RARE-EARTH INFORMATION CENTER NEWS

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C.N.R.S. Part I —

Laboratoire des Terres Rares

SENIOR STAFF — Pictured from left are Drs. J.-C. Achard, G. Schiffmacher, P. E. Caro, H. Makram, Mrs. Domine, J. Loriers, L. Vichr, Mrs. Jonkierre, A. Percheron, and J. P. Briffaut. Senior Staff member Dr. Charlotte Henry La Blanchetais is not shown.

The national rare-earth research laboratory of the French National Center for Scientific Research (C.N.R.S.), also known as the Laboratoire Georges Urbain, is located in Bellevue near Paris, France. The parent agency (C.N.R.S.) operates several laboratories, each conducting research in sharply defined fields, and also supports university research.

The Laboratory is named after Georges Urbain who in the first quarter of the 20th Century did a tremendous amount of work in rare-earth separation by fractional crystallization. He also studied many of the properties of rare earths and, as early as 1909, discovered the red europium fluorescence of today's color television fame.

Rare-earth research has a long standing history in France where many of these elements were discovered or first isolated: samarium, 1879, and dysprosium, 1886, by Lecoq de Boisbaudran; europium, isolated by E. A. Demarcay in 1901; ytterbium, 1878, and gadolinium, 1880, by J. C. G. de Marignac; thulium, 1879, by P. T. Cleve; holmium, 1879, Cleve and J. L. Soret; and lutetium, 1907, by G. Urbain.

Prof. Urbain's early work on rare earths was continued by Félix Trombe, one of Urbain's students, who prepared some of the metals and in 1934 discovered the ferro-

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RIC Supporters

To date 16 of the world's leading rare-earth producers and manufacturers of rare-earth products have contributed or pledged to contribute to the support of RIC during the fiscal year, July 1970 through June 1971. Currently financial support is being received from:

- American Metallurgical Products Co., U.S.A.
- American Potash and Chemical Corp., a subsidiary of Kerr-McGee Corp., U.S.A.
- Forskningsgruppe For Sjeldne Jordarter, Norway.
- Th. Goldschmidt A.-G., Germany.
- W. R. Grace and Co., U.S.A.
- Indian Rare Earths, Ltd., India.
- Leico Industries, Inc., U.S.A.
- Michigan Chemical Corp., U.S.A.
- Molybdenum Corporation of America, U.S.A.
- Research Chemicals Division, Nuclear Corporation of America, U.S.A.
- Ronson Metals Corp., U.S.A.
- Royal Sulphuric Acid Works Ketjen, Ltd., The Netherlands.
- Sylvania Electric Products, Inc., U.S.A.
- Typpi Oy, Finland.
- United States Radium Corp., U.S.A.
- Wako Bussan Co., Ltd., Japan.

Although Royal Sulphuric Acid Works Ketjen, Sylvania, and U.S. Radium as new contributors are helping RIC reach its operating goal of $11,000, additional funds are still needed to meet minimum objectives of publishing *RIC News* and answering information inquiries.

Coryell Honored With AEC Citation

Charles D. Coryell, professor of chemistry at the Massachusetts Institute of Technology (MIT), has been awarded a U. S. Atomic Energy Commission Citation for his "distinguished contributions to the nation's atomic energy program in the field of fission products research and radiation chemistry."

Dr. Coryell is widely known for his pioneer work in nuclear chemistry and in 1945 co-discovered the rare-earth element promethium, the last rare-earth element to be separated and identified. His research interests center on those aspects of physical, inorganic, and structural chemistry which are basic to nuclear science, and in the chemistry of nuclear transmutation, particularly of nuclear fission.

AEC Citations are presented to persons not in the employ of the Commission who have made meritorious contributions to, or have been outstanding in the U. S. nuclear energy program.

New Publication

X-Ray Fluorescence Spectrometry Abstracts is a new quarterly publication which surveys the international literature including conference proceedings and unpublished reports on the theory and practical applications of x-ray fluorescence spectrometry.

