RARE-EARTH INFORMATION CENTER NEWS

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French National Rare Earth Research Laboratory

(Editor's note: This is the second of two articles describing the work being carried out at the French national rare earth research laboratory. The first article, which dealt with the history and an overview of the laboratory's program, was presented in the September 1970 issue. The photograph included with that issue featured the senior staff members only; the photograph shown here is of the entire staff.)

The studies at the Laboratoire des Terres Rares of the French National Center for Scientific Research in Bellevue, France, are concerned with the relation between the properties of the rare earth $4f^n$ configurations and the solid state structural environment. The main goals of investigations of concentrated and doped rare earth materials are: 1) the use of the rare earth optical properties as a tool for understanding some problems in solid state chemistry such as the nature of bonding (orbital overlap), nonstoichiometry and solid solutions, and 2) the selection of structural conditions needed to obtain optimum properties of the rare earths in phosphors, imaging devices and lasers.

Absorption and fluorescence spectra are used to determine the energy levels of the $4f^n$ configurations, especially $4f^3$ (Nd) and $4f^6$ (Eu) for a large number of structural situations in a variety of compounds. The $^{2S+1}L_J$ free ion levels retain their identity in the solid state and are split a few hundred cm^{-1} by the crystal field.

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Rare Earth ♫ And ♫ Bread

Did you attempt to call RIC around the 24th of March to get some scientific information but didn't have our telephone number handy so tried to reach us via the University operator? And instead of reaching RIC you were connected to a person trying to sell you tickets to a rock concert here at the Iowa State University campus given by the "Rare Earth" and "Bread". These two rock groups played to about 12,000 persons at the Hilton Coliseum on Saturday, March 25.

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Weathering Effect

In a study of the evolution of Scandinavian glacial loams and clays, E. Roaldset and I. Th. Rosenqvist discovered an unusual lanthanide distribution in the gneisses found in upper Numedalen, Eastern Norway, *Nature, Phys. Sci.* 231, 153-154 (1971).

The gneisses represent deeper parts of the weathering profile. An examination of the micaceous fractions of these rocks showed the micas to be extremely enriched in lanthanides compared to the host rock. Moreover, the lanthanide distribution showed a more pronounced odd-even effect than in the earth's crust. X-ray data showed that the lanthanides were present in an adsorbed state and not in the mineral lattice proper.

The authors assumed that the enrichment on the surface of the mica minerals was initiated by the liberation of rare earths from the primary minerals during weathering on the top of the profile. The ions then diffused through the underlying rock and then precipitated by adsorption. By some mechanism, still not clearly defined, those lanthanides present in small amounts in the host mineral had a lower probability of being transported and deposited than those present in large amounts. As a result of the scarcity of the odd numbered lanthanides in the original material, an underrepresentation of these elements occurred in the micas.

Magnificent Magnets

Did you know that there is a rare earth material which has an energy product about three times that of the best $SmCo_5$ permanent magnet prepared to date? Before you get too excited about this material, we must inform you that its Curie temperature is, alas, only 100°K.

The compound Dy_3Al_2 was found to have an energy product of 73 MG·Oe at 4.2°K. This compound and its unusual magnetic properties have been studied by B. Barbara, C. Bécle, R. Lemaire and D. Paccard of the Laboratoire de Magnetisme in Grenoble, France, and their results have been published in several journals—*J. Phys. (Paris) Suppl.* 32, Cl-299 to Cl-304 (1971); *Z. angew. Phys.* 32, 113-116 (1971); and *IEEE Trans. Mag.* MAG-7, 654-656 (1971).

This compound and $TbNi_{1-x}Cu_x$ have a new type of domain wall whereby a large remanent magnetization coexists with a large coercive field. It is quite possible that these and similar materials may be useful permanent magnets.

Creative Invention Award to H. T. Hall

Hall

H. Tracy Hall, distinguished professor of chemistry at Brigham Young University, has been awarded the 1972 American Chemical Society (ACS) Award for creative invention. The ACS cited Prof. Hall for his development of high-pressure, high-temperature technology for the production of synthetic diamonds.

Hall's latest process made possible the production of industrial diamonds in a variety of molded shapes and in sizes ranging from 0.01 to 20 carats. Prior to the Hall process, synthetic industrial diamonds were made in sizes of 0.000001 to 1 carat.

Hall's high-temperature, high-pressure work has been applied to the preparation, identification and determination of the crystal structures of rare earth compounds.

Named Dean at Rolla

Adrian H. Daane, head of the chemistry department at Kansas State University, will become dean of the College of Arts and Sciences, University of Missouri at Rolla, July 1.

FERRITES

The latest advances in experimental and applied ferrite technology are presented in *Ferrites. Proceedings of the International Conference,* Y. Hoshino, S. Iida and M. Sugimoto, eds. (University Park Press, Baltimore, 1971) 660 pp., $36. The conference was held in Kyoto, Japan, July 1970.

