

RARE-EARTH INFORMATION CENTER NEWS

INSTITUTE FOR ATOMIC RESEARCH
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March 1, 1970

No. 1

Rare Earths In the News

FERRIMAGNETS

Ferrimagnets, the odd magnetic materials widely used in radar circuits and computers, may find new applications as microwave signal amplifiers. Experiments at the Lockheed Research Laboratory in Palo Alto, Calif., have shown that resonance echoes in yttrium iron garnet ferrimagnets can amplify microwave signals by 50 db.

SOLID ELECTROLYTES

Tubes of a thoria: yttria composition, acting as solid electrolytes or high temperature semiconductors, are used in high temperature fuel cells and as e.m.f. cells for measuring oxygen solubility in molten materials. The tubes were developed by Micropure, Ltd. of London.

SUPERALLOYS

Yttrium, gadolinium, and thorium, which markedly improve surface stability of nickel superalloys, seriously degrade mechanical properties of cast alloys and narrow the hot working range of wrought alloys, according to studies by General Electric.

A vanadium alloy (V-20-Mo-10Ti) containing 0.5% yttrium has a tensile strength of 175,000 psi at room temperature and 21,000 psi at 1200°C, and at 815°C has a strength/density ratio superior to that of some well-known superalloys, reports the U.S. Bureau of Mines, Reno, Nev.

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Rare Earths in Lunar Samples

The relative abundances of the rare earths in lunar samples may provide clues to unravel the complex chemistry of the moon. The results of the investigation of the 22 kg of lunar samples collected by Apollo 11 were presented at the Lunar Science Conference Jan. 5-8 and published in a special Jan. 30 issue of *Science*.

In general the distribution of rare earths in the lunar material resembles terrestrial oceanic andesite, Ca-rich achondrite, or abyssal basalt with the striking exception that the Eu content is about 60% lower relative to Sm and Gd. This Eu depletion could have been produced by
(Continued on Page 4)

Rare Earths Aid Pollution Fight

An application using Nd lasers to help solve air pollution problems has recently been developed by Culkowski, Swisher and Gifford of the Atomic Energy Commission's Oak Ridge National Laboratory. The system consists of a pulsed laser and associated optical and detector equipment, known as LIDAR for Light Detection and Ranging.

When LIDAR in conjunction with a telescopic system is aimed at a nearly invisible source of pollution, such as chimney effluents, the dispersion or behavior of particles in the effluent is revealed by means of projection and reflection of high intensity beams of light.

Van Vleck Retires

Harvard University Professor John H. Van Vleck has retired from full-time teaching and research and is now Hollis Professor of Mathematics, Emeritus. He is well-known in the scientific community for his studies on magnetism and quantum theory of atomic structure.



Van Vleck

To us (the rare-earth community) he is the "father of rare-earth magnetism" for his contributions to the scientific foundation of the theory of the magnetic properties of the rare-earths. He was the keynote speaker at Fourth Rare-Earth Research Conference, Phoenix, April, 1964.

Among his many honors, Van Vleck was president of American Physical Society in 1952, and he has received the Langmuir Prize (American Physical Society), the Michelson Award (Case Institute of Technology), and the National Medal of Science.

RE Products Make Top 100

The continuing progress of rare-earth technology was well represented when Industrial Research, Inc. named what it considered the 100 outstanding products of the past year's technical efforts. The IR 100, now seven years old, listed three products for 1969 employing rare earths.

(Continued on Page 2)

ACS Award to Banks

Dr. Charles V.

Banks, professor of chemistry at Iowa State University, has won the 1970 American Chemical Society (ACS)



Banks

Award in Analytical Chemistry. Dr. Banks is also chemistry section chief at the Atomic Energy Commission's Ames Laboratory, Ames, Iowa.

The \$2,000 award, sponsored by Fisher Scientific Company, was presented to Banks at the ACS Spring Meeting in Houston on February 23.

Banks was nominated primarily for his over-all contributions to the science of analytical chemistry, including rare-earth materials.

YTTRIUM

Yttrium-Properties, Phase Diagrams, Industrial Applications by V. F. Terekhova and E. M. Savitskii is now available as an English translation, 167 pages.

The authors have attempted to generalize the available literature data on the preparation and properties of yttrium, and the phase diagrams and properties of its alloys. The technological and mechanical properties as well as the physical, chemical, magnetic and electrical properties are discussed along with such topics as recrystallization, metallography, and single crystals. Almost all of the available binary and ternary phase diagrams are presented in the alloy section.

Although the authors believe that yttrium has not been studied on a sufficiently wide scale, the limited research has developed uses in the fields of metallurgy, nuclear energy, refractory materials, and medicine which are surveyed in the last section.

The translation, which includes 280 references, is available for \$3.00 from the Clearinghouse for Federal and Scientific Technical Information, Springfield, Virginia 22151, U.S.A.

Rare-Earth Polymer

A rare-earth polymer (MG_3) has been prepared by extracting the metallic ions from RE chloride or nitrate solutions with di(2-ethylhexyl)phosphoric acid (G).

T. Harada, M. Smutz, and R. G. Bautista of Ames Laboratory, Iowa State University, measured the physical and chemical properties of this polymer in which $M=Y, Yb, Dy, Ho, Sm, Nd,$ and La. Molecular weight determinations for the yttrium polymer show the formula to be $(YG_3)_{6000}$.

To our knowledge this is the first report of a rare-earth polymer.

RE Mineral Specimens

The Hoyt company has made available an 18-specimen case of rare-earth and reactive metal minerals for \$27.50. Purchasers have a choice of 18 of 27 rare-earth and reactive metal minerals. For more information write to: Hoyt, Mineral Specimens Division, 3049 N. Marigold Drive, Phoenix, Arizona 85018, U.S.A.

RE Enrichment

The effect of geological environment on the composition of the rare earths in minerals has been illustrated by data on monazite, sphene, and apatite, compiled by M. Fleischer and Z. S. Altschuler in *Geochim. Cosmochim. Acta* 33, 725 (1969).

Alkalic and mafic rocks have been shown to be enriched by the light lanthanides in igneous processes, while the same process enriches granitic rocks, especially pegmatites, with the heavy rare earths. The effects of geological environment were found to be greater for minerals in which the rare earths appeared as minor constituents.

It was suggested that the geological source of monazite from various types of rocks could be determined by the average composition of the rare earths.

IR Radiation To Visible Light

Several papers by L. G. Van Uitert, L. F. Johnson and their co-workers have described the materials, their preparation and mechanisms for converting infrared radiation to visible light. These papers appeared in *Appl. Phys. Letters*, 15, 48-50, 51-52, and 53-54 (1969) and *Mater. Res. Bull.* 4, 381-390 (1969).

In general the infrared radiation from a Si-doped GaAs diode (0.93μ) is converted to visible light by a rare-earth oxyhalide phosphor. The rare-earth oxyhalide contains Yb which absorbs infrared radiation and then transfers the energy to another lanthanide ion (generally Ho, Er or Tm) which emits visible radiation. A $BaRF_5$ compound where R is Y or Lu can also be used as the host material instead of Y_3OCl_7 . The Yb^{+3}, Er^{+3} -doped $BaRF_5$ yields a green light, while the Yb^{+3}, Er^{+3} -doped Y_3OCl_7 emits a red light.

The authors furthermore point out that a "tunable" color can be obtained for certain Er-activated Y_3OCl_7 phosphors by varying the GaAs diode excitation output. Color variations can also be obtained by varying the Yb concentration and/or by varying the lanthanide activator ion.

RE Products Make Top 100
(Continued from Page 1)

One of these products was a samarium-cobalt permanent magnet, which has twice the strength of any conventional permanent-magnet material. Also in the list was a YIG-tuned "Gunn Effect" oscillator, used for microwave sweepers, analyzers, and broadband microwave receiver local oscillators. The third rare-earth development was an yttrium aluminum garnet laser utilizing a neodymium doped YAG rod. The laser, primarily for cutting and welding materials such as aluminum and silicon, can be frequency-doubled for high power uses.

Iron RE Source

Rare earth-containing mineral piles at Republic Steel's Port Henry, NY, iron ore mine may be purchased by Molybdenum Corp. of America.



The apatite constituting 10% of the tailings includes the heavy rare earths yttrium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, europium, and gadolinium.

Molycorp's final decision to exercise its option and begin recovery and processing will depend partially upon further market development for these rare earths.

Rare Earths in the News
(Continued from Page 1)

TENNIS ANYONE?

British producer Magnesium Elektron (MEL) is making paddle tennis rackets from a 1% rare earth-magnesium alloy. MEL hopes to capture one-third of the market within three years by selling the rackets—which offer durability, attractiveness, and light-weight, flexible design—for about \$20.

LIQUID SCINTILLATOR

Mineral-oil based gadolinium-loaded neutron scintillation detectors with efficiencies of 80% have been prepared at the Ames Laboratory. A gadolinium-2-ethylhexanoate and tri-n-octylphosphine oxide complex which is soluble in mineral oil is more stable and can be prepared more safely.

RE-Doped Compounds

World-wide interest on the optical properties of another class of rare-earth doped materials is evident in several recent publications.

In Japan H. Komiya (*J. Phys. Soc. Japan*, 27, 893-901 1969) writes about the optical spectra of Tm^{+3} , Li^+ and Tm^{+3} , Cu^+ -doped ZnSe. He describes the crystal field effects and presents a model to account for the observed spectra.

The luminescent properties of lanthanide-activated CdS, with Cu as a co-dopant, is described by English investigators (Apperson, Garlick, Lamb and Lunn) in *Phys. Stat. Solidi*, 34, 537-544 (1969). Of the 11 lanthanides studied, seven exhibit line emissions. In these materials the luminescence is due to the lanthanide ion, which receives the energy absorbed at a Cu site via resonance transfer.

The electroluminescence of ZnS thin films containing lanthanide metal fluorides is discussed by American scientists (Chase, Heppelwhite, Krupka and Kahng) in *J. Appl. Phys.* 40, 2512-2519 (1969). They found that of the 12 fluorides investigated the ZnS/TbF₃ device had the brightest illumination, more than 50 ft-lamberts. Spectra for the 12 devices and energy level schemes were also given.