The publication contains abstracts of all major papers arranged under key subject headings. Numerous references to rare-earth work are included in the current volume.

Published in English, this journal is available from Science and Technology Agency, 3 Dyers Buildings, London E. C. 1, England, at an annual subscription rate of $58.00.

MEETING

Another conference on Rare Earths and Actinides will be held at the University of Durham, England, July 5, 6 and 7, 1971, under the sponsorship of the Solid State Physics Sub-Committee of the Institute of Physics and The Physical Society.

Preliminary plans call for a program with emphasis on properties which are similar in the two goups of elements. The scope of the conference will be restricted to pure metals, intermetallic compounds and alloys, and simple compounds with nonmetals.

For more information about the Durham Conference write to the:

Institute of Physics and The Physical Society
47 Belgrave Square
London, S.W. 1, England

Report on Magnetic Semiconductor Meeting

Last November a two-day meeting was held on magnetic semiconductors at the IBM Research Center in Yorktown Heights, New York. A summary of this meeting by J. B. Goodenough appeared in the June 1970 issue of *Physics Today*, pp. 79-83.

At this meeting compounds such as the europium chalcogenides (EuO, EuS, EuSe and EuTe), $Pr_{1+x}O_2$, $LaCoO_3$, $La_{1-x}Ca_xMnO_3$ and the ferrogarnets ($Y_3Fe_{5-x}Si_xO_{12}$) were discussed along with a number of other non-rare earth compounds.

1100 WATT CW LASER

The Laser Products Division of Holobeam, Inc., Peramus, New Jersey, USA, has announced the successful demonstration of a Nd:YAG laser which generates 1100 W continuous wave (CW).

RE GAS LASERS

Infrared laser lines have been obtained for the first time from metallic samarium and europium vapors, according to Ph. Cahuzac, *Phys. Letters* 31A, 541-542 (1970).

Promethium Review

The technology surrounding the development of promethium as a lightly shielded heat and radiation source as well as the chemistry and properties of promethium are reviewed by H. T. Fullam and H. H. Van Tuyl in *Isotopes Radiation Tech.*, 7, 207-221 (1969-70).

Promethium is now available in kilogram quantities, and work is underway to determine properties of the metal not previously measured. For the first time the structure and the lattice constants of metallic Pm have been reported. Since only the chemistry of the metal and the sesquioxide have been studied in any detail, many scientists are awaiting the results of chemical and physical studies on Pm and its compounds to see how well Pm fits in with current theories on the nature of the lanthanide series.

Promethium is the only fission product that has potential application as a lightly shielded radioisotope power source, and this is thought to be its largest market potential. Other applications as well as the availability, nuclear properties, shielding, production, and heat-source fabrication are also described in this review.

HANDBOOK

The mechanical and physical-chemical properties of the rare-earth metals are tabulated in the *Handbook of the Rare Elements. Vol. III. Radioactive and Rare Earth Elements,* M. A. Filyand and E. I. Semenova, translated and edited by M. E. Alferieff, (Boston Technical Publishers, Inc., Cambridge, Mass., 1970). The price is $22.50.

The 170-page chapter on rare earths contains a general section comparing the physical, magnetic, and mechanical properties of the rare earths plus sections on each individual element. Nuclear properties, crystal forms, thermodynamic values, and technological properties are listed for each element as well as the major uses and commercial alloys of the element. References are included for all data.

Molecular Engineering in Garnets

The crystal structure of microwave garnets can be designed to obtain different combinations of magnetic properties according to A. S. Hudson, *Review of Physics in Technology* 1, 9-26 (1970).

By adjusting the molecular composition parameters in the general formula

$$(Y_{3-a-b-c}Gd_aR_bCe_c)\ (Fe_{2-z-d}In_zMn_d)\ (Fe_{3-y}M_y)O_{12}$$

c-sites a-sites d-sites

where R=Dy, Ho, Tb and M=Al or Ga it is possible to control magnetization, magnetization *vs* temperature, resonance linewidth, spinwave linewidth, magnetostriction constant, and dielectric properties. However, in optimizing several properties conflicts occur between competing requirements so that the final design of the garnet will represent a compromise between the various conflicting requirements.

