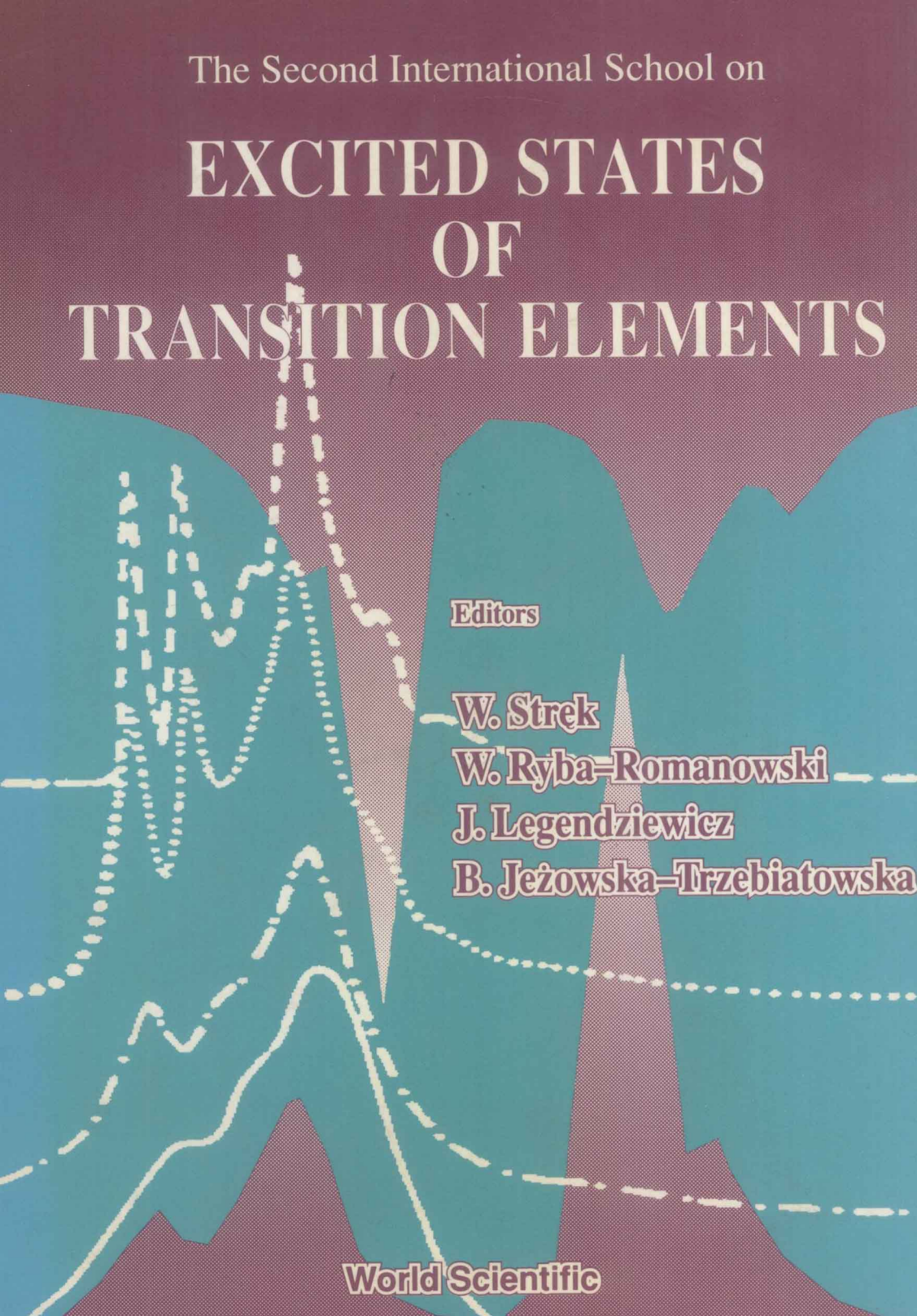


The Second International School on

EXCITED STATES OF TRANSITION ELEMENTS



Editors

W. Stręk

W. Ryba-Romanowski

J. Legendziewicz

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World Scientific

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**THE SECOND INTERNATIONAL SCHOOL ON
EXCITED STATES OF TRANSITION ELEMENTS**

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PREFACE

The Second International School on Excited States of Transition Elements was held in Karpacz, Poland, September 2–6, 1991. It was a continuation of the first meeting held three years earlier in Książ Castle, Poland. The School was sponsored by the Polish Academy of Sciences, the University of Wrocław, the Technical University of Wrocław, Lumonics, Inc. Ltd. and Coherent Physik.

The purpose of the School was to bring together outstanding specialists and young scientists working in the field of spectroscopy of rare earth and transition metal ions. These elements find broad applications in optoelectronics, quantum electronics and luminophores.

