

# RARE-EARTH INFORMATION CENTER NEWS

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

Volume VII

March 1, 1972

No. 1

## Giant Magnetostrictions

The discovery of giant room-temperature magnetostrictions in polycrystalline materials was announced by A. E. Clark and H. S. Belson of the U.S. Naval Ordnance Laboratory, Silver Spring, Md., at the Magnetism Conference in Chicago, Ill., Nov. 16-19, 1971. The largest magnetically-induced strains found to date ( $\sim 2000 \times 10^{-6}$  for  $TbFe_2$ ) are ten times larger than the largest value previously reported for any polycrystalline substance and 100 times larger than for typical magnetostrictive strains.

The origin of the magnetostrictions in the  $RFe_2$  and  $RFe_3$  compounds is due to the anisotropy of the rare earth ion and not the iron ion. The magnetostriction remains large at room temperature because the iron ion aligns the rare earth spins at temperatures well above room temperature ( $>500^\circ C$ ). The corresponding cobalt and nickel compounds have small room temperature values because the cobalt or nickel ion does not, or only weakly, aligns the rare-earth spins.

Magnetostrictions of  $5600 \times 10^{-6}$  and  $-3500 \times 10^{-6}$  are predicted for  $CeFe_2$  and  $TmFe_2$ , respectively, at absolute zero. The magnetostrictions are defined as the difference between the strains parallel and the strains perpendicular to the applied field direction.

Some of the results reported by Clark and Belson have been recently confirmed by N. C. Koon, A. I. Schindler and F. L. Carter, *Phys. Letters* 37A, 413-414 (1971).

## Rare Earths Are Fluorescent Probes

Rare earth ions are finding increasing use as biological probes. Besides being used as NMR probes [*RIC News* VI [2] 4 (1971)], the lanthanide ions are now serving as fluorescent probes in determining the nature of metal-binding sites and the conformation of proteins.

C. K. Luk used  $Pr^{+3}$ ,  $Nd^{+3}$ ,  $Eu^{+3}$ ,  $Tb^{+3}$ ,  $Ho^{+3}$  and  $Er^{+3}$  in a study of human serum transferrin, an iron-binding protein which acts as an iron buffer and an iron carrier, *Biochemistry* 10, 2838-2843 (1971). From titration curves determined from the ultraviolet absorption spectrum of the rare earth ion added to transferrin, it was found that the two metal binding sites in transferrin are not equivalent as was earlier thought. The larger ionic radii of  $Nd^{+3}$  and  $Pr^{+3}$  allowed these ions to bind in only one site per protein molecule, while  $Eu^{+3}$ ,  $Tb^{+3}$ ,  $Ho^{+3}$  and  $Er^{+3}$  could fit into both binding sites.

In the same study, fluorescence lifetime measurements of the  $Tb^{+3}$ -transferrin complex and the  $Tb^{+3}$ -transferrin- $Fe^{+3}$  complex showed that the distance between binding sites was greater than  $43\text{\AA}$ . This is a refinement of earlier studies which showed that the two sites were greater than  $9\text{\AA}$  apart.

## Cresson Award to Van Vleck

Harvard University's John H. Van Vleck has received one of two Elliot Cresson Medals awarded for 1971 by the Franklin Institute.



Van Vleck

Established in 1848, the Cresson award is the oldest of the Franklin Institute's awards.

Van Vleck, now Hollis Professor of Mathematics, Emeritus, was cited for his contributions to magnetism and other aspects of solid-state physics and for his training of physical scientists. Known to the rare earth community as the father of rare earth magnetism, Van Vleck has also gained renown for his studies of the quantum theory of atomic structure.

Van Vleck has received the American Physical Society's Langmuir Prize and served as president of the Society in 1952. He is a past winner of the Michelson Award of the Case Institute of Technology, and the National Medal of Science.

## 27 Firms Back RIC

Two more rare earth firms have become Fiscal 1972 financial backers of RIC. They are Nippon Yttrium Co., Japan, now in its second year of RIC support, and a new contributor APROMON, Administracao da Producao da Monazita, Brazil. The addition of these two companies to the ranks of Center backers brings to 27 the number of firms contributing this year.