A number of the 170 papers in this volume deal with rare earth ferrites, garnets and chalcogenides. New photomagnetic effects observed in Si^{+4} and Sr^{+2} doped YIG's, GdIG and europium chalcogenides were presented and discussed in light of their application to memory devices. An entire session was devoted to bubble domain technology including the dynamic properties of bubble domains and controllable pattern printing effects in rare earth orthoferrites. Cobalt substitution in $RFeO_3$ was reported to alter the temperature dependence of the uniaxial anisotropy. Uses for YIG's in integrated circuits were explored in the session on microwave ferrites and their applications.

Other topics of interest to rare earthers include the magnetic and semiconducting properties of europium chalcogenides, the preparation and crystal chemistry of the ferrites, and the growth of single crystals of ferrites and garnets.

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MEETINGS

USSR ACADEMY SETS RE CONFERENCE

The USSR Academy of Sciences has scheduled its 7th Conference on Rare Earth Metals for Sept. 12-17, 1972, in Moscow. The focus of this year's Conference is on the role of rare earth metals, alloys and compounds in science and technology.

Topics to be discussed in particular are magnetism, superconductors and semiconductors, electronics and lighting, alloys, refractory compounds, nuclear applications, catalysts, and applications in agriculture, biology and medicine.

Plans are to publish an annotated proceedings. Details of its availability will be published in *RIC News*.

For additional information concerning the Conference contact Dr. V. F. Terekhova, scientific secretary, Leninski Prospect 49, Institute of Metallurgy, USSR Academy of Sciences, Moscow B-334.

ANALYSIS AND APPLICATION

Analysis and Application of Rare Earth Materials will be the topic of a NATO Advanced Study Institute to be held at Kjeller, Norway, Aug. 23-29, 1972. The Institute is organized by The Netherlands-Norwegian Reactor School, Instituut for Atomenergi.

The six-day program will consist entirely of invited papers and will cover 1. RE properties and their relation to specific applications and analytical methods, 2. survey of analytical techniques, 3. analysis of various RE materials, and 4. survey of applications of RE materials with discussion of analytical requirements.

The deadline for registration was June 1, 1972, but interested persons may wish to inquire about late registration. Write Mr. E. Andersen, Reactor School, Instituut for Atomenergi, P.O.B. 40, 2007 Kjeller, Norway. Information about the conference proceedings will be published as soon as it is available to *RIC News*.

Magnetic Fields In Superconductors

The use of rare earth magnetic insulators or semiconductors has enabled scientists at the Argonne National Laboratory to visually examine magnetic fields in superconducting materials. An understanding of their behavior is essential if superconducting systems are to be utilized for electric power distribution.

Dr. R. P. Huebener and his coworkers have coated superconducting materials with a thin film of an EuS and EuF_2 mixture which has a high Faraday rotation. That is, these rare earth compounds rotate a polarized beam of light in the presence of a magnetic field; the amount of rotation is proportional to the magnetic field strength. The Faraday rotation can be used to watch and photograph the beginning, growth and motion of the magnetic field and to calculate field strength.

As pointed out by Dr. Huebener, this technique was originally developed by H. Krichner at the Siemens Laboratory in Munich, Germany (*Phys. Letters* **26A**, 651-652 [1968] and **30A**, 437-438 [1969]). More details concerning the work can be found in a paper by R. P. Huebener, R. T. Kampwirth and J. R. Clem, *J. Low Temp. Phys.* **6**, 275-285 (1972) and in *Cryogenics* **12**, 100-108 (1972) by Huebener, Kampwirth and V. A. Rowe.

Final Fiscal '72 Support

A Malaysian rare earth company, Lim Fong Seng Sdn. Bhd., has become the 28th firm to provide RIC support for the current fiscal year.

Cunningham is VP

Nucor Corp. has elected James W. Cunningham a vice president of the firm. He will continue as general manager of the company's Research Chemicals Division in Phoenix, Arizona.

Electro-optic Images

Researchers at the Sandia Laboratories have developed a thin ceramic sheet which can be used to display images either directly or by projection as in a transparency. The sheet called "Cerampic," is a composite of a photoconductive film (PVK polyvinyl carbazole) deposited on one side of a thin electro-optic plate of lanthanum-modified lead zirconate-lead titanate (PLZT). Transparent electrodes (tin oxide doped with indium oxide) are deposited on both sides of the composite plate.

Cerampic creates an image by aligning ferroelectric domains in the PLZT in various orientations corresponding to the details of the image. Bright areas are formed by domains aligned in the direction of the incident light, while the dark areas result from domains orientated in other directions which scatter light away from the field of view.