These proceedings collect invited and contributed papers presented at the School. The School was attended by 90 scientists from Austria, Byelorussia, Brazil, Canada, Czechoslovakia, Denmark, England, Estonia, Finland, France, Germany, Ireland, Israel, Italy, Lithuania, the Netherlands, Romania, Russia, Switzerland, Vietnam and Poland.

Numerous people contributed to the success of the School. In particular we would like to thank our colleagues from the Organizing Committee for their effort and enthusiasm. Special thanks are due to M. Błażej, P. Dereń, G. Dominiak-Dzik, S. Gołąb, M. Gałczyński and E. Łukowiak.

December 1991

B. Jeżowska-Trzebiatowska
J. Legendziewicz
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GARNETS' PUZZLE [§]

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ABSTRACT The absorption, dye laser excitation and luminescence spectra of the Pr^{3+} ion in yttrium gallium (YGG) and aluminum (YAG) garnets as well as in gadolinium gallium garnet (GGG) were measured at temperatures from 4.2 to 300 K. The superimposed spectra obtained by conventional methods could be separated into several individual ones by site selective dye laser excitation. The garnets seem to possess several optically active sites as follows: YGG: 2, GGG: 4, and YAG: 5. The possible origins of the different sites as well as the mechanisms leading to the observed spectra are discussed.

1. INTRODUCTION

The rare earth aluminum or gallium garnets corresponding to a general formula $\text{RE}_3\text{M}_5\text{O}_{12}$ have found wide applications as laser materials (YAG: Nd^{3+}) as well as proposed as substrate materials for magnetic memories, *cf. e.g.* [1]. Due to these existing or potential advantages the different garnets have been subject to extensive studies in almost every conceivable field.

[§] Paper presented at the 2nd International School on Excited States of Transition Elements, Karpacz, Poland, Sept. 2-6, 1992.

¶ On sabbatical leave from Department of Chemistry, University of Turku, SF - 20500 Turku, FINLAND

Because of the utmost importance of the purity and perfect crystal structure for most applications the occurrence and nature of the structural disorder as well as crystal imperfections and defects have been under keen interest from the very beginning of the study of garnets. This is readily comprehensible since both the impurities and crystal imperfections offer a possibility to unpleasant processes, *e.g.* to a creation of radiative or non-radiative relaxation pathways which decrease the efficiency of lasers. In magnetic materials the imperfections may cause either global or local disturbances in the magnetic field.

In this paper we describe the use of the trivalent rare earth ions (RE^{3+}) in monitoring the properties of different garnet materials. The present study utilizes the sensitivity of the optical properties of the RE^{3+} ions to even very slight structural modifications not only in the immediate environment of the RE^{3+} ion but also further away. In order to achieve our goal we have employed the absorption, excitation and luminescence spectroscopy of the Pr^{3+} doped $\text{Y}_3\text{Ga}_5\text{O}_{12}$ (YGG), $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG), and $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ (GGG) host matrices. Finally, the aim of this paper is to throw some light on the puzzling optical properties of the RE^{3+} ions in garnets.

2. EXPERIMENTAL

2.1 Sample Preparation

The different garnets were studied both in single crystal and powder forms. The powder samples, kindly provided by Dr. J.P. Coutures [2], were prepared by heating stoichiometric mixtures of corresponding oxides. Single crystals obtained from a flux were provided by Dr. J.M. Desvignes [3]. For the YGG: Pr^{3+} samples the concentration of the dopant ion, Pr^{3+} , varied from 0.001 to the pure praseodymium compound. For the other systems, the x_{Pr} equaled to 1 %. All powder as well as single crystal samples were checked by X-ray diffraction analysis and no extra phases were found.

2.2 Optical Measurements

The visible and IR absorption of the Pr^{3+} ion was measured with a commercial Cary 2400 spectrometer. The transitions from the crystal field split ground $2^{\text{S}+1}\text{L}_{\text{J}}$ level, $^3\text{H}_4$, to the excited $^3\text{P}_{0-2}$, $^1\text{I}_6$, $^1\text{D}_2$, $^1\text{G}_4$, and $^3\text{F}_{2-4}$ levels could be observed - at least partially.

The site selective excitation spectra of the $^3\text{P}_0 \rightarrow ^3\text{H}_4$ and $^1\text{D}_2 \rightarrow ^3\text{H}_4$ transitions was carried out by a Lambda-Physics FL 2001/2 dye laser pumped by a SOPRA nitrogen laser which arrangement yields a 3 mJ dye laser pulse of 12 ns duration at a repetition rate of 4 to 100 Hz. The band width of the dye laser was around 2 cm^{-1} .