L A S E R

The optical properties of Nd-doped crystalline and glass laser materials have recently been studied at 25°-200°C in an attempt to further the development of laser materials, *Applied Optics* 8, 1087-1102 (1969). In the first portion of their article, Thornton, Fountain, Flint and Crow made an extensive survey of the existing information on Nd-laser materials.

In the latter portion they described some of the more promising YAG and glass hosts. YAG-Nd was found to be more appropriate for high repetition rate Q-switched applications, although glass-Nd would also be good, if the optical

Two More RIC Grants

Santoku Kinzoku Kogyo Co. Ltd. of Kobe, Japan, and Ban Eng Hong Tin Mining Co. Sdn. Bhd., of Ipoh, Malaysia, have joined the ranks of private industrial firms which provide financial assistance to RIC. The Center now receives support from 19 leading rare-earth companies from eight countries throughout the world.

distortion and birefringence caused by thermal effects could be improved. Further results showed that Cr^{+3} , as a sensitizer, enhanced the 1.06 μ fluorescence of YAG by as much as 20% 120 μ sec after initiation of the pump pulse.

Recent plasma research employing Nd-doped lasers was reported in *Physics Today* 22, 55 (Nov. 1969). High-temperature plasmas are being produced by Nd-doped glass laser systems which produce hundreds of joules in pulses lasting nanoseconds to picoseconds. University of Rochester scientists have produced 10⁴ to 10⁶ neutrons/pulse by focusing the laser on a solid droplet of deuterium.

At Lawrence Radiation Laboratory a tilted-disc laser amplifier system which contains 15 Nd-doped glass discs is expected to produce 1000 joules with a 50 cm² cross section for a few nanoseconds. The laser will be used to investigate high temperature (1-10keV) plasmas and sharp x-ray lines produced by focusing the laser output on a high-atomic number target.

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Staff Writers

Liquid Lanthanum

The structure factor of liquid lanthanum has been measured by neutron diffraction by M. Breuil and G. Tourand, *Phys. Letters* 29A, 506-507 (1969). They noted that the structure factor is significantly different from that of other metals. Two unusual features are the absence of oscillations in the intensity vs k (the distance in reciprocal space) plot below the critical k value, and the anomalous low intensity value for the strongest peak at a temperature close to the melting point.

The radial distribution function shows that there are 11 nearest neighbors at a distance of 3.75 Å. These values are essentially the same as in the solid.

As far as we are aware this is the first determination of the radial distribution and structure factor for a liquid rare-earth metal. Results on other rare-earth metals would be of interest too, to see if they are similar to or different from lanthanum.

RE Chromites

The unique properties of the rare-earth chromites may lead to their use as electrode materials for magnetohydrodynamic (MHD) power generation. The chromites are not only refractory materials with melting points between 2310°C and 2490°C but also very good p-type electrical conductors, especially when doped with aliovalent impurities.

The ceramic and electrical properties of lanthanum chromite can be improved by doping with strontium carbonate according to D. B. Meadowcroft, *J. Phys. D.* 2, 1225-1233 (1969). The maximum density, hardness, strength, and thermal shock resistance were achieved by adding up to 4 mol% SrCO₃ to La_{0.84}Sr_{0.16}CrO₃ before final fabrication and firing in a reducing atmosphere at over 2030°C. The doped product has an electrical resistivity less than 10⁻² ohm m above room temperature, a

thermal conductivity of 5.1 w m⁻¹ degK⁻¹ between 830° and 1730°C, a thermal expansion coefficient of 9.0x10⁻⁶ deg⁻¹ between 25°C and 830°C, and also excellent corrosion resistance.

The chromites of the rare-earth elements except Ce can be prepared by calcining the corresponding nitrates at 1000-1100°C as reported by Portnoy and Timofeyeva, English trans., AD-694,792 (April 1969). The melting point of the chromites decreases linearly with atomic number. All of the chromites were more resistant to corrosion than the corresponding sesquioxides.

Rare Earth in Lunar Samples (Continued from Page 1)

partial melting (less than 20%) of the lunar mantle composed of feldspar, olivene, orthopyroxene, and opaque oxides; the lunar rocks would then represent liquids from different stages of this equilibrium melting. The relatively high abundance of the rare earths on the moon lends strength to another interesting speculation—that the lunar material is a condensate of solar nebula formed at temperatures which lie between the condensation temperatures of iron and nickel on the one hand and of sulfides and proton-rich materials on the other.

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Burnup Monitor

The determination of La, Ce, Pr, and Nd fission products by an x-ray spectrometric method was reported to be a new and accurate means of monitoring fast reactor oxide fuel performance by Dr. R. P. Larsen at the 158th American Chemical Society meeting in New York, Sept. 1969.

Because a number of fission product nuclides with successive mass numbers are determined, this method is less subject to changes in neutron energy and in concentration, which can result from transmutation by neutron capture. A further advantage is that complete chemical and radiochemical separations of the lanthanides from the more active fission products are not necessary, since terbium is added as an internal standard. Both the K- and L- spectra can be used in rare-earth x-ray spectroscopy.

CONFERENCE REPORT

The February 1970 issue of *Physics Today* contains a summary of papers presented at the 1969 International Conference on Luminescence held at the University of Delaware Aug. 25-29. A number of papers, which may be of interest to some of our readers, are reviewed on pages 91 and 93 of this issue.



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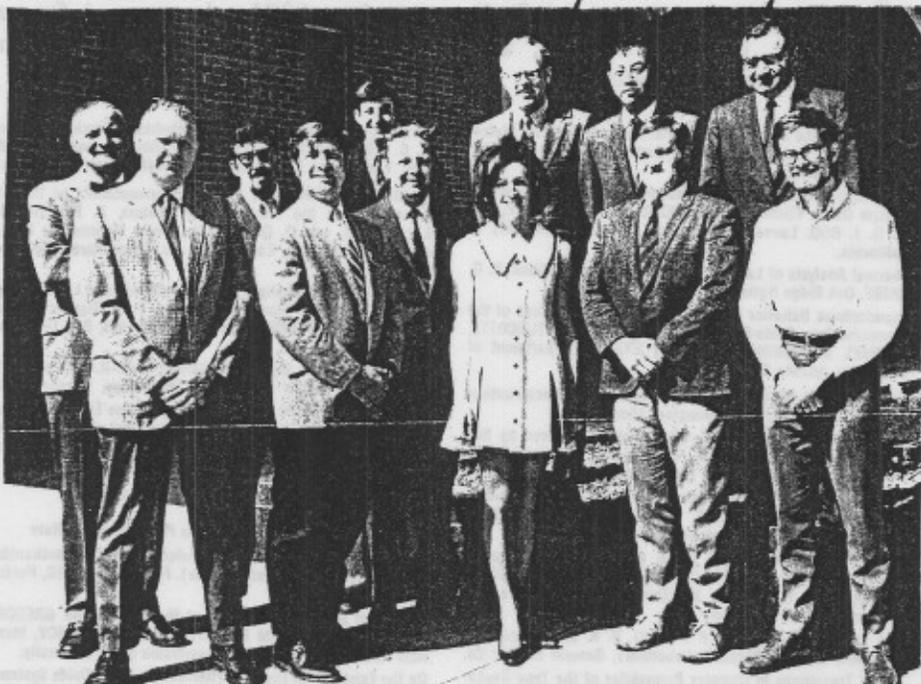
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No. 2

Emphasis on Magnets—

RE Work at University of Dayton



RARE EARTH RESEARCH GROUP — In the front row from left are David Walsh, Alden Ray, Herbert Mildrum, Helen Rice, Robert Leasure and Charles Shanley. Pictured in the back row from left are Adolf Biermann, Norman Hecht, Andrew Kraus, Joyce Wild, James Tsui and Karl Strnat.

Rare-earth research at the University of Dayton has been concerned mostly with rare earth-transition metal alloys, their physical metallurgy, crystallography, basic magnetic properties and application as permanent magnets. New work deals with the structure of flame-sprayed rare-earth oxide coatings and their compatibility with molten metals.

The Physical Metallurgy Group under Alden Ray has constructed phase diagrams of the rare-earth metals with iron and cobalt and has investigated the crystal structures of the intermediate phases in these systems. The work also is extended to include multi-component alloys because of the intense interest in some of these phases for magnetic uses. Alloys of the types R_2B_7 , RB_5 and R_2B_{17} are under study, where R is an individual light lanthanide element or a mixture of several, and B is primarily cobalt with substitutions of other metals, such as iron, copper and manganese. Of primary concern are the factors determining the stability of these phases and the tolerance of the structures for such substitutions. The precipitation and spinodal decompositions which occur in some systems are technologically significant as mechanisms for magnetic hardening.

(Continued on Page 7)

RE's STOP POLLUTION

Rare-earth ions have been found to almost completely remove simple and condensed phosphates in a new approach to wastewater treatment. This significant new use for mixed cerium group rare earths was reported by Recht, Ghassemi and Kleber at the 8th Rare Earth Research Conference.

Present methods of wastewater treatment do not significantly remove phosphorus, which in concentrations greater than 0.01 mg/l leads to massive algae growth and accelerates eutrophication of natural waters.

Phosphorus can now be separated by treating the wastewater with RCl_3 , $R_2(SO_4)_3$ or $R(OH)_3$. The insoluble RPO_4 can then be removed by filtration, and the rare earth can be recovered and recycled with losses in the range of 0.1 to 0.5%. Residual phosphate phosphorus and lanthanide concentrations are anticipated to be less than 0.01 mg/l.

If the wastewater from the entire U.S. population were treated using this process, the rare earth requirement would be about 28,000 tons/yr. Preliminary estimates indicate a total cost for phosphate removal by this process to be less than \$.10/1000 gal.

This economic method for phosphate removal is a proprietary development of North American Rockwell Corp.

8th Rare Earth Research Conference

The 8th Rare Earth Research Conference was held in Reno, Nevada, April 19-22, 1970. The Conference was well attended with approximately 225 participants (40 from non-U.S. countries) listening to and discussing the 90 papers which were presented during the three-day meeting. A complete listing of the papers appears below.

The keynote address was presented by Dr. Henry Eyring of the University of Utah. In the early portion of his address, he recalled

his experiences with some of the early rare-earth pioneers with whom he has had contact during his scientific career. The latter portion of his stimulating talk dealt with his work and ideas on rate processes.

