RARE-EARTH INFORMATION CENTER NEWS

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MIGRATING HOLES

L. Ozawa studied the excitation mechanisms of various rare earth activator ions by electron beam irradiation of phosphor crystals [*J. Electrochem. Soc.*, **128,** 140-5 (1981)]. The time-averaged luminescence intensities of the phosphors were plotted versus the concentration of various activator ions. These curves, referred to as concentration dependence (CD) curves, were used to indicate the manner of excitation. It was found that if the initial slope of the CD curve was 1.0, the excitation was by direct interaction of the incident electrons, but if the slope was less than 1.0 the excitation involved recombination centers for electrons and holes. Upon examination of the curves it was discovered that rare earths that possess both +3 and +2 valencies (Eu, Dy and Sm) [*Editor's note:* The Dy^{2+} state is unusual and difficult to obtain.] act as recombination centers in all three phosphors (Y_2O_3, YVO_4 and Y_2O_2S) tested while rare earths that possess both +3 and +4 valencies (Pr and Tb) act as recombination centers in Y_2O_2S only. Rare earths that possess only the +3 valency failed to act as recombination centers in any of the three phosphors. It was further determined that Eu, Dy and Sm first trap an electron then capture a hole while Pr and Tb trap a hole then capture an electron. It is the excited +3 form of the ion that luminesces.

After studying the general systems, Ozawa concentrated his efforts on Y_2O_2S using Eu and Tb as the activator ion impurities [*J. Electrochem. Soc.*, **128,** 2984-5 (1981) and **129,** 1535-40 (1982)]. In the first Y_2O_2S paper he compares the CD curve from electron beam excitation to the CD curves using radiations of 200, 320 and 417 nm. From comparison of intensities it is concluded that only one percent of the luminescence of Eu^{3+} is from direct excitation. In the second Y_2O_2S paper, Ozawa studied the migration of electrons and holes, the effect of electron beam pulse width on CD curves and the lifetimes of the excited activator ions. It was found that the electrons and holes migrate in only one direction, apparently under the influence of some indirect field. Terbium ions were used to measure hole migration and europium to measure electron migration. The lifetime of the excited ions was found to be about 500 μs. The author believes that further experiments using a single crystal or a thin film are necessary to get a complete picture of the motion of carriers in highly insulated phosphor crystals.

ALBERT SAUVEUR AWARD

Dr. Frank H. Spedding, professor emeritus, Iowa State University, was the recipient of the Albert Sauveur achievement award presented by the American Society for Metals at its annual awards dinner in St. Louis, Missouri, October 25, 1982.

The award, established in 1934 in honor of the distinguished teacher, metallographer, and metallurgist, recognizes pioneering metallurgical achievements that have stimulated organized work along similar lines to such an extent that a marked basic advance has been made in metallurgical knowledge. Dr. Spedding was cited for his pioneering achievements in the production of the lanthanide elements, scandium, yttrium, uranium and thorium.

Rotating Faradays

M. J. Weber has compiled into a report, M-103, some data on various "Faraday Rotator Materials." A limited number of the loose leaf reports are available from the author at Lawrence Livermore Laboratory, P.O. Box 808, Mail Code L-472, Livermore, CA 94550 (U.S.A.). The report, issued in June 1982, includes the following sections: introduction; measurement techniques and data analysis; tables of Faraday rotator materials; description of data sheets; glass data sheets and crystal data sheets.

The author describes the report in the Preface as follows:

"This manual presents data on Faraday rotation properties for a number of different materials examined during the past four years. It is not a comprehensive survey. Although it may have the appearance of being an eclectic selection of materials, the samples are representative of the many materials of conceivable interest for isolators for high power lasers and other applications. Because laser applications were the primary motivation for this survey, data on the absorption and nonlinear optical properties of the materials are also included. The wavelength region of interest was limited to the near-infrared through the near-ultra-violet. The Faraday rotator materials considered include diamagnetic and paramagnetic-doped glasses and crystals. Therefore Faraday rotation in ferromagnetic materials, such as rare-earth iron garnets, or in chalcogenide materials for 10μm applicatinos are not covered."

According to the author, Faraday rotation is covered in many standard textbooks and only a brief review is presented in the introduction. References that provide more extensive

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LETTER TO THE EDITOR

Dear Editor:

I have a comment on a small point in the latest *RIC News* [September 1, 1982]. On page 2, in the article on "Amorphous Magnetism" noting the recent Soviet review, there is the phrase at the end of the leading paragraph "the appearance of the new field of amorphous magnetism." If you'll forgive me, I found it embarrassing to read this in 1982 because the effort in this area of research has been going very strongly for about a decade, with origins that go back even farther.

