

RARE EARTHS SPECTROSCOPY

Proceedings of the International Symposium on Rare Earths Spectroscopy Wrodaw, Poland, September 10-15, 1984.

Editors:

B. Jeżowska-Trzebiatowsk**b** J. Legendziewicz W. Stręk



Published by

World Scientific Publishing Co. Pte. Ltd.
P. O. Box 128, Farrer Road, Singapore 9128
242, Cherry Street, Philadelphia PA 19106-1906, USA

Library of Congress Cataloging in Publication Data

International Symposium on Rare Earths
Spectroscopy (1984: Wrocław, Poland)
Rare Earths Spectroscopy.

- 1. Earths, Rare Spectra Congresses.
- Rare Earth Metal Compounds Spectra —
 Congresses.
 Phosphors Spectra Congresses.
- I. Jeżowska-Trzebiatowska, Boguslawa.
- II. Legendziewicz, J. III. Stręk, W. IV. Title. QC462.R2157 1984 546'.4 85-16927 ISBN 9971-978-38-5

Copyright © 1985 by World Scientific Publishing Co Pte Ltd.

All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the Publisher.

Printed in Singapore by Kim Hup Lee Printing Co. Pte. Ltd.

RARE EARTHS SPECTROSCOPY

PREFACE

The International Symposium "Rare Earths Spectroscopy" was held in Wrocław, Poland, September 10-15, 1984.

The Symposium was addressed to physicists and chemists interested in rare earths spectroscopy. The main aim of the Symposium was the presentation of the new achievements in spectroscopy of RE ions in solution and solid state and possibilities of their applications in the field of laser technology.

The Symposium covered the following areas in rare earth spectroscopy: spectroscopy methods in structural studies of lanthanide compounds, intensities of f-f transitions, f-d transitions, hypersensitivity, environment effects, luminescence, non-radiative transitions, energy transfer and technology of laser and phosphors.

The Symposium was attended by 120 scientists representing Austria, Brazil, China, GDR, England, Finland, France, India, Israel, Hungary, Holland, Poland, Rumania, USA, USSR and Vietnam. The plenary lectures and posters have provided a broad view of what is new in the rare earths spectroscopy and the excellent mixture of theory and experiment made this Symposium a stimulating one.

The warmest gratitude and an appreciation is expressed to all those taking part in the Symposium, who by their valuable and interesting papers and by taking an active part in discussions as well as by their freedness have greatly contributed to the success of the RES Symposium.

The Organizers acknowledge financial support from the Polish Academy of Sciences, the Technical University of Wrocław and University of Wrocław.

Furthermore we thank our colleagues from the Organizing Committee for their efforts, enthusiasm and energy without which this Symposium would not have been successful.

Wrocław, 20th March, 1985

B Jeżowska-Trzebiatowska J Legendziewicz W Stręk

CONTENTS

Pre	face	v
I	SPECTROSCOPY METHODS IN STRUCTURAL STUDY OF LANTHANIDE COMPOUNDS	
	Free-ion spectra of interest to solid and solution spectroscopists $J\ G\ Conway$	3
	Regularities in the lanthanide and actinide properties G V Ionova and V I Spitsyn	21
	Electron correlation effects in rare earth systems K Jankowski	39
	Analogies and differences in spectral properties of ions with 4f ³ and 5f ³ electronic configurations J Drożdżyński	57
	Lanthanide ions as NMR probes L Banci, I Bertini and C Luchinat	80
	Chemical NMR spectroscopy of the lanthanide nuclei J Mason	100
	Optical activity of lanthanide single crystals M Chowdhury and B Karmakar	114
	Stability constants and absorption spectra of the europium (II)-aminopolycarboxylate complexes G Laurenczy and E Brücher	127
	Energy levels of Er ³⁺ in KY ₃ F ₁₀ E Antic-Fidancev, M Lemaitre-Blaise and P Porcher	134