## Rare Earths In the News

### Y<sub>2</sub>O<sub>3</sub>-AlN COMPOSITE

A dense, high strength, fiber-reinforced product has been produced by K. Komeya and H. Inoue by sintering 25 wt % Y<sub>2</sub>O<sub>3</sub> with AlN at 1700°C [*Trans. Brit. Ceram. Soc.* 70, 107-113 (1971)]. The reaction product consisted of Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>, and possibly Y<sub>4</sub>Al<sub>2</sub>O<sub>9</sub>, and well-developed, randomly oriented AlN fibers.

### SPACE SHUTTLE

Four rare earth containing alloys, TD (thoria dispersed) Ni-Cr-Al-Y, Haynes alloy No. 188 (39Co-22Ni-22Cr-14W-2Fe-1Mn-0.2Si-0.1La), GE-1541 (80Fe-15Cr-4Al-1Y) and GE 2541 (70Fe-25Cr-4Al-1Y) are among several candidates for the metallic heat shields for the U.S. space shuttle vehicle which was recently given presidential approval for development.

### ORE ANALYZERS

Rare earth radioisotopes, <sup>147</sup>Pm and <sup>153</sup>Gd, are being used to detect tin and barium, and tungsten and lead, respectively, in ores. The radiation from the isotope excites fluorescent X-rays from the materials in the ore and the emitted X-rays are detected in a portable spectrometer.

### HELICOPTER PARTS

Parts made from a 9Y-1Zn-Mg alloy which was developed by the Frankford Arsenal are being tested in Sikorsky helicopters. The alloy has favorable strength and elongation properties, excellent corrosion resistance, and parts made from the alloy can be manufactured by conventional techniques.

### FREE

Copies of *Rare-Earth Metals in Steels*, IS-RIC-4, and *Thermo-Chemistry of the Rare Earth Carbides, Nitrides and Sulfides for Steelmaking*, IS-RIC-5, are available from RIC.

## Ferroelectric Molybdates

Considerable disagreement exists in the literature on the structure of gadolinium molybdate. This question as well as the physical properties and possible uses of Gd<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> are considered by L. A. Drobyshev, A. Z. Rabinovich and Yu. N. Venetsev in their review of rare earth molybdates, *Izv. Akad. Nauk SSSR, Ser. Fiz.* 34, 2528-2540 (1970); Eng. transl., *Bull. Acad. Sci. USSR-Phys. Ser.* 34, 2250-2261 (1970).

Much work has been published on the L-form of the rare earth molybdates since this is the only form which exhibits spontaneous polarization. Some investigators propose that the structure of L-gadolinium molybdate is tetragonal, while others assert that it is orthorhombic. The authors believe that both structures can be obtained by varying the conditions of growth. The conditions of formation, phase transformations, and the growth of single crystals are reviewed in detail, as well as the unusual properties of the rare earth molybdates which could lead to exotic uses for these materials.

The coexistence of ferroelectric properties and laser activity in single crystals of Gd<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>:Nd suggest that this compound could be used to obtain internally modulated laser radiation. The authors also suggest that the rare earth molybdates could find application in light and color gates controlled by low voltages or relatively small mechanical stresses, optical pressure sensors, controlled pyroelectric sensors and memory devices.

## Distorted Nuclei

Recent measurements of the *E*<sub>4</sub> moments in <sup>152</sup>Sm and <sup>154</sup>Sm suggest a departure of about 10% from a purely ellipsoidal shape for the nuclei, F. S. Stephens, R. M. Diamond and J. de Boer, *Phys. Rev. Letters* 27, 1151-1154 (1971).

The *E*<sub>4</sub> transition moments between the ground state and the 4+ rotational state in the Sm nuclei were determined from Coulomb excitation experiments with 10-12

## LETTER

To the Editor:

In your recent issue of 1 December 1971, it was interesting to note that promethium-147 has been confirmed in nature. I think it is interesting to note that in the same year that Erämetsä (1965) reported promethium-147 in a rare earth concentrate, promethium-147 was also detected in African (Katanga) pitchblende as a spontaneous fission product. These three experiments now give evidence to support the idea that promethium should be classified in the same manner as such elements as astatine, francium, etc. rather than being classified as being "extinct". It appears now that promethium has several sources of production in nature: cosmic ray production and spontaneous fission production from uranium-238 (and possibly induced fission production from uranium-235).