From our discussions with many attendees it was evident this was another highly successful Rare Earth Research Conference — the eighth in a row. Our congratulations go to Tom Henrie and R. E. Lindstrom, their co-workers, and the organizing committee.

The Conference proceedings are available at a cost of \$16.00 from: Dr. T. A. Henrie
Reno Metallurgy Res. Center
U.S. Bureau of Mines
Reno, Nevada 89505 U.S.A.

The Ninth Rare Earth Research Conference is being organized by Dr. Alan F. Clifford, Virginia Polytechnic Institute, Blacksburg, Virginia, and it will be held in October 1971. As more information becomes available it will be announced in RIC News.

KEYNOTE ADDRESS —

Chairman: T. A. HENRIE, U.S. Bureau of Mines

Introductory Address. HENRY EYRING, University of Utah.

SOLID STATE I —

Chairman: K. A. GSCHNEIDNER, JR. — Iowa State University and Ames Institute for Atomic Research

Spin Wave Spectrum for Holmium Metal. (Session Keynote). R. M. NICKLOW, J. C. G. HOUMANN, H. A. MOOK, and M. K. WILKINSON, Oak Ridge National Laboratory.

Permanent Magnet Properties of PrCo₅ Alloy Powders. KARL STRNAT and JAMES TSUI, University of Dayton.

SOLID STATE II —

Chairman: W. C. KOEHLER, Oak Ridge National Laboratory

Structural and Magnetic Properties of Intermetallic Compounds in the Ternary System Y-Fe-Co. (Session Keynote). HANS R. KIRCHMAYR, Institut für Experimentalphysik, Ruhr-Universität, Bochum, Germany.

Magnetic Aftereffect and Aging of Sm(Co, Cu, Fe)₅ Permanent Magnet Alloys. H. MILDORF, A. E. RAY, and K. STRNAT, University of Dayton.

Magnetic Structure of HoFe₂. J-M MOREAU, C. MICHEL, M. SIMMONS, T. O'KEEFE, and W. J. JAMES, University of Missouri. Magnetic and Structural Characteristics of the Ternary Intermetallic Systems Containing Lanthanides. BURKE LEON and W. E. WALLACE, University of Pittsburgh.

Magnetic Susceptibility and Nuclear Magnetic Resonance of Some R₂Cu₃ Compounds. K. H. J. BUSCHOW, A. M. van DIEPEN, and H. W. de WIJN, University of Pittsburgh.

Magnetic Properties of Dysprosium Thallium Three. CLAYTON E. OLSEN, GEORGE P. ARNOLD, and NORRIS G. NERSON, University of California, Los Alamos Scientific Laboratory.

Magnetic Properties and Specific Heat of Monochalcogenides of La, Pr, and Tm. E. BUCHER, A. C. GOSSARD, K. ANDRES, J. P. MAITA, and A. S. COOPER, Bell Telephone Laboratories. Rare Earth Ions in a Hexagonal Field I. E. SEGAL and W. E. WALLACE, University of Pittsburgh.

Magnetic Interactions and Crystalline Field in Equiatomic Rare Earth-Noble Metals Compounds. J. PIERRE, Laboratoire d'Electrostatique et de Physique du Métal, C. N. R. S., Grenoble, France.

CHEMISTRY I —

Chairman: L. EYRING, Arizona State University

Mixed Crystal Phases in the System ThO₂-PrO₃. (Session Keynote). G. BRAUER and B. WILLAREDT, Chemisches Laboratorium d. Universität Freiburg, Germany.

Fluorosulfides, Sulfobromides, and Sulfoiodides of the Rare Earth Elements. C. DAGRON, J. ETIENNE, J. FLAHAUT, M. JULIEN-POUZOL, P. LARUELLE, N. RYSANEK, N. SAVIGNY, G. SFEZ, F. THEVET, Faculté de Pharmacie, Paris, France.

CHEMISTRY II —

Chairman: T. MOELLER, Arizona State University

Electron Diffraction Studies on Thin Films of Samarium Sesquioxide. (Session Keynote). C. BOULESTEIX, PAUL E. CARO, M. GASGNIER, Miss C. HENRY LA BLANCHETAI, and B. PARDO, Centre National de la Recherche Scientifique, Laboratoire des Terres Rares, Bellevue, France.

Reactions of the Sesquioxides of Pm, Nd, and Sm With Water. H. T. FULLAM and F. P. ROBERTS, Battelle Memorial Institute, Pacific Northwest Laboratory.

Complexes of the Rare Earth Sesquioxides With Divalent Europium Oxide. EDWARD CATALANO, BETTIE L. SHROYER, and W. O. J. BOO, Lawrence Radiation Laboratory, University of California.

Thermal Analysis of Lanthanide Hydroxide Preparations. R. G. HAIRE, Oak Ridge National Laboratory.

Pseudophase Behavior in the Epsilon and Iota Regions of the Praseodymium Oxide-Oxygen System. RHEAL P. TURCOTTE, MICHAEL S. JENKINS, and LEROY EYRING, Department of Chemistry, Arizona State University.

Thulium Oxide Microsphere Preparation and Characterization. C. J. AMBROSE, Donald W. Douglas Laboratories.

Properties of Thulium Oxide Microspheres Prepared by Sol-Gel Methods. S. R. BUXTON, M. H. LLOYD, and T. E. WILLMARTH, Oak Ridge National Laboratory.

Studies of the Europium-Oxygen-Fluorine and Samarium-Oxygen-Fluorine Systems. R. G. BEDFORD and E. CATALANO, University of California, Lawrence Radiation Laboratory.

The Relative Stabilities of the B and C Forms of Sm₂O₃, Eu₂O₃, and Gd₂O₃. GEORGE C. FITZGIBBON, DANIEL PAVONE, and CHARLES E. HOLLEY, JR., University of California, Los Alamos Scientific Laboratory.

The Systems Bi₂O₃-R₂O₃ (R = Y, Gd). R. K. DATTA and J. P. MEEHAN, Lighting Research Laboratory, General Electric Co. Phase Transitions in Complex Perovskites of the Type Ba₂LnMoO₆. C. D. BRANDLE and H. STEINFINK, University of Texas.

CHEMISTRY III —

Chairman: D. J. MAC DONALD, U.S. Bureau of Mines

A Comparison of Eluting Agents for the Ion-Exchange Purification of Promethium. (Session Keynote). E. J. WHEELWRIGHT, Battelle Memorial Institute, Pacific Northwest Laboratory.

Infrared and Raman Spectra of Trivalent Lanthanide — Di-(2-Ethylhexyl) Phosphoric Acid Solvent Extraction Organic Equilibrium Phases. ROBERT C. LLOYD and HARRY BOSTIAN, University of Mississippi.

Tricyclopentadienyl Complexes of Promethium, Curium, Berkelium, and Californium: Their Preparation and Identification by Microtechniques. P. G. LAUBEREAU and J. H. BURNS, Oak Ridge National Laboratory.

On the Formation Constants of the Rare-Earth Complex Species. YASUO SUZUKI and MARIKO MIKADO, Radioisotope School, Japan Atomic Energy Research Institute, Tokyo, Japan. Different Hydrated Forms of the Ethylenediaminetetraacetate Complexes of the Rare Earths. J. LINN MACKKEY, DAVID E. GOODNEY, and JAMES R. CAST, Austin College.

Analysis of the Elution System of Rare Earths With Chelating Agent as Eluent. ZENZI HAGIWARA and SUSUMU SAKAGUCHI, Faculty of Engineering, Tohoku University, Sendai, Japan.

Mobilities of Rare Earth Cations by Bromine Redox Electrolysis With Porous Carbon Electrodes. E. I. ONSTOTT, University of California, Los Alamos Scientific Laboratory.

SOLID STATE III —

Chairman: E. F. WESTRUM, JR. University of Michigan

An Electronic Transition in Cerium Hydride. (Session Keynote). G. G. LIBOWITZ, J. G. PACK, D. H. HOWLING, and W. P. BINNIE, Ledgemont Laboratory, Kennecott Copper Corporation.

Electrical Resistivity and Magnetic Susceptibility of Definite Compounds in the Tin-Samarium System. A. PERCHERON, J. L. FERON, and O. GOROCHEV, Centre National de la Recherche Scientifique, Laboratoire des Terres Rares, Bellevue, France.

Pressure-Induced Changes in the Electronic and Lattice Properties of Thulium Monotelluride and Their Significance. A. JAYARAMAN, E. BUCHER, and D. B. MC WHAN, Bell Telephone Laboratories.

Semiconduction in Rare Earth Oxides. C. N. R. RAO and G. V. SUBBA RAO, Indian Institute of Technology, Kanpur, India. Kondo Effect and the Influence of Crystalline Electric Field on the Electrical Resistivities of the Intermetallic Compounds CeAl₃ and CeAl₂. Y. U. S. RAO, W. SUSKI, R. S. CRAIG, and W. E. WALLACE, University of Pittsburgh.

CHEMISTRY IV —

Chairman: A. F. CLIFFORD, Virginia Polytechnic Institute

Chemistry and Physics of Lower Valence States of Lanthanides in Ionic Crystals. (Session Keynote). FRANCIS K. FONG, Purdue University.

Studies of the Divalent Oxides of the Rare Earths. GREGORY J. MCCARTHY, WILLIAM B. WHITE, and RUSTUM ROY, Materials Research Laboratory, Pennsylvania State University.

On the Existence of Divalent Ytterbium in Some Oxide Systems. J. C. ACHARD and O. de POUS, Centre National de la Recherche Scientifique, Laboratoire des Terres Rares, Bellevue, France.

An Investigation of the Eu-Eu₂O₃ System and the Equilibria Between the Europium Oxides and the Eu-Pt System, With Related Studies of the Sm-Sm₂O₃ and the Yb-Yb₂O₃ Systems. R. G. BEDFORD and E. CATALANO, University of California, Lawrence Radiation Laboratory.

A Study of the Binary Systems SmF₂-SmF₃, EuF₂-EuF₃, and YbF₂-YbF₃ and Their Equilibria With Corresponding Ln-Pt Systems. R. G. BEDFORD and E. CATALANO, University of California, Lawrence Radiation Laboratory.

Growth and Properties of Lanthanum Oxyfluoride Crystals. L. E. SOBON, K. A. WICKERSHEIM, R. A. BUCHANAN, and R. V. ALVES, Lockheed Palo Alto Research Laboratory.