Charge transfer at Eu impurity in CdF ₂ crystals M Godlewski, D Hommel, J M Langer and H Przybylińska	140
Absorption and luminescence spectra of lanthanide compounds with alanine, correlation with X-ray data J Legendziewicz, T Głowiak, E Huskowska and Dao-Cong-Ngoan	146
Hyperfine structure of the f-electron ions in the crystal field of cubic symmetry B Wróbel and W Wojciechowski	156
Correlations in spectroscopy of trivalent lanthanide ions in solutions of complexes S V Beltyukova, N A Nazarenko and N S Poluektov	162
Spectroscopy of Nd ³⁺ complexes with NTA K Bukietyńska and A Mondry	167
Local distortions around Eu^{2+} ions in PbF_2 single crystals J Kuriata	174
Microscopic simulation of a locally compensated centre of Eu ³⁺ in CdF ₂ K Leśniak	180
The template synthesis and spectral characterization of nitrogen donor macrocyclic complexes of lanthanides W Radecka-Paryzek	186
Theoretically improved INDO method including resonance integrals derived from Heisenberg equation of motion for ground and excited state properties of f-electron elements J Leszczyński	191
Infrared spectra of rare earth complexes of 1-(2-pyridylazo)- 2-naphthol PM Drożdżewski	196

	Relativistic effects in the zero-field splitting of ${}^8S_{7/2}$ (4f ⁷) ions in MeF ₂ single crystals W Pastusiak and J Kuriata	202
	Spectroscopic properties of the $\mathrm{Dy^{3}}^+$ ions in single $\mathrm{KY_xDy_{1-x}(MoO_4)_2}$ crystals J Hanuza, L Macalik, P Dereń, W Ryba-Romanowski, W Stręk and B Jeżowska-Trzebiatowska	209
	Ultrasonic velocity dispersion study in aqueous solutions of lanthanide salts B Voleišienė, A Voleišis and E Yaronis	219
	Crystal-field three-parameter model of Er ³⁺ , Nd ³⁺ in phosphate S Xia, P Xu and S Liu	225
	The calculation of the splitting chain of crystal-field energy levels of Pr ³⁺ in LiYF ₄ crystal S Xia, F Huang, P Xu and S Liu	230
	Comparison of the effect of rare earths, d-transition metals and some metals of the main groups on the aromatic system of benzoic acid W Lewandowski	236
II	INTENSITIES OF f-f TRANSITIONS, f-d TRANSITIONS, HYPERSENSITIVITY	
	Lanthanide (III) f-f transition probabilities S F Mason and B Stewart	245
	A systematic view of transition intensities in the spectra of actinides and lanthanides in condensed phases W T Carnall, H Crosswhite and K Rajnak	267
	What do f-f electric dipole intensity parameters tell us about mechanism? MFReid and FSRichardson	298

Vacuum ultraviolet absorption spectra of CaF_2 : RE^{3+} crystals T Szczurek and M Schlesinger	309
Intensity analysis and luminescence spectra of lanthanide compounds in solution and in solid state J Legendziewicz, G Oczko and B Keller	331
Intensity analysis of f-f transitions of the PrP ₅ O ₁₄ crystal W Stręk, C Szafrański, P Dereń, K Jabłoński and B Jeżowska-Trzebiatowska	340
Spectroscopic properties of KPr _x Y _{1-x} P ₄ O ₁₂ crystals M Malinowski	348
Vibronic structure of the neodymium hypersensitive transitions in vanadates E Antic-Fidancev, M Lemaitre-Blaise, P Caro, B Piriou and W Stręk	354
Relations between the hypersensitive transitions intensity and position in spectra and LJ designations of ground levels of trivalent lanthanide ions NS Poluektov, NA Nazarenko, VT Mischenko and SV Beltyukova	363
Electron correlation third-order contributions to the forced electric-dipole transition probabilities in f^N systems L $Smentek-Mielczarek$	368
Determination of oscillator strengths of La II lines excited in a plasma generated near a ferroelectric surface A Goly, J Kusz and S Weniger	373
Spectroscopic properties of neodymium ion-intensity and band shift Q Su and Y Lu	379
Spectral parameters of Tm ³⁺ in crystal TmP ₅ O ₁₄ calculated by Judd-Ofelt theory Q Su, Q Wang, S Wu, G Hong and S Yue	385