Moses Attrep, Jr.  
Chemistry Department  
East Texas State University  
Commerce, TX 75428

*Editor's note: The natural occurrence of Pm due to fission of <sup>235</sup>U and <sup>238</sup>U was reported in RIC News II [1] 2 (March 1, 1967).*

MeV <sup>4</sup>He projectiles. The *E*<sub>4</sub> moment is of interest because it results from the intrinsic shape of the nucleus and can give detailed information about that shape.

The experimental data were subjected to quantum mechanical corrections. The resulting β<sub>4</sub> values for the nuclear charge distribution were about twice those obtained for the nuclear field from *a*, *a'* measurements above the Coulomb barrier, and also larger than expected on the basis of present calculations of nuclear shapes. Assuming that the nucleus is a rigid, uniformly-charged rotor, the large *E*<sub>4</sub> moment indicates a large hexadecapole deformation.

The authors described the exact meaning of the β<sub>4</sub> values as an open and interesting problem, and indicated that more experiments were necessary.

## 10th Rare Earth Research Conference

The 10th Rare Earth Research Conference has been scheduled for April 30-May 3, 1973, at Carefree Inn, Carefree, Arizona 85331. The general plan of the Conference will follow that of preceding conferences, and details of programming will be made available as they develop.

Professor Glenn Seaborg has agreed to present a keynote address interrelating lanthanide and actinide chemistry. To complement his discussion, a session or two dealing with lanthanide-actinide chemistry will be included. A continuation of the bioinorganic program inaugurated at the 9th Conference will be arranged by Drs. D. W. Darnell and E. R. Birnbaum, New Mexico State University, Las Cruces, New Mexico. Other sessions will be announced later when details are complete, but they will most certainly allow for the inclusion of papers on chemistry, metallurgy, industrial applications, spectroscopy, magnetic properties, crystal and molecular structure, solid-state chemistry and physics, etc. It is to be hoped that this conference can maintain the international flavor of the preceding ones.

Planning will be assisted materially if each person who is interested in attending will complete and return before May 1 the preliminary information form included below.

(Detach)

### 10TH RARE EARTH RESEARCH CONFERENCE

Carefree, Arizona, U.S.A.

April 30-May 3, 1973

Please complete the following and send before May 1, 1972, to Dr. Therald Moeller, Department of Chemistry, Arizona State University, Tempe, Arizona 85281, U.S.A. This form is for information only and carries no final commitment.

Plan to attend.     Yes     No                      Plan to present paper.     Yes     No  
(Please type or print)

Special interest area (s). \_\_\_\_\_

Name \_\_\_\_\_

Address \_\_\_\_\_

\_\_\_\_\_

## Previous RE Conference Proceedings

ASM-AEC Symposium on Rare Earths, Chicago, Illinois, November, 1959.

*The Rare Earths*, F. H. Spedding and A. H. Daane, eds., John Wiley and Sons, Inc., New York (1961). Reprinted and available from R. E. Krieger Publishing Co., Inc., P. O. Box 542, Huntington, NY 11743; \$16.50.

First Rare Earth Research Conference, Lake Arrowhead, California, October, 1960

*Rare Earth Research*, E. V. Kleber, ed., Macmillan Co., 60 Fifth Avenue, New York, NY 10011. Price unknown.

Second Rare Earth Research Conference, Glenwood Springs, Colorado, September 24-27, 1961

*Rare Earth Research*, J. F. Nachman, C. E. Lundin, eds., Gordon and Breach Science Publishers, Inc., 150 Fifth Avenue, New York, NY 10011. Ref. \$24.50/prof. \$18.50 (1968-69 price).

Third Rare Earth Research Conference, Clearwater, Florida, April 21-24, 1963

*Rare Earth Research II*, K. S. Vorres, ed., Gordon and Breach Science Publishers, Inc., 150 Fifth Avenue, New York, NY 10011. Ref. \$34.50/prof. \$15.60 (1968-69 price).

Fourth Rare Earth Research Conference, Phoenix, Arizona, April 22-25, 1964

*Rare Earth Research III*, L. Eyring, ed., Gordon and Breach Science Publishers, Inc., 150 Fifth Avenue, New York, NY 10011. Ref. \$44.50/prof. \$22.50 (1968-69 price).