Recently new types of YIG's have been developed in which calcium or bismuth is substituted for yttrium and vanadium is substituted for iron. These garnets have higher Curie temperatures than those containing other nonmagnetic substitutions while still retaining comparable resonance properties. These new materials are expected to eventually replace some of the more expensive conventional substituted garnets.

Transparent Ferromagnets

Recent investigations of transparent ferromagnets are reviewed by G. S. Krinchik and M. V. Chetkin in *Soviet Physics Uspekhi* 12, 307-319 (1969).

A number of rare-earth ferromagnetic dielectrics, including EuO, EuSe, $R_3Fe_5O_{12}$ and $RFeO_3$ have been found to transmit infrared and visible light, and some interesting physical effects have appeared in optical investigations of these compounds. Various types of temperature-dependent, collective-exchange reasonances were observed in $Yb_3Fe_5O_{12}$ at ll kOe in the interval 6.6 to 100 cm^{-1} at 2 to 70°K. In a separate study the anisotropy of exchange splitting of rare-earth ions in certain ferromagnetic crystals was found to be caused by nonequivalent sites of the rare-earth ions in the iron-garnet lattice. The mechanism of the Faraday effect in $R_3Fe_5O_{12}$ was also investigated and found to consist of an exchange mechanism and a mechanism connected with the precession of the ferromagnet at optical frequencies as well as the usual spin-orbit mechanism.

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Cathode Material

$PrCoO_3$ is presently the most promising cathode material for high-temperature zirconia electrolyte fuel cells. These fuel cells had previously been limited in performance and range of potential application by the lack of suitable materials for electrodes and electrode leads.

In a study conducted by C. S. Tedmon, Jr., and co-workers, *J. Electrochem. Soc.* 116, 1170-1175 (1969), fuel cells with porous $PrCoO_3$ cathodes gave satisfactory performance at 1100°C for more than 5000 hours. Power densities of 300 MW/cm^2 at 1000°C and 600 MW/cm^2 at 1100°C were generated in zirconia electrolyte fuel cells with $PrCoO_3$ cathodes using hydrogen as the fuel and air as the oxidant. These cells, however, did not survive thermal cycling. Since the thermal expansion coefficient of $PrCoO_3$ is about 2.5 to 3 times larger than that of zirconia, interfacial stresses and spalling of the cathode occurred during cooling.

$LaCoO_3$ and Sr-doped $LaCoO_3$ were also examined as electrode materials in this study. These materials were unsatisfactory because $LaCoO_3$ reacted with the electrolyte and produced nonconducting products.

Perovskite Book

F. S. Galasso in *Structure, Properties, and Preparation of Perovskite-Type Compounds,* Pergamon Press, Inc., 1969, presents detailed information on more than 500 compounds, a number of which contain rare earths.

Structural data on ternary, ABO_3 type, and complex, $A(B'_xB''_y)O_3$, compounds is presented in a systematic manner for easy reference. The chapter on x-ray diffraction techniques includes identification of distortions in the structure of ABO_3 compounds as well as ordering in complex perovskite-type compounds.

In discussing the properties of perovskite-type compounds—electrical conductivity, ferroelectricity, ferromagnetism, optical transmittances, catalytic properties, melting points, heats of formation, thermal expansion, and mechanical properties—the author points out structure-property relationships and the importance of perovskite-type compounds for ferroelectric and piezoelectric applications and more recently as superconductors, laser modulators and catalysts. A section has also been included on the preparation of these compounds as powders, thin films and single crystals.

A formula index is included in this 207-page volume; the price is $9.00.