The image can be stored by applying a voltage to the electrodes, since the dark areas act as insulators and the light areas as conductors. This device has many potential uses, such as generating images, which only take a few seconds to develop from signals received by telephone or radio.

G & D IN '71

"The year 1971 was one of substantial growth and diversification for the rare-earth industry," reports J. G. Cannon, *E. & M.J.* 173, 187-200 (1972).

Tons of rare earth materials shipped for consumption increased 31% over 1970. Metallurgical applications made the most significant gains with the largest increase in demand being for the use of rare earth silicides in the steel industry. During the last half of 1971 it was necessary to import mischmetal from England, Germany and Japan to meet U.S. market needs; as a result U.S. mischmetal producers were reported to be considering expansion.

Liquid Lasers

The chemical problems concerned with using Nd, Eu, Gd and Tb complexes in liquid lasers are reviewed by I. M. Batyaev, *Uspekhi Khim.* **40**, 1333-1350 (1971); Eng. transl., *Russ. Chem. Rev.* **40**, 622-631 (1971).

One of the problems involved is the competition between solvation and complex formation in laser systems. The author presents current theories on the mechanism of action, the nature of the active species and the relation of structure to luminescent properties. Difficulties in the preparation of laser systems are also considered. Tables summarize the properties of current liquid laser systems, the solvents used and the coordination numbers of the lanthanides in various systems. The authors conclude that the best liquid system developed so far consists of Nd_2O_3 dissolved in selenium oxycholoride with the addition of the aprotic acid, $SnCl_4$. This system has laser properties comparable to the best specimens of solid systems based on Nd^{+3} in $CaWO_4$ and glasses.

The study of lanthanide complexes in aprotic solvents has led to the development of new views on their structure and the discovery of a relation between the dissipation of energy from the excited ions to the surrounding medium as a function of bond type.

Rare Earth and Bread

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Next time you wish to call us remember our phone number is no further away than the *RIC News* you are reading–see our mailing block on page 2. U.S. Government phones can be used to call us direct on FTS (Federal Telecommunications System).

P.S. We've informed our University operators that we really do exist, and if you don't have our number readily available they should be able to connect you without any difficulties–we hope. Amen.

French National RE Research Laboratory

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The nature of the splitting yields information on the lanthanide ion site symmetry, and the amount the barycenter of the levels is shifted from compound to compound is proportional to the covalency of the bonding (nephelauxetic effect). The intensity of the forbidden internal $4f^n$ transitions, together with the lifetime of the excited states, also gives important information.

The optical data are correlated with the structural characteristics which are determined by high resolution electron microscopy, and x-ray and electron diffraction. Of special interest are refractory rare earth compounds whose structure is of a layered nature. These are the A- and B-forms of the lanthanide (Ln) oxides, which are prepared as textured thin films for electron microscopy; and "oxysalts," such as the oxysulfides and oxychlorides which are the salts of the two hexagonal and tetragonal "lanthanyl" cations $(LnO)_n^{n+}$ (a layered entity made of OLn_4 tetrahedra sharing edges). The three-dimensional frameworks of OLn_4 tetrahedra found in the C-form Ln_2O_3 are also investigated. Several structural relations between the Ln_2O_3 polymorphs, e.g., epitaxy, twinning or phase transitions, are studied by electron microscopy. The $(LnO)_n^{n+}$ materials exhibit the largest nephelauxetic effect known and have large transition probabilities. As a consequence they are considered to be some of the best of the industrial rare earth phosphors.

Other types of materials being investigated include garnets, aluminates, phosphates and members of the Ln_2O_3-SiO_2, Ln_2O_3-$LnCl_3$, and Ln_2O_3-CO_2-H_2O systems. By using Ce, Nd, Eu and Tb as structural probes, attempts are being made to understand the reasons for better quality phosphors from a structural viewpoint. The growth of garnet and spinel single crystals is also important in this regard.

Special attention is given to the intense allowed $4f^{n-1}\,5d \leftrightarrows 4f^n$ transitions of Ce^{3+}, Tb^{3+} and Eu^{2+}. Energy transfer from rare earth to rare earth is also of interest in connection with structure.

The Laboratory is continuing its research on the preparation of ultrapure metals, especially Sm, Eu and Yb. Physical properties of these metals are studied in connection with the electronic structure as a function of temperature and pressure. Rare earth alloys, especially with tin and lead, are investigated by thermochemical, magnetic and resistive methods.

The chemical systems connected with the possible occurrence of the divalent state in Eu, Sm, Yb and Tm are being continually examined. Binary or ternary LnX systems, where X is O, S, N, P or C, are studied by physical methods such as Mössbauer spectroscopy.

The Laboratory has recently become interested in preparing rare earth organic compounds, especially DPM chelates and organic acid salts in the solid state, and studying these materials by optic and electron microscopy.

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