*Proceedings of the 5th Rare Earth Research Conference*, Ames, Iowa, August 30-September 1, 1965, Available from the National Technical Information Service, Springfield, VA 22151, USA.

Book 1 (Spectra)	AD-627 221 [also CONF-650804-(Bk. 1)]
Book 2 (Solid State)	AD-627 222 [also CONF-650804-(Bk. 2)]
Book 3 (Chemistry)	AD-627 223 [also CONF-650804-(Bk. 3)]
Book 4 (Solid State)	AD-627 224 [also CONF-650804-(Bk. 4)]
Book 5 (Metallurgy)	AD-627 225 [also CONF-650804-(Bk. 5)]
Book 6 (Solid State)	AD-627 226 [also CONF-650804-(Bk. 6)]

\$6.00 each book.

Symposium co-sponsored by the Division of Inorganic Chemistry and The Division of Nuclear Chemistry and

Technology, 152nd ACS meeting, New York, New York, September 13-14, 1966

*Advances in Chemistry Series No. 71 Lanthanide/Actinide Chemistry*, P. R. Fields and T. Moeller, symposium chairmen. Available from special issue sales, American Chemical Society, 1155 16th Street N.W. Washington, DC 20036 USA. \$11.00.

*Proceedings of the 6th Rare Earth Research Conference*, Gatlinburg, Tennessee, May 3-5, 1967, CONF-670501.

Available from the National Technical Information Service, Springfield, VA 22151, USA. \$6.00.

*Proceedings of the 7th Rare Earth Research Conference*, Coronado, California, October 28-30, 1968, Sessions A-H

CONF-681020-(Vol. 1) and Sessions I-M, CONF-681020-(Vol. 2). Available from the National Technical Information Service, Springfield, VA 22151, USA., \$6.00 each volume.

French International Rare Earth Conference, May 5-10, 1969, Paris and Grenoble, France

*Les Éléments des Terres Rares*, Tome I and Tome II, Bureau 3A-Service de Presse, Centre National de la Recherche Scientifique, 15 Quai Anatole France, Paris 7<sup>e</sup>, France. Tome I-price unknown, Tome II-107.50 F.

*Proceedings of the 8th Rare Earth Research Conference*, Reno, Nevada, April 19-22, 1970, available from Dr. R. Lindstrom,

Reno Metallurgy Research Center, U.S. Bureau of Mines, Reno, NV, 89505, USA, \$17.00.

Conference on Rare Earths and Actinides, University of Durham, Durham City, England, July 5-7, 1971

*Conference Digest No. 3, Rare Earths and Actinides*, Durham 1971, Institute of Physics, London, England (1971). Available from Dawsons of Pall Mall, Cannon House, Folkestone, Kent, England. £5 (except £3.50 for members of the Institute of Physics).

*Proceedings of the 9th Rare Earth Research Conference*, Blacksburg, Virginia, October 10-14, 1971, available from Dr.

Alan Clifford, Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA, \$20.00.

## REnaissance

"The past few years have seen a renaissance of interest in organometallic compounds of the lanthanide and actinide elements, . . ." report R. G. Hayes and J. L. Thomas, *Organometal. Chem. Rev. A* 7, 1-50 (1971).

In an excellent review paper, the authors discuss the preparation of new compounds, the extension of the chemistry of known systems, and physical measurements directed toward the determination of geometrical and electronic structures. Only the literature from 1964 through Sept. 1970 is covered, since reviews of the earlier literature are available. Tables of physical properties are abundant for the systems included—the cyclopentadienide, cyclooctatetraene and triindene compounds plus aryl and alkyl derivatives of the lanthanides.

The cyclopentadienide compounds are covered extensively, and the authors attempt to determine the nature of these compounds from various lines of evidence. Possible mechanisms for covalent bonding through  $5d$  orbitals are explored in a discussion of the electronic structure of these compounds. In a later section a detailed analysis of the optical spectra shows that there is no appreciable contribution to the bonding from  $f$  orbital covalency, although there may be covalent effects in the  $f$  level splitting.

The mass, optical and NMR spectral studies of the lanthanide organometallic compounds are also discussed in this review and the data tabulated.

## Reviews Neutron Activation Analysis

While still far from being considered an industrial technique, activation analysis is becoming more important with the growing use of rare earth metals. T. Bereznai covers this topic in what he describes as an "application-oriented review," *J. Radioanal. Chem.* 9, 81-100 (1971).

