RARE-EARTH INFORMATION CENTER NEWS

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Rare Earth Research at University of São Paulo

First row, left to right: L. R. F. Carvalho, L. B. Zinner, R. Najjar, and A. M. P. Felicissimo; **Second row:** W. Oliveira and G. Vicentini.

Rare Earth Complexes Examined—

The investigation of complexes of rare earth salts with ligands containing oxygen as donor atom at the Institute of Chemistry, University of São Paulo, Brazil, started in 1960. The research group is headed by Professor G. Vicentini and includes Associate Professor L. B. Zinner and Doctors L. R. F. Carvalho, A. M. P. Felicissimo, R. Najjar, W. Oliveira, and J. C. Prado.

The first investigations, using dioxanne, have been expanded to include a considerable number of amides, cyclic sulfoxides, amine oxides, and other ligands. Salts containing chloride, bromide, iodide, isothiocyanate, nitrate, perchlorate, hexafluorophosphate, methanesulfonate, trifluromethanesulfonate, and trifluoroacetate have been systematically investigated.

The preparation of the complexes is followed by a characterization using microanalytical procedures, x-ray patterns, electrolytic conductance measurements in non-aqueous solvents, and infrared, electronic-absorption and emission spectra. In some cases differential thermal analysis and thermogravimetric techniques are also used. Recently, in collaboration with Professor E. E. Castellano (Physical and Chemical Institute of São Carlos) and Professor R. W. Becker (Federal University of Parana), the structures of several compounds have been studied by single crystal x-ray diffraction methods.

In recent years, special interest has been devoted to: (a) investigation of electronic absorption spectra of the neodymium complexes, both in the solid state and in solution, to obtain information concerning the nature of bonding, environmental effects around the central ions and influence of the basicity of the ligands on the intensity of hypersensitive bands; and (b) the fluorescence, as well as absorption, spectra which is often used to determine coordination numbers, symmetry and geometry of the polyhedra, and nature of bonding.

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1983 Frank H. Spedding Award

The Frank H. Spedding Award, first presented at the Fourteenth Rare Earth Research Conference in 1979, is given in recognition of distinguished contributions in the field of rare earth science and/or technology. Nominations are now being sought from the world-wide community of scientists and engineers for the 1983 Award to be made at the Sixteenth Rare Earth Research Conference, April 1983, at Florida State University, Tallahasse. An individual can present more than one candidate for consideration. Seconding letters are encouraged, particularly if they present significant information not covered by the nominator.

Forms for use in making nominations can be obtained from the Executive Secretary of the Frank H. Spedding Award Committee. Nomination forms, including seconding letters and other supporting documents, must be in the hands of the Executive Secretary by October 1, 1982.

Dr. John B. Gruber, Executive Secretary
Frank H. Spedding Award Committee
Vice President for Academic Affairs
Portland State University
Portland, Oregon 97207
(503) 229-3421

Phase Diagram Project

K. A. Gschneidner, Jr. and coworkers of the Ames Laboratory and Rare-Earth Information Center at Iowa State University have undertaken the sizable job of compiling and evaluating the data on the binary phase relationships of the rare earths with other elements. The first binary systems evaluated will be the intra rare earth alloys; then the binary systems of the

(continued on page 6)

1981 Tswett Medal

R. E. Sievers has been named to receive one of the two 1981 M. S. Tswett Chromatography Medals in recognition of his contributions to the application of chromatography to the environmental sciences. His pioneering research has helped establish chromatography as one of the most broadly applicable tools for environmental analysis.

Sievers received his M.S. (1958) and his Ph.D. (1960) from the University of Illinois. He was one of the principal investigators for the NASA Apollo Lunar Analysis Project. In 1975 he was appointed Professor of Chemistry at the University of Colorado and is currently serving as the Director of the Cooperative Institute for Research in Environmental Sciences at the University. Long time *RIC News* readers will recall our review of a book entitled "NMR Shift Reagents" that was edited by Sievers [see *RIC News* **VIII**, No. 4, 2 (1973)].