The luminescence of the Pr^{3+} ion in the garnet hosts was excited either by different blue lines of a Spectra Physics argon ion laser or selectively on the $^3\text{P}_0$ and $^1\text{D}_2$ levels by the arrangement described in the preceding chapter. The emission was dispersed by a 1 m Jarrell-Ash or a 1 m Jobin-Yvon HR1000 single monochromator equipped with photomultiplier detection. The emission in the visible range studied is dominated by the $^3\text{P}_0 \rightarrow ^3\text{H}_{4-6}$ and $^3\text{P}_0 \rightarrow ^3\text{F}_{2-4}$ transitions together with weak emission from the $^1\text{D}_2$ level to the $^3\text{H}_{\text{J}}$ ground multiplet. At 300 K the emission from the $^3\text{P}_1$ levels to the $^3\text{H}_{4-6}$ and $^3\text{F}_{2-4}$ levels could be observed, too.

Most measurements were performed at liquid helium, liquid nitrogen and room temperatures.

3. CRYSTAL STRUCTURE OF GARNETS

The rare earth aluminum and gallium garnets form two mutually isostructural series of compounds with the formula $\text{RE}_3\text{M}_5\text{O}_{12}$. However, not all rare earth elements make up garnets; in both cases some of the lighter ones (excluding yttrium), La and La to Sm, for the gallium and aluminum garnets, respectively, have not been found to yield the title compound [4]. The garnets crystallize in the cubic system (with the axis length around 12 \AA) possessing eight molecular units in the cell. The space group is $\text{Ia}\bar{3}\text{d} - \text{O}_h^{10}$ (N^{A}

230 in [5]). All RE^{3+} ions occupy an eight-coordinated site of D_2 point symmetry while 40 % of the lighter host cations reside in a six coordinated site of S_6 point symmetry. The remaining 60 % of the gallium or aluminum ions lie in a four coordinated site of S_4 symmetry. The six and four coordinated sites are rather undistorted and can be considered close to the ideal polyhedra, octahedron and tetrahedron, respectively. The coordination around the RE^{3+} ions is, on the contrary, much more distorted from the ideal dodecahedron [6].

The Pr^{3+} can be considered to replace the RE^{3+} host cation without difficulties owing to the only slight difference in the ionic radii (Pr^{3+} : $r_{\text{VIII}} = 1.126$, Gd^{3+} : $r_{\text{VIII}} = 1.053$, and Y^{3+} : $r_{\text{VIII}} = 1.019 \text{ \AA}$ [7]). On the contrary, the insertion of the RE^{3+} ions in the M^{3+} site would prove to be much more difficult due to the unusually low coordination numbers, six and four, as well as because of the large difference in the ionic radii (Ga^{3+} : $r_{\text{IV}} = 0.47$ and $r_{\text{VI}} = 0.62$; Al^{3+} : $r_{\text{IV}} = 0.39$ and $r_{\text{VI}} = 0.54 \text{ \AA}$ [7]). The insertion of the RE^{3+} ions into the six-coordinated M^{3+} site cannot, however, be ruled out owing to some previous reports dealing with the single crystals grown by the Czochralski method [8, 9].

4. RESULTS AND DISCUSSION

A general - but not unknown - observation made in the course of our studies of RE garnets is that the optical spectra of single crystal samples are more complex than those of the polycrystalline materials. This is somewhat confusing since taken into account the greater surface area of the powders they should also present a greater number of distorted RE sites. On the other hand, the single crystals prepared from high temperature melts may inherently possess more disorder of atoms between different sites because of the effect of the high entropy at higher temperatures [9]. Also the simple crystal defects due to *e.g.* occlusions of the melt may partially explain the complexity of the spectra. The preceding reasoning does not, however, exclude other effects.

Earlier reports on the RE^{3+} doped garnet systems indicate at least two (or more) different sites [8 - 11]. Our previous studies of gadolinium gallium garnet concluded the presence of a supplementary but unidentified site from the absorption spectrum of the Gd^{3+} ion [12]. The supplementary sites have been attributed to the partial occupation of the M^{3+} sites (mainly the S_6 sites) by the RE^{3+} ions [9]. This has been ascertained by the optical spectra since only the magnetic dipole transitions are then allowed obeying the selection rules $\Delta J = 0, \pm 1$. Unfortunately, the magnetic dipole transitions are very sparse for the Pr^{3+} ion and - especially at low temperature - the observation of these transitions is next to impossible. Even if the Pr^{3+} ions were to occupy the S_6 sites of the M^{3+} ions they would not be observed directly. Further more, the difference in the ionic radii between the Pr^{3+} and the RE^{3+} host cations would ascertain that the M^{3+} sites would be preferentially occupied by the latter. Since the direct observation of the occupation of the M^{3+} sites by the RE^{3+} ions seems improbable by the spectroscopy of the Pr^{3+} ions one should content to the indirect way. One possibility is offered by observing the effect of the nearby M^{3+} site occupied by a RE^{3+} ion on the symmetry and the strength of the crystal field (c.f.) felt by the Pr^{3+} ion in the regular RE site.