The nuclear problems of activation analysis, including detection limits and interferences due to reactor activation, are described in detail and summarized in several tables. The second part of the review deals with nondestructive activation analysis and the problems and methods involved. Some mention is also made of the chemical separation methods which can be used to obtain maximum sensitivity.

The samples which have been subjected to activation analysis are listed in the final table which includes the up-to-date methods used and the features of each method.

## 4f BONDING

A new model was proposed for the electronic configuration of the lanthanide metals [K. A. Gschneidner, Jr., *J. Less-Common Metals* 25, 405-422 (1971)]. He suggested that the metals have two kinds of  $4f$  electrons, the "atomic"  $4f$  electrons which account for the magnetic properties found for these metals, and the  $4f$  "band" electrons which occupy the valence band along with the  $6s$ ,  $5p$  and  $5d$  electrons and contribute to the bonding.

The  $4f$  concentration in the valence band was estimated to vary from 0.7 of an electron per atom for the light lanthanides (La, Ce, Pr, . . .) to 0.1 or less for the heavy lanthanides (. . . Er, Tm, Yb, Lu). In making these calculations, the energies of the electronic configurations of the neutral lanthanide atoms (see accompanying story on Electronic Configurations, p. 6) were essential in determining

## CORROSION

The performance of rare earth-modified, heat-resistant alloys was discussed in several papers presented at the Conference on Corrosion by Hot Gases and Combustion Products, Dec. 9-10, 1970, Düsseldorf, Germany, and published in *Werkstoff. Korr.* 20 [6] (1971).

The theory of the effect of RE's in improving scale resistance was presented by G. C. Wood, pp. 491-503, and illustrated by the behavior of Fe-, Ni-, and Co-Cr alloys in oxygen. Although it is generally known that the addition of trace amounts of Ce increases the life of electrical heater alloys, the mechanism is still unknown. The work in this area was reviewed by H. Hillinger, pp. 504-509, and a possible mechanism was proposed.

A. Rahmel and N. Scholz, pp. 510-513, reported improved adhesion of scale during temperature cycling and water quenching of a 0.1-0.3% Ce mischmetal Ni-Cr-Mo steel. The oxidation resistance of a Cr-Ni-Nb steel containing 0.3% Y was improved only at 1000-1100°C and intergranular oxidation was noted at higher temperatures, according to J. E. Antill, pp. 513-517.

The corrosion mechanism of Co-Cr alloys was studied in air,  $H_2S$  and combustion gases by A. Davin, D. Coutsouradis and L. Habraken, pp. 517-527, who found that Y additions decreased the depth of oxide or sulfide penetration. P. Elliot and T. K. Ross, pp. 531-540, reported that the oxide form of the rare earths is responsible for the hot corrosion resistance of rare earth-modified superalloys and acts as a sulfur getter.

the fractional number of  $4f$  electrons in the valence band. According to the author, this dual electron model explains the crystal structure sequence found in these metals, their melting points and heats of sublimation, and it is the only model which is capable of explaining all three of these properties.

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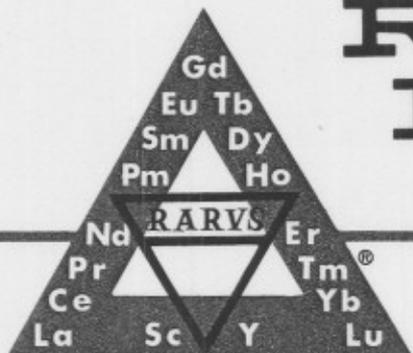
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# RARE-EARTH INFORMATION CENTER NEWS

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No. 2

## French National Rare Earth Research Laboratory



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

The studies at the Laboratoire des Terres Rares of the French National Center for Scientific Research in Bellevue, France, are concerned with the relation between the properties of the rare earth  $4f^n$  configurations and the solid state structural environment. The main goals of investigations of concentrated and doped rare earth materials are: 1) the use of the rare earth optical properties as a tool for

understanding some problems in solid state chemistry such as the nature of bonding (orbital overlap), nonstoichiometry and solid solutions, and 2) the selection of structural conditions needed to obtain optimum properties of the rare earths in phosphors, imaging devices and lasers.