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Editor's Comment:

In this article we were paraphrasing the author, G. A. Petrakovskii. We apologize for any false impressions this may have given our readers.

Spinning Electrons

F. Mehran and K. W. H. Stevens are the authors of a review [*Phys. Reports* **85**, 123-160 (1982)] entitled "Electron Spin Resonance of Impurities in Magnetic Insulators." While the title and abstract reads ESR the paper talks of EPR which might be confusing to some people new to the field.

Electron paramagnetic resonance (EPR) studies of impurities are usually carried out in diamagnetic compounds to reduce the magnetic interactions between the impurity and the host ions. This review covers the spin resonance of impurities in paramagnetic hosts and, more particularly, impurity S-state ions in compounds with paramagnetic host ions of the lanthanides. Among the interesting phenomena observable and measurable in these experiments are: (1) symmetric and antisymmetric exchange interactions between the impurities and the host ions determined from the indirect superhyperfine and pseudo-Zeeman interactions and pseudo-crystal field effects: (2) the Jahn-Teller induced random strains effects which result in the fine structure linewidths being dependent on the magnetic field; and (3) the nature

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Lanthanide Chelation

University of Florida chemists Linda Hirschy, Eric Dose and James Winefordner believe lanthanide sensitized luminescence will be a notable addition to the list of analytical techniques. Hirschy, in her presentation at the American Chemical Society's meeting in Kansas City, reported the group has used the technique to analyze for tetracycline and its analogs with detection limits of about 1 ppm. They are now working to extend the method to other organic species.

The Florida team's method makes use of a technique widely used to improve the sensitivity for luminescence detection of the lanthanides themselves. The organic ligands have broadband absorption spectra which absorb energy at a characteristic wavelength. The absorbed energy is transferred from the lowest triplet level of the complex to the 4*f* level of the ion (specifically Eu^{3+} in this application) by intramolecular energy transfer. The energy is then emitted in a narrow linelike band (615 nm for Eu^{3+}) and measured to quantify the ligand involved. Selectivity can be obtained by choosing the appropriate excitation wavelength for the organic ligand of interest.

BUSINESS NEWS

Molycorp, Inc.

Molycorp, Inc. has announced the completion of a two-year, $36 million plant expansion and environmental control program at its Washington, Pennsylvania facility. Included in the expansion was a new rare earth metals plant to produce high-purity samarium metal from the oxide using a controlled-atmosphere induction furnace. Permanent employment at the facility will increase by 25 percent when full production is achieved.

Rotating Faradays

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treatment of magnetooptical effects in solids as well as references to other tabulations of Verdet constants for Faraday rotator materials are listed at the end of the introduction.

All the paramagnetic Faraday rotator materials listed in this report have rare earths as the active ion.

3rd REMST - 15th RERCP

The Proceedings of the 15th Rare Earth Research Conference, held June 15-18, 1981 at Rolla, Missouri are available in a single volume entitled "The Rare Earths in Modern Science and Technology. Volume 3." The 120 papers are classified and divided into the following sections: Spedding Award address (1), bioinorganic chemistry (9), organometallic and coordination chemistry (10), spectroscopy (26), phase equilibrium and thermodynamics (16), structural and solid state chemistry (14), magnetic properties (23), hydrides (8), purification and analysis (8), and new applications (5). Included in this volume are the first contributions from scientists in the People's Republic of China to a Rare Earth Research Conference.

Edited by G. J. McCarthy, H. B. Silber and J. J. Rhyne, the Proceedings were published by Plenum Press (1982) in a volume containing 611 pages. The cost of the book is $59.50 and copies may be obtained from Customer Services, Plenum Press, 233 Spring Street, New York, NY 10013 (U.S.A.).

Bibliography Under Ceramics?

As previously reported [*RIC News*, **XVII**, No. 1, p4 (1982)] Molycorp is working on a projected four volume set of bibliographies on the use of rare earths in glass and ceramics. The first two were on glasses, the third on ceramics. Volume Three, alias Application Report 8210, is entitled "Abstracts of Major Work Concerning Lanthanides (Rare Earths) in Refractories, Engineering Ceramics and Polishing Compounds." The sections in this bibliography include silicon nitride, zirconia and hafnia, alumina, basic refractories, rare earth ceramics, mixed oxide ceramics, polishing compounds, and miscellaneous. Entries consist of the title, author(s), reference and a brief summary of the article. A special locater section at the end of the report lists the abstract number, rare earth involved, author(s) and country, and source, or if patent, to whom it was assigned. These Application Reports are available free from Molycorp, Inc., 709 Westchester Avenue, White Plains, NY 10604 (U.S.A.), telephone (914)-997-8880.