In the YGG host [13] two sites for the Pr^{3+} ion have been found. The sites possess rather similar c.f. splittings of the energy level schemes. The decay times of the 3P_0 level of the sites are close to each other, 19 and 17 μs , indicating the basic similarity of the sites. However, the spectra show a lowering in symmetry of the additional site as revealed by the appearance of additional lines resulting from the breakdown of the selection rules valid for the D_2 symmetry. The concentration of the Pr^{3+} ion seems to intensify the emission from the additional site as should be expected if the additional site results from a formation of a $Pr^{3+}(RE^{3+}\text{-site}) - Pr^{3+}(M^{3+}\text{-site})$ pair.

The studies of the $YAG:Pr^{3+}$ deal with single crystals with x_{Pr} equal to 1 % [14, 15]. This material yields complicated emission and excitation

spectra, especially for the transitions terminating to or originating from the 3H_4 ground level. Several $^3P_0 \rightarrow ^3H_4$ transitions have very similar line spacings indicating the same c.f. splitting of the 3H_4 level. The transitions from different sites have slightly (a few cm^{-1}) different energies seemingly due to the different position of the emitting level, 3P_0 . This behavior has been connected to the electron-phonon coupling within the 3H_4 ground level which can be able to displace the electronic transitions by up to $10 - 20 \text{ cm}^{-1}$ [16]. The emission from the 1D_2 level to the 3H_4 one is even more complex, and, moreover, depends highly on the experimental conditions.

In contrast to the emission to the ground level, the transitions to the other levels, 3H_5 and 3H_6 , of the ground multiplet show more simple behavior, in fact rather similar to the YGG case above. The studies of the YAG:Pr^{3+} system is further complicated by the possibility of minor impurity components (impossible to observe by routine X-ray analysis) since the pure praseodymium aluminum garnet does not exist.

The site selective excitation spectra of the $^3P_0 \rightarrow ^3H_4$ transition in GGG:Pr^{3+} (Figure) shows similar complex behavior to the YAG:Pr^{3+} *a priori* suggesting the presence of at least four different sites [17]. The origin of the three

Excitation spectra of the $^3P_0 \rightarrow ^3H_4$ transitions in GGG:Pr^{3+}
 $^3H_4 \rightarrow ^3P_1$ and $^3H_4 \rightarrow ^1I_6$ transitions at 4.2 K

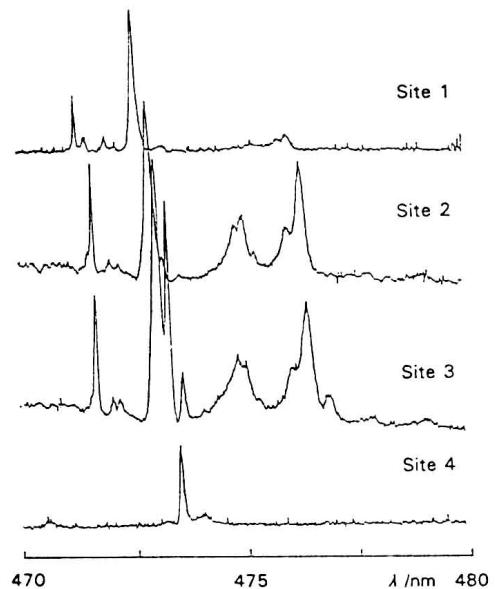


Figure The excitation spectra of the $^3P_0 \rightarrow ^3H_4$ transitions in GGG:Pr^{3+} .

sites with very similar c.f. splittings is probably similar to that in the YAG host discussed above. The fourth site being completely different from the three others might be caused by an impurity phase. In any case, it is highly improbable that this site results from the occupation of the Ga^{3+} site by a Pr^{3+} ion.

5. CONCLUSIONS

The present paper describes some features of the usually complicated absorption, excitation and luminescence spectra of the Pr^{3+} ion in three different garnets, YGG, YAG and GGG. Some suggestions to the origin of the complexity, *e.g.* the phonon-electron coupling within the $^3\text{H}_4$ ground level of the Pr^{3+} ion, the occupation of the M^{3+} sites by the RE^{3+} ions and/or simply the presence of minor impurity phases, are offered. However, no definite solution(s) to the garnets' puzzle could be obtained.

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