FIRST CONFERENCE

The Metals Society, London, and the Chinese Society of Metals, Beijing, are pleased to announce the first International Conference on the Production and Applications of Less Common Metals to be held November 8-10, 1982 in Hangzhou, The People's Republic of China. The conference hopes to provide an appraisal of recent developments in the production and application of less common metals, including the rare earths, and to create the opportunity to establish contacts between specialists from China and the other countries. Topics include corrosion-resistant alloys, superconductivity, superplasticity, memory alloys, energy generation, and storage and catalysis. Visits to industrial, academic, and research organizations may be arranged after the conference and product literature will be exhibited during the meetings. English is the official conference language. For more information contact: K. L. Wakelam—marketing director, The Metals Society, 1 Carlton House, Terrace, London SW1Y 5DB. Telephone 01-

Contributors

Six companies have contributed to the Center during the last 3 months bringing the total number of contributors to 34 for the year. Five companies renewed their support and one new member was added. This quarter's companies are listed below. The number in parentheses is the number of years that company has supported the Center.

Allied Chemical Corporation, U.S.A. (10)
Atomergic Chemetals, Inc., U.S.A. (10)
GTE Laboratories, Inc., U.S.A. (10)
MCI-Megon, A.S., Norway (11)
Metserv, Inc., U.S.A. (1)
Research Chemicals, U.S.A. (14)

Thermal Stability

Amorphous Gd-Fe alloys have a sharply lower thermal stability than do Zr-Fe and Th-Fe alloys even though Zr and Th have metallic radii and electronegativities similar to Gd. The Gd-Fe system also seems to be the exception to the rule that states: "the tendency to glass formation is generally highest near deep eutectics." These previously reported facts led K. H. J. Buschow and A. G. Dirks to investigate a series of amorphous alloys of rare earths with transition metals. [*J. Electrochem. Soc.* **127**, 2430-2 (1980)]. They investigated the $R_{69}Ni_{31}$ alloys with R = La, Nd, Gd, Tb, Dy, and Er; the $Gd_{0.6}M_{0.4}$ alloys with M = Fe, Mn, Co, and Ni; and the Tb-Fe and Er-Fe systems.

Using the first peak maximum in the differential scanning calorimeter (DSC) tracing as the crystallization temperature (T_{cr}) they found that the T_{cr} in the $R_{69}Ni_{31}$ alloy varies linearly from 400 K to 630 K on going from La to Er. The thermal stabilities of the $Gd_{0.6}M_{0.4}$ alloys were found to follow the pattern Fe<Mn<Co<Ni. The DSC tracings for the rare earth rich portions of the Tb-Fe and Er-Fe systems were found to be similar within each system regardless of the compositions.

They concluded that the thermal stability of an amorphous alloy will be largely determined by the temperature dependence of the viscosity. Crystallization sets in whenever the temperature is high enough to match ΔE, which is the energy needed to cre- [illegible] of the smallest atom in the alloy. It can be shown that the enthalpy of formation of a hole of the size of a 3*d* atom (ΔH_{3d}) in rare earth rich $R_{1-x}M_x$ alloys is less than the ΔH_{3d} in the pure 3*d* metals. Furthermore, in alloys with a fixed transition metal, the values of ΔH_{3d} increase on going from La to Lu.

RE's in the News

Nice Reflection

C. Buckwalter, Jr. of Battelle's Northwest Laboatory has developed a better mirror using a rare earth solution. The process involves coating the glass substrate with the rare earth solution before coating it with silver. The rare earths inhibit corrosion on the substrate which usually causes the silver backing to separate. The process was originally developed to improve the weatherability of solar collecting mirrors but could also be used to improve mirrors for consumers.

RE Phosphors in NDT

Once a new material is developed for a particular application, other applications are developed to make use of the new material. Such is the case with rare earth oxysulfide phosphors. First developed for x-ray intensifying screens in medical diagnostic radiology, they have now been incorporated, by the Lockheed Missles & Space Corporation, into a filmless, real-time inspection system for non-destructive testing of such things as strategic missile motors. The rare earth screen converts x-ray images to optical images which are then converted to electronic signals for either monitor observation or video recording. Under optimum conditions the system can detect flaws as small as 0.5 percent of the object's thickness.

