188.
[17] F. Zhao, S. Gao, J. Mater. Chem. 18 (2008) 949.
[18] A.R. Strzelecki, P.A. Timinski, B.A. Helsel, P.A. Bianconi, J. Am. Chem. Soc. 114 (1992) 3159.
[19] W.J. Evans, N.T. Allen, J.W. Ziller, J. Am. Chem. Soc. 122 (2000) 11749.
[20] M.C. Cassani, M.F. Lappert, F. Laschi, Chem. Commun. (1997) 1563.

[21] F. Jaroschik, F. Nief, X.F. Le Goff, L. Ricard, Organometallics 26 (2007) 1123.
[22] R.D. Shannon, Acta Cryst. A32 (1976) 751.
[23] P. Pyykko, Chem. Rev. 88 (1988) 563.
[24] G. Meyer, Prog. Solid State Chem. 14 (1982) 141.
[25] G.-L. Law, K.-L. Wong, K.-K. Lau, S.-T. Lap, P.A. Tanner, W.-T. Wong, J. Mater. Chem. 20 (2010) 4074–4079.
[26] Y. Kaizu, K. Miyakawa, K. Okada, H. Kobayashi, M. Sumitani, K. Yoshihara, J. Am. Chem. Soc. 107 (1985) 2626.

Peter A. Tanner*
Chang-Kui Duan
Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong S.A.R., PR China

* Corresponding author.
E-mail address: bhtan@cityu.edu.hk (P.A. Tanner)

19 March 2010
Available online 24 May 2010
doi:10.1016/j.ccr.2010.05.009

Reply to "Luminescent lanthanide complexes: Selection rules and design"

The letter by Tanner et al. represents a timely and detailed discussion of the spectroscopic properties of lanthanide elements and of their complexes in general, which is a necessary requisite whenever a study dealing with such properties is presented in literature.

The focus of the study by Armelao et al. [1] was specifically on innovative lanthanides antenna complexes, describing the basic principles of ligands design to yield systems featuring a coordination site for the metal cation with appended suitable chromophores as sensitizers, and their use to prepare efficient light emitting materials by soft chemical solution routes. Thus, within this scope, the spectroscopy of rare earth elements as well as other aspects related to materials synthesis were treated to an intermediate level, at the same time referring the reader to the extended available literature for a deeper insight into specific issues.

Reference

[1] L. Armelao, S. Quici, F. Barigelletti, G. Accorsi, G. Bottaro, M. Cavazzini, E. Tondello, Coord. Chem. Rev. 254 (2010) 487.

L. Armelao [a,*]
S. Quici [b]
F. Barigelletti [c]
G. Accorsi [c]
G. Bottaro [d]
M. Cavazzini [b]
E. Tondello [e]
[a] *ISTM – CNR and INSTM, Dipartimento di Scienze Chimiche, Università di Padova, Via F. Marzolo 1, 35131 Padova, Italy*
[b] *ISTM – CNR, Via C. Golgi 19, 20133 Milano, Italy*
[c] *ISOF – CNR, Via P. Gobetti 101, 40129 Bologna, Italy*
[d] *IMIP – CNR and INSTM, Dipartimento di Scienze Chimiche, Università di Bari, Via E. Orabona 4, 70126 Bari, Italy*
[e] *Dipartimento di Scienze Chimiche, Università di Padova and INSTM, Via F. Marzolo 1, 35131 Padova, Italy*

* Corresponding author.
E-mail address: lidia.armelao@unipd.it (L. Armelao)

14 May 2010
Available online 24 May 2010
doi:10.1016/j.ccr.2010.05.011