Vacancy and Charge Ordering in the Th₃P₄ Structure. FORREST L. CARTER and M. O'HARA, U.S. Naval Research Laboratory.

The Ytterbium-Carbon System: Vaporization of YbC_{1.25}±y. JOHN M. HASCHKE and HARRY A. EICK, Michigan State University.

Vapor Pressure Measurements in the SmC₂-C and TmC₂-C Systems. ROBERT L. SEIVER and HARRY A. EICK, Michigan State University.

Isotopic Enrichment of the Product of a Lanthanide Neutron Capture Reaction. D. O. CAMPBELL, Oak Ridge National Laboratory.

CHEMISTRY V —

Chairman: R. K. DATTA, Lighting Research Laboratory, General Electric Co.

Predicting the Fermi Surface of Rare Earth Compounds Using Simple Chemical Concepts. (Session Keynote). FORREST L. CARTER, U.S. Naval Research Laboratory.

The Dissociation Energy of Diatomic Cerium and Predicted Stability of Gaseous Intermetallic Cerium Compounds. K. A. GINGERICH and H. C. FINKBEINER, Texas A and M University.

Electron-Transfer Absorption in Some Actinide (III) and Lanthanide (III) Tricyclopentadienides and the Standard II-III Cation Oxidation Potentials. L. J. NUGENT, P. G. LAUBEREAU, G. K. WERNER, and K. L. VANDER SLUIS, Oak Ridge National Laboratory.

Energy Transfer in Rare Earth Activated Systems. R. C. ROOP, Westinghouse Electric Corporation.

The Heat Capacity of Scandium From 6 to 300K. B. C. GERSTEIN, W. A. TAYLOR, W. D. SHICKELL, and F. H. SPEDDING, Ames Laboratory, USAEC, Iowa State University.

Thermal Study of Absolute Ionic Entropies and Crystal Field Splittings in Heavy Rare Earth Trichloro-Hexahydrates. Heat Capacities From 5-300° K. F. H. SPEDDING, D. C. RULF, and B. C. GERSTEIN, Iowa State University.

Distribution 4f et 5d-6s du Gadolinium et de l'Europium dans le Metal et l'Oxyde. C. BONNELLE and R. C. KARNATAK, Laboratoire de Chimie Physique de la Faculté des Sciences de Paris, France.

EPR of Gd³⁺ in Hydrated and Deuterated Rare Earth Double Nitrates and Ethyl Sulphates. H. A. BUCKMASTER, Y. SHING, University of Calgary, Calgary, Alberta, Canada.

A Structural and Thermogravimetric Investigation of the Rare Earth Formates. RHEAL P. TURCOTTE, MICHAEL S. JENKINS, JOHN M. HASCHKE, and LEROY EYRING, Arizona State University.

A New Room-Temperature Phase of Europium (II) — Orthosilicate. G. BUSCH, E. KALDIS, and R. VERREAULT, Laboratorium für Festkörperphysik, Zurich, Switzerland.

Europium Bromides and Hydrated Bromides. HARRY A. EICK and JOHN M. HASCHKE, Michigan State University.

METALLURGY —

Chairman: C. E. LUNDIN, Denver Research Institute

Phase Diagrams for the Ce-Co, Pr-Co, and Nd-Co Alloy Systems. (Session Keynote). ALDEN E. RAY and GARY I. HOFFER, University of Dayton

A Comparison of Sublimation and Vaporization for Purification of Samarium Metal. J. E. MURPHY, E. MORRICE, and M. M. WONG, Reno Metallurgy Research Center, U.S. Bureau of Mines.

The Proper Handling of Rare Earth Metals and Alloys for Lattice Parameter Studies. F. H. SPEDDING and B. J. BEAUDRY, Ames Laboratory, USAEC, Iowa State University.

Preparation of ¹⁴⁷Pm Metal and Determination of the Density and Melting Point. E. J. WHEELWRIGHT, Battelle Memorial Institute, Pacific Northwest Laboratory.

The Prediction of the Rare Earth Compounds With Other Elements by Means of Electronic Computers. E. M. SAVITSKY and V. B. GRIBULJA, Institute of Metallurgy of Banku, Academy of Sciences, USSR, Moscow.

Effect of the Sixth Period Elements on the Melting and Transformation Temperatures of Praseodymium. R. B. GRIFFIN and K. A. GSCHNEIDNER, JR., Ames Laboratory, Iowa State University.

High Pressure Synthesis of New Heavy Rare Earth Carbides. M. C. KRUPKA, N. H. KRUKORIAN, University of California, Los Alamos Scientific Laboratory.

The Reaction of Selected Lanthanide Carbides With Platinum and Iridium. N. H. KRUKORIAN, University of California, Los Alamos Scientific Laboratory.

Correlations Between Systems of Yttrium With the Groups IVB and VB Elements. O. N. CARLSON, O. D. McMASTERS, and F. A. SCHMIDT, Ames Laboratory of U.S. Atomic Energy Commission.

SOLID STATE IV —

Chairman: H. A. EICK, Michigan State University

The Effect of Co³⁺ on the Magnetic Properties of Yttrium Iron Garnet Single Crystals. (Session Keynote). G. WALLEZ, H. MAKRAM, and J. LORIER, Laboratoire de Recherche sur les Terres Rares, Centre National de la Recherche Scientifique, Bellevue, France.

Magnetic Properties of Transition Metal — Rare Earth Chalcogenide Spinels. LAWRENCE SUCHOW and ALFRED A. ANDO, Newark College of Engineering.

Crystal Field, g-Factor and Magnetic Susceptibility Calculations for Eu³⁺ and Tb³⁺ in the Rare-Earth Oxyfluorides. J. J. PEARSON, R. V. ALVES, K. A. WICKERSHEIM, and R. A. BUCHANAN, Lockheed Palo Alto Research Laboratory.

Mössbauer Effect Studies on Eu¹⁵¹ in Mixed Oxide Structures. G. W. DULANEY and A. F. CLIFFORD, Virginia Polytechnic Institute.

Optical, Electrical Transport and Dielectric Studies of Rare Earth Perovskites. C. N. R. RAD and G. V. SUBBA RAD, Department of Chemistry, Indian Institute of Technology, Kanpur, India.

X-Ray Study of Coloration Phenomenon in Lanthanum Oxide. STAFFAN A. BERGWALL and ARUN S. NIGAVEKAR, Institute of Physics, University of Uppsala, Uppsala, Sweden.

An Elevated Temperature X-Ray Diffraction and an Electron Microscopy Study of the Transformations to the Samarium-Type Structure in Gadolinium-Cerium Alloys. C. C. KOCH, P. G. MARDON, and C. J. MCHARGUE, Oak Ridge National Laboratory.

Vibrational Spectra of the C-Type Rare Earth Oxide Structure. WILLIAM B. WHITE, Materials Research Laboratory, Pennsylvania State University.

Radiative and Radiationless Transitions from ⁴F_{5/2} State of the Nd³⁺ Ion. S. A. POLLACK, TRW Systems Group.

SOLID STATE V —

Chairman: R. O. ELLIOTT, University of California Los Alamos Scientific Laboratory

Some Optical and Crystallographic Properties of Eu₂SiO₄. (Session Keynote). G. BUSCH and R. VERREAULT, Laboratorium für Festkörperphysik ETH, Zurich, Switzerland.

Crystal Chemistry of the Rare Earth Silicates. J. FELSECH, Swiss Federal Institute of Technology, Zurich, Switzerland.

Effect of Composition on the Europium Charge-Transfer-Band Absorption in the (Y, La, Eu)₂O₂S System. R. E. SHRAEDER and P. N. YOCOM, RCA Laboratories, David Sarnoff Research Center.

Zeeman Studies of Eu³⁺ and Tb³⁺ in Rare-Earth Oxyfluoride Hosts. R. V. ALVES, J. J. PEARSON, K. A. WICKERSHEIM, and R. A. BUCHANAN, Lockheed Palo Alto Research Laboratory.

Energy Transfer From Y₂O₂S Host to Tb³⁺ and Pr³⁺ at Very Low Concentrations. HAJIME YAMAMOTO, TSUYOSHI KANO, and YOSHIRO OTOMO, Central Research Laboratory, Hitachi, Ltd., Kokubunji, Tokyo, Japan.

Photoluminescence of Rare-Earth Oxides and Orthovanadates Activated by Bi³⁺. Study of the Energy Transfer Processes. G. BOULON and F. GAUME-MAHN, Faculté des Sciences, Laboratoire de Spectroscopie et Luminescence, Villeurbanne, France.

Fluorescence Spectrum of Eu³⁺ Ion in the Site of D₃ Symmetry of LaAlO₃ — Selection Rules — Crystal Field Parameters. F. GAUME-MAHN, C. LINARES, J. C. SOUILLAT, Université de Lyon, Laboratoire de Spectroscopie et de Luminescence, Villeurbanne, France.

Trivalent Rare Earths Luminescent Characteristics in Different Inorganic Glass Hosts. R. REISFELD, E. GREENBERG, L. KIRSHENBAUM, and G. MICHAELI, Department of Inorganic and Analytical Chemistry, Hebrew University of Jerusalem, Israel.

Infrared Spectra of Matrix Isolated Lanthanide Trifluorides. R. H. HAUGE, J. W. HASTIE, and J. L. MARGRAVE, Department of Chemistry, Rice University.

Cerium (III) — Sensitized Terbium (III) Luminescence in Thorium-Orthophosphate. R. HEINDL, V. GUÉRIN and J. LORIER, Centre National de la Recherche Scientifique, Laboratoire de Bellevue, France.

INDUSTRIAL PROCESSES AND GEOCHEMISTRY

Chairman: J. F. NACHMAN, Solar Division of International Harvester Company

Recent Developments in the Applications of the Rare Earth Metals in Nonferrous Metallurgy. (Session Keynote). I. S. HIRSCHHORN, Ronson Metals Corporation.

Rare-Earth Element Distributions in the Apollo 11 and Apollo 12 Lunar Samples. C. C. SCHNETZLER and J. A. PHILPOTTS, NASA-Goddard Space Flight Center.

The Use of a Mixer-Settler to Up-Grade a Rare Earth Mixture for Promethium Purification. J. A. PARTRIDGE, Battelle Memorial Institute, Pacific Northwest Laboratory.