Measuring Neutrino Mass. . .

. . .must be harder than it sounds since researchers have been at it for over 30 years! Relatively recently holmium-163 got into the act. One way of measuring neutrinos is to measure the shape of the photon spectra resulting when an orbital electron has been captured by the nucleus. As it turns out the optimal electron-capturing isotope is holmium-163. The problem really must be difficult since even with the help of holmium researchers have not been able to agree on an upper limit for the neutrino's mass and some have even reported a *non-zero* lower limit.

16th Rare Earth Research Conference

The 16th Rare Earth Research Conference is scheduled for April 18-21, 1983 at Florida State University, located in Tallahassee, Florida, with good airline service from Atlanta, Tampa, and Miami. April is mid-Spring for Tallahassee with the probability of mild, warm days and nights.

The program will include the following major topics: general and analytical chemistry, solutions and solvation, biochemistry, organometallic chemistry, geochemistry, spectroscopy, metallurgy, crystal growth, intermetallic compounds, phase studies and diagrams, solid state physics, x-ray diffraction, neutron scattering, magnetism, thermal and transport properties, surface and interface phenomena, rare earth technology, industrial processes, applications, and actinide chemistry as compared to lanthanides.

The third Frank H. Spedding Award for excellence in research and leadership in rare earth science and technology will be bestowed at this meeting. For more information, see the article entitled "1983 Frank H. Spedding Award" on page 1.

We expect to have many of the leading international experts in rare earth science and technology at the conference. The strong interdisciplinary character of the previous conferences will be continued with substantial representations from government, academic, and industrial institutions worldwide.

To assist the Program Committee in detail planning, please complete and return before July 1, 1982, the preliminary information form provided below.

(detach)

16th Rare Earth Research Conference

Florida State University April 18-21, 1983

Please complete the following and send before July 1, 1982 to:

Professor G. R. Choppin
Department of Chemistry
Florida State University
Tallahassee, Florida 32306, U.S.A.
Phone: (904) 644-3875

This form is for information only and carries no final commitment.

Plan to attend ☐ Yes ☐ No Plan to present paper ☐ Yes ☐ No

Spouse attending? ☐ Yes ☐ No Total no. in your party _____

Special interest area(s). _____

_____

Name _____

Address _____

_____

Previous RE Conference Proceedings†

French International Rare Earth Conference, May 5-10, 1969. Paris and Grenoble, France
Les Éléments des Terres Rares, Tome I and Tome II, Bureau 3A-Service de Presse, Centre National de la Recherche Scientifique, 15 Quai Anatole France, Paris 7e, France. Tome I—price unknown, Tome II—107.50 F.

Proceedings of the 8th Rare Earth Research Conference, Reno, Nevada, April 19-22, 1970, available free from Reno Metallurgy Research Center, U.S. Bureau of Mines, Reno, NV, 89505, USA.

Conference on Rare Earths and Actinides, University of Durham, Durham City, England, July 5-7, 1971.
Conference Digest No. 3, Rare Earths and Actinides, Durham 1971, Institute of Physics, London, England (1971). Available from the Institute of Physics, Distribution Center, Blackhorse Road, Letchworth, Herts SG6 1HN, England. £7.50 (except 3.75 for members of the Institute of Physics).

Proceedings of the 9th Rare Earth Research Conference, Blacksburg, Virginia, October 10-14, 1971, available from Dr. Larry Taylor, Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA. $20.00

NATO Advanced Study Institute on Analysis and Application of Rare Earth Materials, Kjeller, Norway, August 23-29, 1972.
Analysis and Application of Rare Earth Materials, O. B. Michelsen, ed., Universitetsforlaget, Oslo, Norway (1973), available from Universitetsforlaget, P.O. Box 307, Blindern, Oslo 3, Norway or from Universitetsforlaget, P.O. Box 142, Boston, MA 02113. $28.00.