III	LUMINESCENCE OF LANTHANIDE IONS	
	Chemical aspects of rare-earth luminescence G Blasse	393
	Fluorescence enhancement induced by the presence of small silver particles in Eu ³⁺ doped materials O L Malta, P A Santa-Cruz, G F de Sá and F Auzel	405
	Charge transfer excitation of the Nd ³⁺ , Sm ³⁺ , Dy ³⁺ , Ho ³⁺ , Er ³⁺ and Tm ³⁺ emission in sulfides A Garcia, R Ibañez and C Fouassier	412
	Stokes and Anti-Stokes luminescence of Er ³⁺ in yttrium orthoborates N P Efryushina, V P Dotsenko, E A Zhikhareva and S V Ermakova	427
	Inhomogeneity of $KNd_xRE_{1-x}P_4O_{12}$ (RE = Y, Pr and Gd) system studied by the site selection time-resolved spectroscopy technique M Malinowski	433
	Luminescence of zinc sulphide-type phosphors I. Luminescence of Cu activated ZnS phosphors containing Sm³ + or Eu³ + ions M Aneculăese, E J Popovici, D Macarovici and V Ursu	437
	Chemiluminescent reactions of the systems: Eu ²⁺ /Eu ³⁺ -ATP or ADP, AMP, c-AMP-H ₂ O ₂ of biological interest <i>M Elbanowski, M Paetz and J Sławiński</i>	443
	The investigation of Eu(III), Gd(III), Tb(III) and Dy(III) fluorescence in aqueous solutions M Elbanowski, S Lis, B Mąkowska and J Konarski	449
	Some effects in KMnCl ₃ and KMnCl ₃ : Sm ³⁺ luminescence M Pawłowska, W Stręk, B Jeżowska-Trzebiatowska and W Wojciechowski	455

	Temperature localization of Yb ³⁺ excitation in CdF ₂ : Er, Yb crystals A Stapor	461
IV	NON-RADIATIVE PROCESSES IN LUMINESCENT MATERIALS Effects of electron-phonon interaction on optical spectra of TR-ions activated crystals Yu E Perlin	469
	Spatial and spectral migration of energy of rare earth ions in insulators WM Yen	484
	UP-conversion by energy transfers (APTE effect): processes, recent results and role in applied systems F Auzel	502
	The Auger effect — a new nonradiative quenching mechanism of rare earth impurities luminescence JM Langer	523
	Conversion of 1.06 μ m Nd ³⁺ : YAG laser radiation into green fluorescence in Cs ₂ NaEr _{0.1} Yb _{0.9} Cl ₆ single crystals W Ryba-Romanowski, F BenBouzid, Z Mazurak and B Jeżowska-Trzebiatowska	545
	Eu ²⁺ -Mn ²⁺ energy transfer in doubly doped KCl crystals R Cywiński and E Mugeński	551
	Electron transfer quenching and outer-sphere charge transfer transitions in the $[Eu \subset 2.2.1]^{3+}$ -M(CN) ₆ ⁴⁻ systems N Sabbatini, A Bonazzi, M Ciano and V Balzani	559
	Phonon-assisted exciton energy transfer in GaP: N M Bugajski, W Lewandowski and H Mariette	563