DOE Recognition

The research efforts of two rare earth oriented groups were among the eight recognized by the Department of Energy (DOE) as winners in the 1982 Materials Sciences Research Competition. This competition takes place annually and reviews research accomplishments submitted by all DOE laboratories.

S. K. Sinha, G. W. Crabtree, D. G. Hinks of Argonne National Laboratory and H. A. Mook of Oak Ridge National Laboratory won the Outstanding Scientific Accomplishment award in the Solid State Physics category. The subject of their research presentation is "Coexistence of Superconductivity and Magnetism in Single Crystal $ErRh_4B_4$."

The team of K. A. Gschneidner, Jr. and K. Ikeda of Ames Laboratory, Iowa State University, were co-winners of the Outstanding Scientific Accomplishment award in the Metallurgy and Ceramics category. The subject of their research presentation is "Quenching of Spin Fluctuations and Inducing of Magnetic Moments in Metamagnetic Materials."

The purpose of the competition is to identify individual laboratory scientists who have achieved outstanding research results. These research achievements are judged by the DOE's Materials Sciences staff and the Laboratory Managers. The winners' reward consists primarily of recognition by the DOE community of the outstanding research result plus a small amount of additional research funding.

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GMELIN HANDBOOKS

The first volume of the 8th Edition of the *Gmelin Handbooks* was published in 1926 and dealt with the noble gases. Since then about 440 other volumes or supplements have been published with 31 more scheduled for 1982-1983. Twenty five of these published or proposed books deal with the rare earths.

The latest two rare earth books (both in English) are about the chlorides and are volumes C4a and C4b of system number 39. Volume C4a (December 1981) includes comparative and broadly valid data for the rare earth chlorides and chloride systems while volume C4b (April 1982) includes data on individual chlorides and chloride systems.

Molecules and ions in the gas phase or as matrix-isolated species are described in the first part of volume C4a. The following sections treat the properties of chlorides in the solid state, solutions and melts. The longest section describes anhydrous trichlorides. Main topics in this section are preparation, crystallographic properties, resonance spectroscopy, thermal properties, and chemical reactions. Similar data are presented for the hydrated trichlorides. Another large section covers the physical properties of trichloride solutions.

The sections on the individual chlorides in volume C4b deal mainly with the preparation, properties, and chemical reactions of the various rare earth chloride compounds starting with the lowest valence states. Phase diagrams and solutions are discussed in separate parts of the section. References to C4a, the comparative volume, are at the head of each section.

The physical properties of rare earth ions in crystal lattices and the chemistry of rare earth complexes are only briefly described in these two volumes. According to the publisher these topics will be covered fully in later volumes of the *Handbook*.

The prices for volumes C4a (286 pages) and C4b (342 pages) are DM 851 and DM 876 or about $405 and $415, respectively. Information about the *Gmelin Handbooks* and addresses of their dealers may be obtained from Springer-Verlag, 4005-Marketing Gmelin, Heidelberger Platz 3, D-1000 Berlin 33, West Germany.

6th REPM Workshop

The combined proceedings of the 6th International Workshop on Rare Earth-Cobalt Permanent Magnets and Their Applications (Aug. 31-Sept. 2, 1982) and the 3rd International Symposium on Magnetic Anisotrophy and Coercivity in Rare Earth-Transition Metal Alloys (Sept. 3, 1982) have been published. The 46 papers from the Workshop cover the production of these magnets, the measurement and evaluation of their properties, standards, and applications. Also covered are the problems concerning the availability of raw materials and the development of new materials and processes with commercial applications in mind. The Symposium is closely connected with the Workshop and the 21 papers deal with the basic understanding of the relationship between magnetocrystalline anisotropy and coercivity achieved in laboratory specimens as well as industrial magnets. According to H. R. Kirchmayer, Technical University of Vienna, in his introductory remarks, the seemingly pure scientific effort to evaluate and measure the anisotropy and coercivity of rare earth intermetallic compounds has been one of the main driving forces behind the effort to achieve better and better rare earth permanent magnets.

The 6th REPM proceedings are edited and distributed by Dr. Josef Fidler, Institut für Angewandte Physik, Technische Universität Wien, Karlsplatz 13, A-1040 Wien (Austria). The price is $40.00 plus postage. They can also be acquired by writing to Dr. K. Strnat, University of Dayton, School of Engineering, Magnetics Laboratory KL-365, Dayton, Ohio 45469 (U.S.A.).