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K. A. Gschneidner, Jr. . . . . Editor
Nancy Kippenhan and W. H. Smith
Staff Writers

FERROELASTIC-FERROELECTRIC COMPOUND

Information has recently come to our attention concerning a rare-earth compound with the unusual properties of being both a ferroelectric and ferroeleastic material. This compound is $Gd_2(MoO_4)_3$, gadolinium molybdate.

The prefix *ferro* means that the property of interest arises spontaneously in a manner analogous to the spontaneous magnetic field in a ferromagnet. That is, $Gd_2(MoO_4)_3$ possesses simultaneously a spontaneous polarization (electric dipole moment) and a spontaneous strain. Since the two vectors associated with the ferroelectricity and ferroelasticity are coupled, this unique material opens up a number of new areas of application such as optical shutters, light modulators and displays.

The Curie temperature is about 160°C. This is the temperature above which the crystal is neither ferroelectric nor ferroelastic. According to Aizu and co-workers [*J. Phys. Soc. Japan* 27, 511 (1969)], the ferroelectricity is induced by the ferroelasticity, which is unusual compared to other ferroelectric-ferroelastic materials, such as KH_2PO_4.

More recently Isomet of Palisades Park, New Jersey has announced the availability of gadolinium molybdate single crystals 5 cm (2 inches) in diameter by 12 cm (5 inches) in length. Other physical properties, such as crystal structure, lattice parameters, optical properties, etc., will be found summarized in the above mentioned article.

RARE! EARTHLY GOOFS

Vol. V, No. 2, June 1970

The volume number on page 1 should read Vol. V. The masthead on page 7, however, contains the correct volume number for the June 1970 issue.

C.N.R.S. Part I –

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magnetism of gadolinium. Following World War II, the newly-created C.N.R.S. appointed Dr. Trombe as the first director of the Laboratoire Georges Urbain. He pursued an active career in rare-earth research until his retirement from that post in 1969. Still active and well, Dr. Trombe now devotes his time to solar energy research, a field in which he is the world-recognized pioneer. Now the Laboratory, which employs 50 people, is directed by Dr. J. Loriers; Dr. P. E. Caro is deputy director.

The Laboratory has devised and employed several methods for ion-exchange separation of the rare earths, mostly under the supervision of Dr. Loriers. A large amount of scandium was prepared for the University of California in 1953. With increasing industrial facilities for rare-earth separation, attention has been directed more towards the specific properties of the rare earths, particularly in the areas of luminescence and metallurgy. Optical properties are being studied by several investigators whose long-range goals are:

1. understanding the connection between absorption and emission spectra of solid compounds and their structure and chemical bonds,
2. testing the various physical theories for crystal field effects in R^{3+},
3. deriving good phosphors with R^{3+} or R^{2+} as the active ions, and
4. preparing good quality, optically active, compounds.

In the field of metallurgy studies are directed towards preparation of pure metal for study either as bulk material or as thin films, and the preparation of alloys with interesting theoretical properties, e.g., rare earth-tin alloys.

The Laboratory maintains a strong background in chemistry for the prepration of compounds, eithere in the 3^+ state or in the divalent state (EuO was first reported in 1957 by Dr. J.-C. Achard), and is also interested in the prepartion of magnetically active compounds (garnets).

(This is the first of two articles dealing with the activities of the Laboratoire des Terres Rares, C.N.R.S. The above summary of the history and general research direction of the Laboratory will be followed by a second article discussing research programs in detail which is scheduled to appear in the December 1, 1970 issue of RIC News. –Ed.)

Transparent Ferromagnets

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Numerous applications are possible for ferromagnets having sufficiently high transparency in the visible and near infrared regions. These materials could be used in control devices such as gyrators, modulators and optical gates, while the Faraday effect in $Y_3Fe_5O_{12}$ could be used to modulate the intensity of laser emission. Ferromagnets could also be used in memory devices or as a medium for lasers.

Rare-Earth Information Center
Institute for Atomic Research
Iowa State University
Ames, Iowa 50010