A New Use for Rare Earths. HOWARD L. RECHT, MASOOD GHASSEMI, and EUGENE V. KLEBER, Atomics International, North American Rockwell.

Separation of Neodymium, Samarium, and Gadolinium by Liquid — Liquid Chromatography. J. OSCAR WINGET and R. E. LINDSTROM, Reno Metallurgy Research Center, U.S. Bureau of Mines.

The Use of Organophosphorus Compounds in the Separation of the Rare Earths. R. E. LONG, JR. and T. K. KIM, Sylvania Electric Products, Inc.

Separation of the Heavy Lanthanides From Yttrium. J. R. GUMP, Central Michigan University.

Activation Analysis of Yttrium in Ores. K. G. BROADHEAD and H. H. HEADY, Reno Metallurgy Research Center, U.S. Bureau of Mines.

Buckley Award to Geballe, Matthias



Geballe



Matthias

The American Physical Society's 1970 Oliver E. Buckley Solid State Physics Prize was awarded to Theodore H. Geballe and Bernd T. Matthias for their work in superconductivity. Geballe is professor of applied physics at Stanford University and Matthias is professor of physics at the University of California, San Diego.

The two were cited for "their joint experimental investigations of superconductivity which challenged theoretical understanding and opened up the technology of high-field superconductors." Geballe and Matthias, working together at Bell Telephone Laboratories, have greatly extended the list of known superconductors.

Among the superconductors discovered by the Buckley Prize recipients are some that remain superconducting in high magnetic fields and have high transition temperatures, up to almost 21° K. Some of their work on superconductors includes studies on rare-earth materials.

Ionization Potential Work Aids Theory

In late 1969 two papers were published, independent of one another, on the third ionization potentials of the lanthanide elements. The availability of these values at long last is greeted with great joy, since this will enable scientists to make various theoretical calculations.

The paper by M. M. Faktor and R. Hanks [*J. Inorg. Nucl. Chem.*, 31, 1649-1659 (1969)] was submitted (Continued on Page 6)

Lawrence Award To Rare Earther

James W. Cobble, professor of chemistry at Purdue University, received the U.S. Atomic Energy Commission's Ernest Orlando Lawrence Memorial Award in ceremonies held May 11 at the University of California in Berkeley.



Cobble

Dr. Cobble was cited for "outstanding contributions to the physical chemistry of aqueous electrolyte solutions and to the chemistry of technetium, the lanthanides, and actinides; for the discovery of ternary fission of ^{238}U , and for his investigations of chemically bound neutrons in LiF at low temperatures." He was one of five scientists honored for their recent meritorious contributions in the field of atomic energy.

The Lawrence Award was established in 1959 to honor the memory of the inventor of the cyclotron and first director of the AEC's radiation laboratory at Berkeley and Livermore, Calif., which now bears his name. The award, made annually to scientists not more than 45 years old who are United States citizens, includes a gold medal, a citation and a cash prize of \$5000.

HOT WINE

In a study of various parts of grapevines for absorption of fission product fallout activity, radiocesium was found in the surface or shallow part of the root [*Rev. Roum. Phys.* 14, 287-301 (1969)]. The authors determined that ^{144}Cs had been absorbed through the foliage surface, but not in the grape.

Although wine dregs were found to contain relatively large amounts of ^{40}K as an insoluble salt, the quantities of ^{90}Sr and other radioactive substances in the raisin were below the maximum allowable amount set by the International Atomic Energy Agency.

RARE EARTHS IN PERIODIC TABLE

Rare-Earth Elements and Their Position in the Periodic System by D. N. Trifonov is now available as an English translation.

Trifonov divides the development of ideas on the position of the rare-earth elements in the periodic system into five stages. The early chemical and analytical stages deal with the discovery of the rare earths, the confirmation of their trivalency and the discovery of the periodic law. Mendeleev's views on the position of the rare earths as well as Brauner's, Meyer's and a number of others are explored. But it is not until the electronic structure of the lanthanides is determined in the physical stage of development that the position of the rare earths is established. Trifonov explains that even today the position of the 4f families remains a problem and requires prolonged and thorough investigations.

This translation, AEC-tr-6875, is available from the Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia 22151, USA, price \$3.00, 240 pages.

RARE-EARTH BIBLIOGRAPHY

Bibliography on Rare-Earth Elements (Including Scandium and Yttrium) 1958-1962, K. E. Mironov and L. A. Chernikova, is now available as an English translation. This volume contains references to 3594 journal articles, monographs, collections, and abstracts pertaining to the rare-earth elements, alloys, and compounds which were published from 1958-1962.

The references are grouped under more than 50 subject headings to assist the reader in finding the desired subject matter. Both a subject and an author index are included in this 426 page volume.

The English translation is available as AEC-tr-6981 from the Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia 22151 U.S.A., price \$3.00.

Rare Earths at High Temperature

A number of papers on the chemistry and physics of refractory rare-earth compounds at elevated temperatures appear in *Chemistry of High-Temperature Materials*, N. A. Toropov, ed., Consultants Bureau, New York, 1969 (\$25.00). This book is the English translation of the Proceedings of the Second All-Union Conference on the High-Temperature Chemistry of Oxides held in Leningrad, 1965.

The use of rare-earth cations to stabilize a ZrO_2 phase may lead to promising materials for high-temperature technology, according to one of the papers. The use of ZrO_2 has been hindered by volume changes during phase transformations, but the addition of 3-7 mol % heavy RE oxides produces solid solutions which are stable in various gaseous environments and undergo no phase transformations up to 2000°C. Another interesting paper on new materials proposes that RE doped niobates and tantalates could be used as laser materials because of their spectroscopic properties.

A number of papers contain information of interest on rare-earth oxides including electrical properties, polymorphic transformations under vacuum at high temperatures, a direct method for computing lattice sums of distorted and complex cubic lattices, and a superpositional method for computing Madelung constants of defect lattices.

In mixed oxide systems one paper describes the use of statistics and probability theory to establish a dependence between composition and density, melting, and liquidus temperature for the rare-earth oxide-silicate system. Another paper discusses the ionic and electronic conductivity of the $\text{ZrO}_2\text{-PrO}_{1.83}$ system over a broad composition and temperature range. RE chromites are also discussed in several papers covering the synthesis and physicochemical properties of the chromites and the phase transformations of chromite single crystals.

Rare Earths In the News

DISTRIBUTOR

Royal Sulphuric Acid Works Ketjen, Ltd., Amsterdam, The Netherlands, has been named the exclusive agent in Europe and Israel for Shin-Etsu Chemical Industry Co., Ltd., Japan. Ketjen, Europe's largest manufacturer of petroleum cracking catalysts, plans to begin rare-earth production soon. Ketjen is a member of the Akzo group of companies of The Netherlands.

MERGER

Kerr-McGee and Vulcan Materials have announced plans to merge, bringing together the complementary product lines of the two companies. Kerr-McGee is an integrated oil and gas producer and refiner with interests in chemicals while Vulcan makes chemicals, construction materials and metals.

ACQUISITION

International Chemical and Nuclear Corp. has reached an agreement with Koch-Light Laboratories, Ltd., to acquire the Buckinghamshire, England firm outright. Acquisition of Koch-Light will mark International Chemical's first venture outside the United States. Koch-Light produces research chemicals for sale on the world market.

NEW RE ISOTOPES

Rare-earth isotopes ^{151}Er , ^{156}Yb and ^{157}Yb have been discovered by scientists working with the Oak Ridge isochronous cyclotron. The isotopes were made by bombarding ^{162}Er and ^{156}Dy with a helium-3 beam at 100 MeV. Discoverers of the new rare-earth isotopes were Dr. M. A. Ijaz, Virginia Polytechnic Institute, Blacksburg, Va., and Drs. K. S. Toth and R. L. Hahn, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

LANTHANUM CERAMIC

Lanthanum is a key ingredient in what is claimed to be the first truly transparent ferroelectric ceramic ever produced. The ceramic, made

at Sandia Laboratories, Albuquerque, N.M., is said to provide 10 times more contrast than previous ones in black and white image displays, and has a greater color range and lower switching voltages. The ceramic is made by adding 4 wt% or more La to the conventional lead zirconate-lead titanate formulation.

Detection of RE Reactor Poisons

A simple yet extremely sensitive method for determining the "neutron poisons" Gd, Sm, Eu and Dy in reactor materials such as uranium and zirconium has been developed by a team of scientists at the AEC's Ames Laboratory.

Employing quaternary oxide compounds with the empirical formulae $2\text{Li}_2\text{O}\cdot\text{SrO}\cdot\text{UO}_2\cdot\text{WO}_3$ and $\text{Na}_2\text{O}\cdot 2\text{SrO}\cdot 2\text{ZrO}_2\cdot\text{WO}_3$ as hosts for the rare earths under study, P. D'Silva, E. DeKalb and V. A. Fassel were able to detect and determine ultratrace amounts of these elements in the 5 to 10 part per billion (10^9) range in uranium and zirconium. They made their analyses by using x ray-excited, optical fluorescence techniques. Previous analytical methods required lengthy chemical preconcentration procedures to bring the rare-earth concentration up to the detectability level of other instrumental techniques.

Analytical methods for determining Gd, Sm, Eu and Dy in the range of one part per 10 million down to one part per billion are essential in the development of reactor materials. Because of their exceptionally high thermal-neutron capture cross sections (46000, 5600, 4300 and 950 barns, respectively, for Gd, Sm, Eu and Dy), their presence in reactor materials at levels of even less than part per billion amounts can reduce the thermal neutron economy in nuclear reactors.

Rare Earths in the Sun

For the first time the solar abundances of Er, Tm, and Lu have been determined. N. Grevesse and G. Blanquet used data from a new high-resolution solar spectrum obtained at the International Scientific

Station of the Jungfrauoch, Switzerland, to measure the abundances of the rare earths in the sun [*Solar Phys.* 8, 5-17 (1969)].

The results obtained in this study are in general agreement with those of earlier authors. However, in comparing solar and meteoritic abundances the authors found agreement only for Eu, Gd, Dy, Er, and Yb. The solar abundances of La, Ce, Pr, Nd, Sm, Tm, and Lu were greater than the meteoritic values.

The abundances of the rare earths are important in testing the s- and r-processes in nucleosynthesis. Unfortunately, the authors concluded, the solar abundances found in this study were unexplainable on the basis of nucleosynthesis theories.