Proceedings of the 10th Rare Earth Research Conference, Carefree, Arizona, April 30-May 3, 1973. CONF-730402-(P 1-2). Available from the National Technical Information Service, Springfield, VA 22151, USA. $27.20.

Seventh Russian Conference on Rare Earth Metals, Moscow, USSR. Sept. 12-17 (1972). *Rare Earth Metals, Alloys and Compounds* [*Redkozemelnye Metally Splavy i Soedineniya*] (Izdatel'stvo Nauk, moscow, 1973) 355 pp. Cost is 1R, 81K (~ $2.00 U.S.) [14 papers in English, 5 in French and 67 in Russian]. Suggest contacting a book store dealing with Soviet publications.

Proceedings of the 11th Rare Earth Research Conference, Traverse City, Michigan, Oct. 7-10, 1974, available from Harry A. Eick, Department of Chemistry, Michigan State University, East Lansing, MI 48824, U.S.A., $25.00

Proceedings of the 12th Rare Earth Research Conference, Vail, Colorado, July 18-22, 1976, available from University Microfilm, 300 N. Zeeb Rd., Ann Arbor, MI 48106. LD-000328, $83.00.

Thirteenth Rare Earth Research Conference, Oglebay Park, West Virginia, October, 1977. *The Rare Earths in Modern Science and Technology*, G. J. McCarthy and J. J. Rhyne, eds., Plenum Publishing Corp., New York (1978), $49.50.

Conference on Rare Earths and Actinides, University of Durham, Durham City, England, July 4-6, 1977. *Institute of Physics Conference Series Number 37*, W. D. Corner and B. K. Tanner, eds., Institute of Physics, London (1978). 22.00.

French International Rare Earth Conference, September 4-7, 1978, St. Pierre-de-Chartreuse, France. *Physics of Metallic Rare Earths, J. Phys. (Paris) Colloque C-5* 40, C5-1-404 (1979), 245 F.

Fourteenth Rare Earth Research Conference, Fargo, North Dakota, June 25-28, 1979. *The Rare Earths in Modern Science and Technology, Vol. 2.*, G. J. McCarthy, J. J. Rhyne and H. B. Silber, eds., Plenum Publishing Corp., New York (to be published in 1980)
(1980) $59.50.

Symposium at the Second Chemical Congress of the North American Continent (180th ACS National Meeting), Las Vegas, Nevada, August 25-26, 1980.
Industrial Applications of Rare Earth Elements, (ACS Symposium Series 164). K. A. Gschneidner, Jr., ed., American Chemical Society, Washington, D.C. (1981). $35.00.

Fifteenth Rare Earth Conference, University of Missouri, Rolla, Missouri, June 15-18, 1981. *The Rare Earths in Modern Science and Technology*, Vol. 3., G. J. McCarthy, J. J. Rhyne, and H. B. Silber, eds., Plenum Publishing Corp., New York (to be published in 1982).

†Published since 1970. For information on earlier conferences see *RIC News* XIII [2], 4 (1978) or contact RIC.

Excited Isotopes

Claiming another first in the use of lasers for isotope separation, G. I. Bekov, A. N. Zherikhin, V. S. Letokhov, V. I. Mishin and V. N. Fedoseev report the observation of selective photoexcitation and ionization of even or odd isotopes of ytterbium using polarized light [*Pis'ma Zh. Eksp. Teor. Fiz.* **33,** 467-70 (1981); Engl. Trans. *JETP Lett.* **33,** 450-3 (1981)].

Ytterbium atoms were excited through three steps using laser beams, and then 50ns later they were ionized using an electric-field pulse of 10 kV/cm. The lasers had linewidths of 0.04, 0.8 and 0.8 cm^{-1} and average beam powers of 30, 6 and 20mW, respectively. The output frequency of the first laser could be tuned over an interval of 0.5 cm^{-1}.

If the beams in the first and second excitation steps are linearly polarized, transitions in the odd isotopes can occur but are forbidden in the even isotopes. However, if either of the laser beams in the first or second step is circularly polarized the even isotopes can become excited and indeed the major part of the ion current is due to even isotopes. While transitions are always possible for the odd isotopes, the ion yield from odd isotopes still depends to some extent on the polarization. A change in polarization changes the number of magnetic sublevels that are excited in intermediate states.