The 5th REPM proceedings are also available from Dr. Strnat or from Mr. T. Kurino, General Manager, The Society of Non-Traditional Technology, Kotohira Kaikan Bldg, No. 2-8 1-Chome, Toranomon, Minato-Ku, Tokyo 105 (Japan). The price for the 5th REPM proceedings is $35.00 plus postage.

$$ SPONSORS $$

The second quarter of fiscal year 1983 was slow. Eight companies renewed their support and we welcomed one new member to our family. This brings to 18 the number of companies that have furnished support for the Center this year. At this time last year 28 companies had pledged their support. To paraphrase the old saying "Now is the time for all men to come to our aid." The eight companies renewing this quarter and the new member of the family are listed below with the number of years that company has supported the Center given in parentheses.

CERAC, Inc., U.S.A. (6)
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Spinning Electrons

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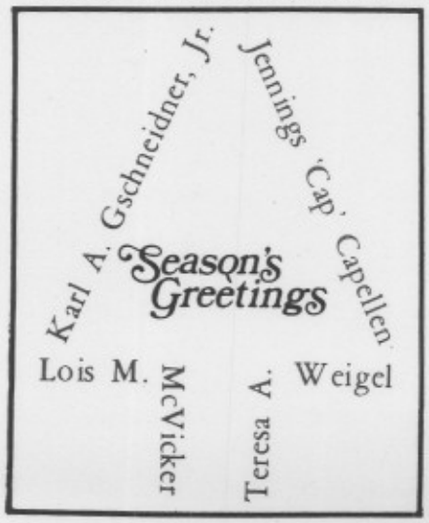
of the dynamical interactions of the host ions which result in lifetime broadenings of the impurity spectra.

The samarium chalcogenides and rare earth zircons are chosen as illustrative examples of paramagnetic insulators for the review. The rare earth zircons considered are those whose rare earth element has an even number of 4*f* electrons.

The review, which contains a bibliography of 215 references, may be purchased directly from the publisher (North-Holland Publishing, Amsterdam) for Dfl. 20.00 (~$7.00).



KRAMERS IONS

In the first of three proposed papers, [*J. Chem. Phys.* **76,** 3877-89 (1982)], N. C. Chang et al. studied the optical absorption and fluorescence spectra of the Kramer ions Ce^{3+}, Sm^{3+}, Dy^{3+}, and Yb^{3+} in the C_2 sites of Y_2O_3. A crystal field analysis of this new data and of previously published data on Nd^{3+} and Er^{3+} was performed by means of a crystal-field Hamiltonian of C_2 symmetry. Parameters were varied to obtain a best root mean square fit of the calculated and experimental levels for Nd, Sm, Dy and Er in Y_2O_3. The resultant crystal-field parameters were used by the authors along with the three-parameter theory of crystal fields to obtain a smoothed set of crystal-field parameters for the entire lanthanide series. Levels computed with these parameters are compared with the authors' experimental results for Ce^{3+} and Yb^{3+} and predictions made for the crystal-field splittings of Gd^{3+}.

Other papers in this series, according to the authors, will cover all R^{3+} non-Kramer ions in C_2 sites and all R^{3+} ions in the C_{3i} sites. Unpublished and extant data, along with crystal field splitting calculations, will be included in each paper.

The optical spectra of tripositive rare earth ions doped into single crystal Y_2O_3 is of interest because the oxide lattice has proven to be an excellent host material for some of the most powerful lasers built.

Electro-Molecular Propulsion

A new separation technique, being developed by Haber, Inc. (Towaco, N.J.), is reported in *Ind. Chem. News,* **3,** [5], 9 (1982). The process is entitled electro-molecular propulsion (EMP) and according to its inventors will perform separations and purifications that cannot be done by conventional solvent extractions and will speed up those separations now carried out by solvent extractions.

The EMP effect was discovered by company president Norman Haber more than 10 years ago and he was granted patents in 1976 and 1979. In EMP, the material to be extracted is first treated, or tailored with different solvents that possess electrical conducting properties similar to the desired material. When an electrical current passes through the separation cell, the molecules of the tailored material separate out from the residual or impure materials, which are immobilized by the current.

EMP is still in the development phase, according to Haber's Robert McPhearson, and has only been tested on small quantities. "However, we have done EMP separations in minutes that would take days using current industrial processes," states McPhearson, "and the process is being scaled up." If the EMP process can be made commercially applicable to the rare earths, McPhearson claims "it will make abundant 16 elements that chemists don't have in commercial quantities today."

Haber, Inc. has set no timetable for commercial production. They do not intend to lease or sell EMP extractors, but rather to enter into joint ventures with other companies.

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