HIGH-PRESSURE ION EXCHANGE

Adjacent lanthanide elements have been separated in less than one hour on a 100 mg scale using a high-pressure ion exchange method developed by Campbell and Buxton [*Ind. Eng. Chem. Process Design Develop.* 9, 89-94 (1970)].

Mixtures of neodymium and praseodymium and of samarium, europium and gadolinium were successfully separated as long as only a small percentage of the resin was loaded with the lanthanides. The authors studied the effects of flow rate, resin loading, eluent composition, and temperature on the separations.

High pressure is required for reasonable flow rates in the system. Glass columns 50 cm in length are suitable for pressures below 800 p.s.i. while stainless steel columns up to 150 cm in length are used at pressures up to 2500 p.s.i. Dowex 50-X12 resin which had been graded to 20- to 40-micron size was used in most of the experiments. Separation was achieved using solutions of α -hydroxyisobutyric acid as the eluent.

The authors anticipate that scale-up of the procedure will be practical, and that high-pressure ion exchange will be applicable to actinide separations.

Ionization Potential

(Continued from Page 3)

ted for publication slightly less than two months before that by D. A. Johnson [*J. Chem. Soc. A.* 1969, 1525-1528]. Basically the authors of both papers determined their values of the third ionization potential in the same manner, however, there were a few minor differences in detail.

The two sets of values were derived from the experimental heats of formation of the lanthanide oxides and heats of sublimation of the lanthanide metals; a knowledge of the first and second ionization potentials; and an estimate of the electron affinity of oxygen and the lattice energy of the lanthanide oxide. Faktor and Hanks also used the heats of formation of the lanthanide arsenides to make their estimates of the third ionization potential.

The two sets of values are in good agreement with each other, generally within 0.2 eV. The authors estimate that the uncertainty in their values range from 0.4 to 0.8 eV.

RIC Issues RE Review

RIC has just published *Reviews on Rare Earths. A Compilation of Books, Journal Articles, Reports, Conference Proceedings, and Bibliographies Published from 1946 to 1968* by C. C. Bertrand and K. A. Gschneidner, Jr.

The bibliography is composed of about 500 general and specific reviews which have been placed in sections best classifying their contents. The reviews in each section are grouped according to books, chapters, journal articles and reports, bibliographies and conference proceedings. A subject and an author-editor index are included.

To obtain a copy, order USAEC Report IS-RIC-3 from the Clearinghouse for Federal and Scientific Technical Information, Springfield, Virginia 22151, U.S.A.; the price is \$3.00.

Rare-Earth Metals in Steels

The effect of rare-earth additions to steels is explored in a special report, IS-RIC-4, prepared by RIC in a study sponsored by Molybdenum Corporation of America.

Rare-Earth Metals in Steels by Nancy Kippenhan and Karl A. Gschneidner, Jr. discusses the question of rare-earth additions to steels by reviewing the literature published on the subject during the 1960's. The information is presented according to increasing complexity of the steels involved. Data on the effect of rare earths on the various characteristics and properties of steel as well as the effect of individual rare earths can be easily located from tables included at the end of each main section. A discussion and summary of the survey has also been included. The 61 page report contains 88 references.

Copies of this report can be obtained without charge from RIC or from Molybdenum Corporation of America, 280 Park Avenue, New York, N.Y. 10017.

Metallic Chlorides

An unusual example of metal-metal bonding has been reported by D. A. Lokken and J. D. Corbett in a lower gadolinium chloride, $GdCl_{1.58 \pm 0.06}$ [*J. Am. Chem. Soc.* 92, 1799-1800 (1970)].

The compound was produced by reacting $GdCl_3$ vapor with gadolinium metal at 610° for several days. The unusual feature of the structure is the presence of chains of gadolinium atoms running parallel to the unique axis. The chains are made up of elongated octahedra sharing opposite edges, with the repeat distance being 3.896\AA , the b dimension. Sheaths of chlorine atoms at distances of 2.71 to 2.83\AA separate the chains of gadolinium atoms from each other.

The structure seems to have features of both metallic and ionic (plus covalent) bonding. The distances within the chain are appropriate for metal-metal bonding, while the geometry and chlorine distances are suitable for $Gd^{3+}-Cl^-$ interactions.

GEOCHEMISTRY

Problems of Geochemistry, N. I. Khitarov, ed., is a special jubilee collection of papers by Soviet and non-Soviet scientists in honor of the 70th birthday of A. P. Vinogradov. Originally published in Russian in 1965, the volume is now available as an English translation, TT-68-50450.

The 754-page volume contains papers in the areas of cosmochemistry and creation of the earth, geochemistry of individual elements and isotopes, genesis of rocks and geochemistry, mineralogy and geochemistry, geochemistry of radioactive elements, biogeochemistry, geochemistry of the ocean, and problems of regional geochemistry.

The papers dealing with rare earths discuss the similarities in the distribution of rare-earth elements in meteorites and in rocks of the earth's crust, the behavior of the rare-earth elements in the hydrothermal process, the separation of the rare earths in the magmatic process, and the abundances of yttrium and ytterbium in igneous rocks.

This translation, TT-68-50450, may be obtained from the Clearinghouse for Federal Scientific and Technical Information, Springfield, Va., 22151, U.S.A.; the price is \$3.00.

Makes Grant to RIC

International Energy Company, Midland, Texas, has become the 20th private industrial concern to provide financial support for RIC. The Center derives its support from grants such as the one by International Energy, and from Iowa State University's Institute for Atomic Research.

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DAVISON CHEMICAL

Davison Chemical, a division of W. R. Grace & Co., has issued two new brochures dealing with rare earths. One, *Rare Earths and Thorium*, describes the processing of rare-earth chemicals and includes a photographic portrayal of the derivation of various rare-earth and thorium products from monazite sand, plus a three dimensional-style illustration showing the relation of rare earths to other elements in the periodic table. The second brochure describes cerium oxide polishing powders, their history, manufacture and uses. Copies may be obtained by writing Davison Chemical Division, W. R. Grace & Co., 4000 N. Hawthorne St., Chattanooga, Tenn. 37406, USA.

CERAC

Cerac, Inc. has product data sheets available for lanthanum boride, rare-earth borides and cerium oxide. The data sheets include information on properties and applications. To obtain copies write: Cerac, Inc., Box 597, Butler, Wisconsin 53007, USA. You can order data sheets by number; LA-569 (lanthanum boride), REB-965 (rare-earth borides), and CEO-568 (cerium oxide).

Photochromics

Z. J. Kiss (*Physics Today* 23, 42-49, Jan. 1970) has described the present state of the art of photochromic materials. In reading the article it is very evident that rare-earth materials play a leading role.

A photochromic material is one which changes color in a reversible manner under illumination by light. The color change is due to a photo-induced charge transfer between deep lying impurity levels or from lattice defects, or combinations of both. With some photochromic materials it is possible to perform

"read", "write" and "erase" operations.

As Kiss points out there are still several problems to be solved, ranging from the need for a better theoretical model to the growth of large high-quality crystals. Utilization of photochromics is possible in optical information storage (especially in conjunction with computers), optical processing and display systems (possibly in a three-dimensional television display).

Plans to Drop RE Stockpile

With Congressional approval the United States Government in Fiscal 1971 will sell 5288 short dry tons (sdt) of its rare-earth stockpile in a move to reduce its present inventory toward the 6500 sdt stockpile objective announced in mid-1969.

As of Dec. 31, 1969 the Government had 13,521 sdt of rare earths on hand — an excess of 7021 sdt over the stockpile objective. Sale of the 5288 sdt will still leave an excess of 1733 sdt over the announced inventory objective. The 5288 sdt excess available for sale in Fiscal 1971 is valued at \$1.9 million. In a later move the Office of Emergency Preparedness, which makes stockpile recommendations for the Government, advised that rare earths be dropped from the list of strategic stockpile materials.

Separation Review

A comprehensive review of the separation methods involving rare-earth elements appears in *Modern Methods for the Separation of Rarer Metal Ions*, J. Korkisch (Pergamon Press, New York, 1969).

Cation and anion exchange separations as well as other chromatographic, extraction, and coprecipitation methods are surveyed in this chapter. References are given for effective separations from a number of mediums including alloys, rocks, meteorites, sea water, biological materials, fission products, and environmental samples. The 58-page chapter contains more than 500 references.

RE Work at Dayton

(Continued from Page 1)

The Magnetics Group directed by Karl Strnat continues to work on a new class of permanent magnet materials based on the RCO_5 phases whose industrial development it has pioneered. This exciting work has stimulated industry and government to organize large development efforts which have already resulted in SmCo_5 magnets with properties far superior to any commercial magnets, with still better and cheaper magnets in store for the future. (This development has been the subject of several previous items published in the *RIC News*, 1, [3], 4; 1, [4], 7 and 3 [3], 1.

Related systematic studies of basic magnetic properties of rare-earth intermetallics are aimed at a better understanding of the spin order and especially the magneto-crystalline anisotropy, a key property for the magnet application.

Norman Hecht is conducting an evaluation of flame-sprayed coatings of Y_2O_3 , La_2O_3 , CeO_2 , Pr_2O_3 and Nd_2O_3 on refractory metals and ceramics. Deposition techniques, crystal and microstructure of the deposits, the strength of their bond to the substrate and their resistance to corrosion by various molten metals (Fe, Ni, Ti, Co) will be studied. Such coatings are of potential technological importance for crucibles and containers for use in the metallurgical processing of steels and high-strength alloys.

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Eu Orthosilicate

Two recent publications on preparation and properties of Eu_2SiO_4 have revealed some interesting characteristics of this material. These papers by G. Busch, E. Kaldis, R. Verreault, and J. Felsche and by Kaldis and Verreault appeared in *Mater. Res. Bull.* 5, 9-18 (1970) and in *J. Less-Common Metals* 20, 177-189 (1970), respectively.

Eu_2SiO_4 is of interest because it is ferromagnetic ($\sim 5^\circ\text{K}$), transparent and an anisotropic semiconductor. In the first paper the authors state that the room temperature form is monoclinic and that it transforms to an orthorhombic modification at 165°C . This phase transformation is accompanied by a color change, a decrease in the semiconducting energy gap of 0.12 eV, and an anomaly in the dielectric constant.