This phenomena can be used to separate odd and even isotopes using laser beams whose linewidth are greater than the isotope shift. It can also be applied to separate and detect isotopes of the alkaline earths and Zn, Cd, Hg, and Pd

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Optical Properties

Issue 18-2 of *Physics Data,* published by Fachinformationszentrum, Karlsruhe, West Germany in 1981, is entitled "Optical Properties of Metals. Part II. Noble Metals, Aluminum, Scandium, Yttrium, the Lanthanides, and the Actinides." The issue contains 288 pages and is priced at $16.00 (DM 35). The compilers are J. H. Weaver, C. Krafka, D. W. Lynch, and E. E. Koch. The bibliography is at the end of the volume and contains 191 entries, each with its own bibliographical code. The optical properties of each metallic element are critically evaluated using data published through 1980. The photon energy range covered is 0.1 to 500 eV with most data falling within the 1 to 6 eV range. Depending on the data available and the properties of the individual element, the presentation for each element evaluated contains all or part of the following: a table listing the author code from the bibliography and the scope of the work in that particular reference; a graph showing the author code and the range of photon energies used in that investigation; and graphs showing optical properties as a function of photon energy. The properties plotted on the graphs include reflectivity, optical conductivity, absorption coefficient, and the real and imaginary parts of the complex dielectric function. For most elements, except for the lighter rare earths, a table of recommended optical data as a function of photon energy is presented.

New Refining Process

A new process to refine rare earth minerals has reportedly been developed by Inoue Japax Research, Inc. (IJR) according to K. Inoue [*Rare Metal News,* No. 1124, p 56 (1981)]. The new physico-chemical process uses sodium hydroxide and electric discharge to produce the rare earth salts from the raw material. The process was developed for the rare earth mineral from the Pai-Yun Mine, Pao-Tow, China. This mineral is a monazite-bastnasite mixture that is difficult to separate by the sulfuric acid method. IJR claims the new technique is capable of producing six nines pure oxides. A pilot plant with a capacity for 1000 tons/year of 60 percent pure rare earth oxide is scheduled to begin operation in Spring 1982 and IJR hopes to have the technology developed to triple that capacity in the next 3 years.

Growing Fast!

Reactive Metals and Alloys Corporation (REMACOR) has been recognized as one of the 100 fastest growing, privately owned companies in the nation by INC. Magazine. Company founder and chairman, J. R. Jackman, attributes the favorable position of REMACOR to the dedication and hard work of the employees in developing and manufacturing products and also the technology to use these products effectively and economically. Sales have increased 200 fold during the past 6 years. Jackman looks for that figure to increase 2 or 3 fold in the next 4 years for a total 500 fold increase for the first 10 years. To increase production a new submerged arc furnace is scheduled for startup early in 1982 with plans for additional furnaces in 1983 and 1985. Another significant aspect of REMACOR's success is a contract with the Republic of China for raw materials, particularly rare earth chloride. REMACOR products are mainly for use in the aluminum, iron and magnesium industries.

4*f* Shell Delocalized

H. K. Mao, R. M. Hazen, P. M. Bell, and J. Wittig have observed a crystallographic transformation in praseodymium under pressure [*J. Appl. Phys.* **52,** 4572-4 (1981)] which, when put together with other observations made by Wittig [*Z. Physik B* **38,** 11-20 (1980) and *Phys. Rev. Letters* **46,** 1431-4 (1981)], indicate a 4*f*-shell delocalization. The praseodymium phase change is accompanied by an approximately 19 percent volume decrease and is thought to be analogous to the γ-α delocalization transition in cerium. Although the praseodymium transition is not isomorphous, the volume decrease is attributed to a collapse of the metallic radius. In support of these conclusions, Wittig has observed a pressure-induced magnetic-to-nonmagnetic transition of praseodymium impurities in lanthanum.