		XIII
	Lattice relaxation in virtual photon process and stimulated non-radiative transitions $ZDLuo$	569
V	TWO-PHOTON TRANSITIONS	
	Two-photon rare-earth spectroscopy BR Judd	575
	Fluorescence dynamics of GdCl ₃ with magnetic field following one and two photon pulsed excitations R Mahiou, B Jacquier and R Moncorgé	579
VI	TECHNOLOGY AND MATERIALS	
	Luminescence and nonradiative relaxation of rare earths in amorphous fluoride materials R Reisfeld	587
	Recent developments in lamp phosphors based on rare earths M Leskelä	617
	Spectroscopic properties of glasses doped with Cr(III) and Nd(III) E Łukowiak, W Stręk, M Szymański, J Sarzyński, E Mugeński, R Cywiński and B Jeżowska-Trzebiatowska	629
	Vibronic transitions in non-centrosymmetric lanthanide complexes W Stręk	636
	Spectroscopy of rare earth impurities in ZnS bulk crystals D Hommel, H Hartmann, M Godlewski, J M Langer and A Stapor	643

Spectroscopic characteristics of trivalent rare-earth in double	
potassium-lanthanide tungstates and molybdates	649
J Hanuza and L Macalik	
Luminescence of ZnS-type phosphors.	
II. Luminescent properties of (Zn, Cd) S and Zn(S, Se)	
phosphors containing Cu and/or Er	666
E J Popovici, M Aneculăese, D Macarovici and V Ursu	

I. Spectroscopy Methods in Structural Study of Lanthanide Compounds

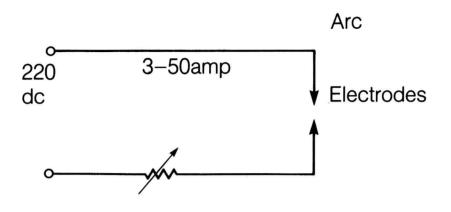
FREE-ION SPECTRA OF INTEREST TO SOLID AND SOLUTION SPECTROSCOPISTS

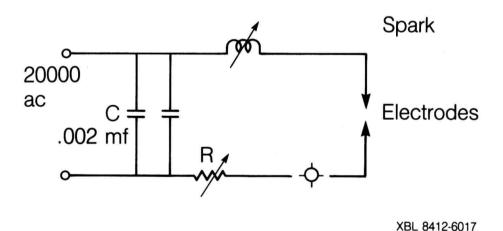
John G. Conway Lawrence Berkeley Laboratory University of California Berkeley, California 94720

A great deal of information is known about the free-ion spectra of the neutral and singly ionized rare earths because of the ease with which these spectra can be produced. Considerably less is known about the doubly and triply ionized rare earths. A discussion of the experimental difficulties, the present state of knowledge, and the predicted information will be given.

1. INTRODUCTION

The first observations of rare earth spectra used arcs and sparks to excite the spectra. These electrical sources excite predominantly the second spectra (II), that is, the first ion (+1). figure 1 is the electrical circuit for such sources. In the 1950's microwave excitation was tried and this type of excitation produced mainly the neutral spectra. These sources are known as electrodeless discharge lamps (EDL). About 70 to 80% of the lines emitted by an electrodeless discharge lamp run at high-atom-density are from the neutral spectrum, however, if run at low-atom-density the spectrum will reduce to less than 50% neutral, the remaining lines are of the first ion. The EDL has other advantages, the material under study is sealed in a quartz tube and has no electrodes and in most cases it is not necessary to have a carrier gas to start the discharge. element under study is added usually as the iodide or some other high vapor pressure compound. This source is particulary good for work with radioactive elements. A typical lamp has dimensions, 5 mm inside diameter and 25 mm long and pressures < 10⁻⁵torr and contains on the order of 50 to 100 micrograms. The EDL will operate in a magnetic field of the order of 30,000 gauss making possible Zeeman studies. A diagram of such an arrangement is shown in figure 2. Another source which requires much larger samples is the hollow cathode. This source dates back to the 1920's. It emits primarily the neutral spectrum but when operated in the pulsed mode can be made to give both the first.





 $\underline{\text{Figure 1}}$: Circuit diagram for a dc arc source and a high frequency spark source.