In the second paper the authors discuss the method of preparing single crystals by a high-temperature chemical transport technique, the stoichiometry, purity and optical properties. The influence of Eu^{+3} ions is also noted in their presentation.

More Bubbles

The Bell Laboratory workers headed by L. G. Van Uitert have reported some more experimental details on the bubble domain devices; *Appl. Phys. Letters*, 16, 84-85 (1970) and *Mater. Res. Bull.*, 5, 153-162 (1970). Both of these papers are concerned with the effect of substituting small quantities of Co for iron in rare-earth orthoferrites, RFeO_3 . The substitution of as little as 5% Co has a marked effect on the magnetocrystalline anisotropy and can reorient the net moment from the *c* axis to the *a* axis.

The bubble domain devices are thin plates about 1 cm (0.4 in.) on an edge and 0.0025 cm (0.001 in.) thick with the easy direction of magnetization normal to the plate. The problem heretofore has been

RARE AIR

The proverbial "breath of fresh air" is becoming rare. A typical sample of urban air was found to contain more than 20 elements including Sc, La, Ce, Sm, Eu, Yb, and Lu [*Anal. Chem.* 42, 257-265 (1970)].

Atmospheric aerosols were analyzed by neutron activation analysis, and the concentrations observed for the rare earths varied from $2 \times 10^{-3} \mu\text{g}/\text{m}^3$ for Ce to $1 \times 10^{-5} \mu\text{g}/\text{m}^3$ for Lu.

Although the rare earth level was extremely low, one of the most notable results of the study was that the unusually high vanadium concentration of 0.4 to $2.0 \mu\text{g}/\text{m}^3$ may constitute a health hazard.

STAMP

The chemical symbol for scandium appears on the 1965 4K Russian stamp commemorating the 20th IUPAC (International Union of Pure and Applied Chemistry) Congress in Moscow. The symbol appears in the spelling of MoScOW.

that the bubble diameter has been too large by a factor of four to be useful in these devices. But by the substitution of cobalt this goal has been achieved.

The authors have also discussed the method of preparing the plate-like crystals by a flux growth technique in the *Mater. Res. Bull.* paper.

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

Second-Class postage
paid at Ames, Iowa.

RIC Display

In recent weeks RIC has been developing a display of rare earths and rare-earth products. The lighted display is located in wall-hung cases in a corridor near the RIC office.

Rare earths on display include oxides, metals, metal products, crystals, ceramic tile, glassware and optical glass, RE-doped light bulbs, industrial chemicals, phosphors and magnets. Display items have been donated by about 12 rare-earth producers and research installations.

We would be happy to receive additional display items from those of you who have rare-earth material available for such purposes. Appropriate credit will be given to each donor.

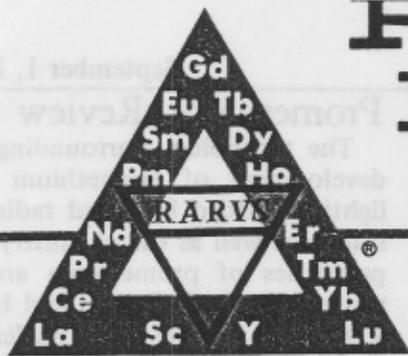
ATOMIC SPECTRA

"Bibliography on the Analysis of Optical Atomic Spectra," C. E. Moore, U.S. National Bureau of Standards Special Publication 306, includes all references necessary to compile tables of atomic energy levels, classified lines and Zeeman data for rare-earth spectra.

The bibliography has been published in four sections; the references on Sc are in section 1, Y in 2, La in 3, and the lanthanides La through Lu in section 4.

This publication is available from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402, U.S.A.; price for section 1—\$1.00, section 2—\$.60, section 3—\$.50, section 4—\$.55.

RARE-EARTH INFORM CTR
AMES LAB USAEC
IOWA STATE UNIVERSITY
AMES, IOWA 50010



RARE-EARTH INFORMATION CENTER NEWS

SUPPORTED BY INSTITUTE FOR ATOMIC RESEARCH
IOWA STATE UNIVERSITY / AMES, IOWA

Volume V

September 1, 1970

No. 3

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 1879, and dysprosium, 1886, by 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-

(Continued on Page 4)

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 groups 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), $\text{Pr}_{1-x}\text{O}_2$, LaCoO_3 , $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ and the ferrogarnets ($\text{Y}_3\text{Fe}_{5-x}\text{Si}_x\text{O}_{12}$) were discussed along with a number of other non-rare earth compounds.

1100 WATT CW LASER

The Laser Products Division of Holobeam, Inc., Paramus, 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

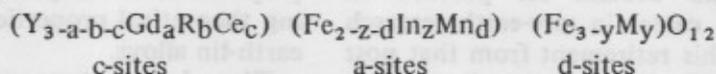
The mechanical and physical-chemical properties of the rare-earth metals are tabulated in the *Handbook of the Rare Elements. Vol. III. Radioactive and Rare Earth Elements*, M. A. Filyand and E. I. Semenova, translated and edited by M. E. Alferieff, (Boston Technical Publishers, Inc., Cambridge, Mass.,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



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 resonances were observed in $Yb_3Fe_5O_{12}$ at 11 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.

(Continued on Page 4)

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/cm² at 1000°C and 600 MW/cm² 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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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 ferroelastic 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 $160^\circ C$. 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 -
(Continued from Page 1)

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. Loriaux; 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. Loriaux. 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 preparation of compounds, either 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 preparation 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 (Continued from Page 3)

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.

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Nobel Rare Earther



Louis Néel

The 1970 Nobel Prize in Physics was awarded to Dr. Louis Néel, director of the Institut Polytechnique de Grenoble and the Centre d'Etudes Nucleaires de Grenoble. Dr. Néel was cited for his "fundamental work and discoveries concerning antiferromagnetism and ferrimagnetism which led to important applications in solid state physics."

The rare-earth garnets were discovered by Dr. Néel and his co-workers in their investigation of the effect of external stimuli, such as heat and electrical charge, on the magnetic properties of ferromagnetic and ferrimagnetic materials. Dr. Néel's research has also involved the magnetic properties of rare-earth metals and ferrites. More recently, Dr. Néel has studied ordered structures created by neu-

Pacemaker Development Tied to Rare Earths

When nuclear-powered cardiac pacemakers reach full development and replace present battery-powered pacemakers, a great deal of their success will be traced to the rare earths. Nuclear-powered pacemakers under development will have a life expectancy of about 10 years compared to the 18-30 month life expectancy of pacemakers powered by mercury batteries.

Promethium-147 may well be the "battery" for nuclear cardiac pacemakers. The Australian Atomic Energy Commission's Research Division has announced the development of a cardiac pacemaker which utilizes alternate layers of ^{147}Pm and silicon for the generation of electricity, and expects to eventually generate a 40 μA current at 5V.

In the United States, Ronson Metals Corporation's CerAlloy 400 has been selected as the getter material for a pacemaker being developed by Nuclear Materials and Equipment Corporation (NUMEC) for the U.S. Atomic Energy Commission. A continuous getter, CerAlloy 400 has the ability to combine with active gases over a wide temperature range. With it, NUMEC engineers hope to maintain a vacuum of 0.1 μ and thus achieve the 10-year life specification of their pacemaker.

tron irradiation and the magnetic properties of fine-grained antiferromagnetics.

We extend our heartiest congratulations to Dr. Néel for being honored by this distinguished prize.

Those f Electrons

Three articles in the June 1970 issue of the *J. Chem. Ed.* 47, 417, 424 and 431, were devoted to the lanthanides and the influence of the 4f electrons.

The first paper by T. Moeller, "Periodicity and the Lanthanides and Actinides," reviewed the regular recurrence in the chemical and physical behavior of these two inner transition series of elements. The periodicity was reviewed from three different approaches: (1) in relation to the periodic table as a whole, (2) between the two series—lanthanides vs actinides, and (3) within each of the series.

In the second paper, "Coordination of Trivalent Lanthanide Ions," D. G. Karraker reviewed lanthanide ion-ligand bonding characteristics, coordination geometry, polymorphism, chelate structures, coordination in solutions and complexes. A comparison between the behavior of the 3d and 4f metal ions indicates that there is little 4f involvement, and that the bonding is essentially electrostatic with high coordination numbers, six or greater.

(Continued on Page 4)



Michigan State University—

Rare Earth Chemistry Group

RARE EARTH RESEARCH GROUP—In the front row from left are Robert Seiver, Sandra Leonard and Carol Biefeld. Pictured in the back row from left are Harry Eick, Alleppey Hariharan, Dale Work and John Smeggil.



Research at Michigan State University under the direction of Harry A. Eick involves phase, crystallographic, and high temperature preparative and thermodynamic studies of binary and ternary lanthanide refractories. Those lanthanides which exhibit divalent tendencies—Sm, Eu, Tm, and Yb—have been studied most recently in the form of carbides, oxide-carbides, halides, oxidehalides, and sulfides. Previous work included borides and chalcogenides. Each phase is examined in three ways: 1. the phases in equilibrium with it are determined, 2. its structure is verified by x-ray diffraction or determined if it is unknown, and 3. the vapor or decomposition pressure of the substance is determined.

The Knudsen effusion target collection technique is used in combination with time-of-flight mass spectrometry to determine equilibrium vapor pressures (and species) as a function of temperature. The microgram condensates are assayed by x-ray fluorescence. From these measurements enthalpies of formation of the phases are calculated. From such studies a consistent set of thermodynamic data may be obtained and, by analogy, the thermodynamics of related reactions may be predicted.

The Michigan State group have recently completed a phase study of the ytterbium-carbon system, and has examined the vaporization behaviors of YbC_2 and an apparently nonstoichiometric $\text{YbC}_{1.25+y}$. Single crystals have been grown and the structure of some of these unusual carbides are being determined by x-ray diffraction techniques. Furthermore, they have demonstrated that previous reports of YbO are erroneous—the phase reported is actually Yb_2OC . They have shown, however, that YbO can be prepared at about room temperature.