Univ. of São Paulo

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During the 21 years of rare earth research more than 100 papers have been published, and 20 Ph.D. and 7 M.Sc. degrees granted. In addition to those shown in the photograph, the group includes 10 graduate and 1 undergraduate students.

Phase Diagrams

(continued from page 1)

rare earths with other elements will be studied. The present plans envision a 4 year time table for the completion of the task.

The data for each system will be evaluated separately and have its own list of references. When available data permits, the discussion will include critical boundaries, invarient points, crystal structures and lattice parameters, thermodynamic properties, metastable phases, and phase diagrams. When sufficient data exists the composite diagrams of mischmetal systems with individual non-rare earth elements will be constructed. A quarterly report will be published containing the information processed and evaluated during that time period. Tentatively evaluated phase diagrams will be submitted to the *Bulletin of Alloy Phase Diagrams* for peer review and publication as part of the National Bureau of Standards/American Society of Metals (NBS/ASM) phase diagram program. Dr. Gschneidner has also agreed to serve the *Bulletin* as Category Editor for binary rare earth alloys. If revisions are needed they will include the suggestions received from the peer review for the *Bulletin* and the input from the NBS/ASM review.

Financial support for the project comes from the National Bureau of Standard's Office of Standard Reference Data (OSRD); and the industrial firms:

Th. Goldschmidt AG, Essen, West Germany;
Molycorp, Inc., Union Oil Co. of California, Los Angeles, CA;
Reactive Metals & Alloys Corp., West Pittsburg, PA;
Ronson Metals Corp., Newark, NJ; and
Santoku Metal Industry Co. Ltd., Kobe, Japan.

Bibliography Under Glass

No, nothing edible, just Volume Two of Molycorp's projected four volume bibliographic series on the use of rare earths in glass and ceramics. Volume Two, alias Application Report 8109, is entitled "Abstracts of Major Work Concerning Rare Earths in Optical & Special Property Glasses Including Decolorization & Analytical Methods." The applications included in this bibliography are optical glass, light filters, colored glass, electrodes, corrosion resistance, decolorizing, analytical methods and miscellaneous. Entries consist of the title, author(s), reference, a brief abstract of the article and, in the case of patents, who the patent was assigned to. A special section at the end of the report aids in locating entries by listing the abstract number, rare earth involved, base glass and source of the reference. Copies of both Volume One, Application Report 8108, and Volume Two are available free by writing to Molycorp, Inc., 709 Westchester Avenue, White Plains, New York 10604, or by calling telephone number (914) 977-8880.

Russian Acquisitions

New Russian publications received by RIC include numbers 13 and 14 of *Redkozemel'nye Poluprovodniki. Tekushchaya Bibliograficheskaya Informatsiya* [Rare Earth Semiconductors. Current Bibliographic Information], V. P. Zhuze, Ed., Fiziko-Teknicheskii Institut im A. F. Ioffe, Akademii Nauk SSSR, Leningrad (1980) and (1981). The thirteenth bibliography has 558 citations while the fourteenth contains 518 citations. References are printed in their original language with an English or Russian notation as to the subject matter. Both issues have an English table of contents and an author index.

Rare Earths Farmed Out

Rumors about rare earth applications going to seed are no longer rumors. RIC has found two applications of rare earth products that are helping farmers get their crops planted in the ground.

In the first application, the U. S. Department of Agriculture has used Super Slurper [see *RIC News* **XIV**, No. 1, 3 (1979)] as a coating for seeds in areas that normally experience shortages of moisture. Super Slurper, which can absorb up to 2000 times its weight in water, holds the available moisture closer to the seed thereby aiding and increasing germination and consequently the final yield. In tests in several different counties in Iowa during 1981 an average yield increase of 5.5% was obtained.

The second application finds International Harvester (IH) using rare earth-treated steel in their disc harrow-blades to increase the hardness/toughness properties. The blades resemble very shallow dishes or plates with sharp edges and are used to break up the surface of the ground in preparation for planting. IH notes that the improved microstructure of the steel in the blades increases the wear and sharpness retention and improves the resistance to cracking or splitting. IH claims the new blades are 30 percent stronger and will last 20 percent longer.

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