☆☆☆☆☆☆☆☆☆☆☆☆☆☆☆☆
 ☆ Reports ☆
 ☆ Booklets ☆
 ☆ Brochures ☆
 ☆☆☆☆☆☆☆☆☆☆☆☆☆☆☆

TYPPI OY—FINLAND

Typpi Oy has recently issued an attractive color brochure, *Rare Earths*. The 41-page booklet contains a comprehensive section on the various uses and applications of the rare earths as well as sections describing the history, facilities, and services of Typpi Oy. Data sheets on rare-earth products are also contained in this brochure which may be obtained free in English or German (*Seltene Erden*) from Typpi Oy, RE-Marketing, Albertinkatu 36D, Box 18175, Helsinki 18, Finland.

Other systems under study include TmC_2 , SmOF , EuS , YbCl_2 , EuCl_2 , and YbOCl . This last phase is particularly interesting in that the c parameter of the unit cell is greater than 50 Å.

High Temperature Oxides

The fabrication, properties, and behavior of yttrium oxide and the lanthanide oxides are reviewed in *High Temperature Oxides, Part II*, A. M., Alper, ed. (Academic Press, New York, 1970) \$16.50.

R. C. Anderson, in the yttrium oxide chapter, discusses some recent technical progress in the preparation and processing of Y_2O_3 as well as the basic structural chemistry, electrical and mechanical properties and applications of this material.

The refractory lanthanide oxides are reviewed by LeRoy Eyring. Eyring emphasizes the importance of the rare-earth oxide series as "a window through which the many facets of solid state and high temperature chemistry may be viewed," as he describes the preparation, crystal structure, thermochemistry, magnetic behaviors and the optical and electrical properties of the oxides.

Analytical Volume

A comprehensive, well-organized volume on the analytical chemistry of the rare earths—*Analytical Chemistry of Yttrium and the Lanthanide Elements* by D. I. Ryabchi'kov and V. A. Ryabukhin—has recently been translated from Russian into English. The English language edition is published by Ann Arbor-Humphrey Science Publishers, Ann Arbor, Michigan, 1970.

The volume includes methods for the determination of the rare-earth elements by gravimetric, polarographic and volumetric procedures, optical methods and activation analysis. The analyses of minerals, alloys, mixtures and compounds are treated separately. Special chapters are also included in the determination of traces of rare earths in high-purity materials and on the analysis of radioactive rare-earth elements.

The more than 2000 references in this volume represent the international literature on the subject through 1964. The price of this book is \$20.00.

High Purity RE Review

The production and application of high purity rare-earth products and their economic importance are reviewed by I. T. Ojima in *Chem. Economy Eng. Rev.*, June 1970, 29-33 and July 1970, 28-33.

Examples of processes for the preparation of high purity europium oxide and yttrium oxide and the corresponding metals are discussed. Typical analyses are included in conjunction with the discussion of techniques for rare-earth analysis and the detection limits of each. Metal production methods yielding 99.9-99.99% pure metals are described.

These high purities are required for use in such applications as phosphors, lasers, bubble memory units and permanent magnets. The properties of the important compounds in these areas are discussed as well as those used as catalysts and in nuclear applications.

Further growth of the rare-earth industry, the author adds, will require economic cooperation between the user and the producer to promote research and development.

RIC News

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Nancy Kippenhan and W. H. Smith
Staff Writers

Ytterbium, atomic number 70, was discovered by J. C. G. Marignac in 1878 and obviously is named for the town of Ytterby.

MEETING

DURHAM RE CONFERENCE

Invited speakers for the Durham Conference on Rare Earths and Actinides to be held at the University of Durham July 5-7, 1971, have been announced. They are R. J. Elliott, Clarendon Laboratory, Oxford; K. A. Gschneidner, Jr., Iowa State University; B. Coqblin, University of Paris; K. H. J. Buschow, Philips Laboratories, Eindhoven; W. C. Koehler, Oak Ridge National Laboratory; J. A. Lee, Atomic Energy Research Establishment, Harwell; and M. B. Brodsky, Argonne National Laboratory.

Inquiries regarding the scientific program and offers of papers are now being accepted. Inquiries should be addressed to the Conference Secretary, W. D. Corner FlinstP, University of Durham, Science Laboratories, South Road, Durham City, ENGLAND. Offers of papers should be accompanied by a 200-word abstract and should be sent as soon as possible, but in no case later than April 3, 1971.

8 More Firms Support RIC

Eight additional rare-earth producers or manufacturers of rare-earth products have contributed their support to RIC for the current fiscal year. This brings to 24 the total of firms which support RIC activities. Those companies which have made contributions since the previous list of RIC supporters was published are:

Elettrochimica Italiana Delle Terre Rare, Italy.

General Electric Company, U.S.A.

International Energy Company, U.S.A.

Lunex Company, U.S.A.

Philipp Brothers, U.S.A.

Rare Earth Corporation of Australia, Ltd., Australia.

Sel-Rex Corporation, U.S.A.
Shin-Etsu Chemical Industry Company, Ltd., Japan.

Five of the eight companies are new contributors to RIC. Elettrochimica Italiana Delle Terre Rare, International Energy and Shin-Etsu have previously supplied financial support for the Center.

Inert Refractories

A recent translation of some Russian work on mixed rare-earth oxides indicates that rare earth tantalates are inert to chemical attack by a variety of mineral acids and sodium hydroxide. N. I. Timofeeva and O. A. Mordovin, *Zhur. Neorg. Khim.* 15, 865-867 (1970); English translation, *Russ. J. Inorg. Chem.* 15, 440-441 (1970), confirm the existence of three of the four previously reported tantalates: Gd_3TaO_7 , $GdTaO_4$ and $GdTa_3O_9$. These compounds are quite refractory with melting points of 2280°, 2050°, and 1840° C, respectively. The Gd_3TaO_7 compound, in addition to being the highest melting ternary compound and whose melting point is 40° C less than that of Gd_2O_3 , has a hardness 4 times that of Gd_2O_3 and is very inert chemically compared to Gd_2O_3 . The crystal structure of Gd_3TaO_7 is of the pyrochlore type.

The chemical inertness of the three gadolinium tantalates according to the authors is the same; however, $GdTa_3O_9$ is about 20% softer than Gd_3TaO_7 , while $GdTaO_4$ has half the hardness of Gd_3TaO_7 .

Other rare earth tantalates and perhaps rare earth niobates may be expected to show properties similar to those found for the gadolinium compounds.

THE AGE OF DISCOVERY

The rare-earth elements were discovered over a 160 year period dating from 1787 to 1947. The most complex element hunt in the history of science began in 1787 when Lt. C. A. Arrhenius stumbled on a unique black mineral near a quarry in Ytterby, Sweden, and was culminated in 1947 with the discovery of promethium.

Rare Earths In the News

ERBIUM SINGLE CRYSTAL

Scientists at the U. S. Atomic Energy Commission's Ames Laboratory have produced what is believed to be the largest, purest single crystal of erbium ever achieved. The crystal, 99.95% pure, measures 1.2 cm (0.5 in.) diameter and is 12.5 cm (5 in.) long. The record single crystal was grown by arc-zone melting, a process which depends upon a large temperature gradient—often as much as 1600° C—that is established when the surface of the metal is melted with an electric arc while the sample is supported in a water-cooled copper mold.

SPEEDY X-RAY

Sylvania has announced the development of an improved phosphor for boosting the speed of diagnostic x-rays by 100%. The Eu-doped phosphor, $Ba_3(PO_4)_2:Eu$, peaks at the spot x-ray film is most sensitive, at the 415 nm peak in the deep blue-violet. This phosphor now makes it possible to take x-ray pictures of moving parts of the body without blurring the image, Sylvania claims, and also reduces the exposure of patients to radiation.

La HI TEMP ALLOY

A lanthanum-bearing cobalt alloy developed by Cabot Corporation's Stellite Division is expected to provide the next incremental improvements over Hastelloy X, a nickel-cobalt alloy presently used in the burner section of gas turbines. Hastelloy X can withstand temperatures up to 870° C and provide a component life of 20,000 hours without protective coatings. The lanthanum-bearing alloy, designated HA-188, can provide an 80° C temperature advantage in creep strength and two to three times better thermal fatigue life at 980° C, although its oxidation resistance at 980° C is somewhat less than that of Hastelloy X at 870° C.

YTTRIUM BOOSTS TEMP LIMIT
NASA's Lewis Research Center reports that small amounts of yttrium, and tantalum or hafnium added to Fe-Cr-Ni alloys impart increased high temperature oxidation resistance to these superalloys up to 1260° C. A 10-mil thick foil of Fe-25Cr-4Al-0.5Ta-0.08Y subjected to this temperature for 800 hours exhibited a weight loss of less than 3.5 mg/cm². This, NASA reports, is a 60° C temperature advantage over commercially available superalloys.

RE Technology

Industrial methods for the separation and preparation of the rare earths are reviewed by E. Greinacher in a chapter in *Chemische Technologie - Band 2 Anorganische Technologie II* (Carl Hanser Verlag, Munich, 1970).

The chapter contains a brief description of the history, aqueous chemical behavior and methods of analysis of the rare earths. The principal applications of the rare earths as alloying agents, lighter flints, glass-polishing materials and catalysts are explored as well as other miscellaneous applications. Beginning with the ore, the production of the metal is described through the various extraction and separation steps to the electrolysis of the chloride or oxide which yields the product metal. The preparation of high purity metals is also briefly reviewed.

Rare-Earth Information Center
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Ames, Iowa 50010

Duwez Named ASM Fellow

Professor Pol E. Duwez, California Institute of Technology, was one of the first 200 members of the American Society for Metals (ASM) to be named ASM Fellows for their distinguished contributions to the field of metals and materials. Professor Duwez has made several contributions to rare-earth metallurgy.

To RESA Governing Board

Hans Borchardt, E. I. du Pont de Nemours & Co., has been named to the governing board of The Scientific Research Society of America (RESA). Rare-earth luminescence is one of his varied professional interests.

(Continued from Page 1)

The last paper by O. Johnson, "Role of *f* Electrons in Chemical Binding," does not deal so much with the lanthanides as it does with the effect of the 4*f* electrons on the properties of the elements beyond the lanthanides. Johnson believes the indirect influence of the *f* electrons is due to the poor screening of the nuclear charge by these electrons, and thus this shows up in the ionization potentials and chemical behaviors of the sixth-period elements as compared to those of the fourth and fifth periods. For example, the first ionization potentials of the elements gold, mercury, thallium and lead are anomalously higher than those expected from the trend established by their respective congeners.

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