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

(Continued on page 4)

## Rare Earth And Bread

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

(Continued on page 4)

## Weathering Effect

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

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

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

## Magnificent Magnets

Did you know that there is a rare earth material which has an energy product about three times that of the best  $\text{SmCo}_5$  permanent magnet prepared to date? Before you get too excited about this material, we must inform you that its Curie temperature is, alas, only  $100^\circ\text{K}$ .

The compound  $\text{Dy}_3\text{Al}_2$  was found to have an energy product of 73 MG·Oe at  $4.2^\circ\text{K}$ . This compound and its unusual magnetic properties have been studied by B.

## Creative Invention Award to H. T. Hall

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



Hall

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

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

## Named Dean at Rolla

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

Barbara, C. Bécle, R. Lemaire and D. Paccard of the Laboratoire de Magnetisme in Grenoble, France, and their results have been published in several journals—*J. Phys. (Paris) Suppl.* 32, C1-299 to C1-304 (1971); *Z. angew. Phys.* 32, 113-116 (1971); and *IEEE Trans. Mag.* MAG-7, 654-656 (1971).

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

# FERRITES

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

A number of the 170 papers in this volume deal with rare earth ferrites, garnets and chalcogenides. New photomagnetic effects observed in  $\text{Si}^{4+}$  and  $\text{Sr}^{2+}$  doped YIG's, GdIG and europium chalcogenides were presented and discussed in light of their application to memory devices. An entire session was devoted to bubble domain technology including the dynamic properties of bubble domains and controllable pattern printing effects in rare earth orthoferrites. Cobalt substitution in  $\text{RFeO}_3$  was reported to alter the temperature dependence of the uniaxial anisotropy. Uses for YIG's in integrated circuits were explored in the session on microwave ferrites and their applications.

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

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# MEETINGS

## USSR ACADEMY SETS

### RE CONFERENCE

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

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

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

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

### ANALYSIS AND APPLICATION

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

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

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

## Magnetic Fields In Superconductors

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

Dr. R. P. Huebener and his co-workers have coated superconducting materials with a thin film of an EuS and EuF<sub>2</sub> mixture which has a high Faraday rotation. That is, these rare earth compounds rotate a polarized beam of light in the presence of a magnetic field; the amount of rotation is proportional to the magnetic field strength. The Faraday rotation can be used to watch and photograph the beginning, growth and motion of the magnetic field and to calculate field strength.

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

## Final Fiscal '72 Support

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

## Cunningham is VP

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

## Electro-optic Images

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

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

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

## G & D IN '71

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

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

## Liquid Lasers

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

One of the problems involved is the competition between solvation and complex formation in laser systems. The author presents current theories on the mechanism of action, the nature of the active species and the relation of structure to luminescent properties. Difficulties in the preparation of laser systems are also considered. Tables summarize the properties of current liquid laser systems, the solvents used and the coordination numbers of the lanthanides in various systems. The authors conclude that the best liquid system developed so far consists of Nd<sub>2</sub>O<sub>3</sub> dissolved in selenium oxychloride with the addition of the aprotic acid, SnCl<sub>4</sub>. This system has laser properties comparable to the best specimens of solid systems based on Nd<sup>3+</sup> in CaWO<sub>4</sub> and glasses.

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

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Rare Earth and Bread  
(Continued from page 1)

Next time you wish to call us remember our phone number is now further away than the *RIC News* you are reading—see our mailing block on page 2. U.S. Government phones can be used to call us direct on FTS (Federal Telecommunications System).

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

French National RE Research Laboratory  
(Continued from page 1)

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

The optical data are correlated with the structural characteristics which are determined by high resolution electron microscopy, and x-ray and electron diffraction. Of special interest are refractory rare earth compounds whose structure is of a layered nature. These are the A- and B-forms of the lanthanide (Ln) oxides, which are prepared as textured thin films for electron microscopy; and "oxysalts," such as the oxysulfides and oxychlorides which are the salts of the two hexagonal and tetragonal "lanthanyl" cations (LnO)<sub>n</sub><sup>+</sup> (a layered entity made of OLn<sub>4</sub> tetrahedra sharing edges). The three-dimensional frameworks of OLn<sub>4</sub> tetrahedra found in the C-form Ln<sub>2</sub>O<sub>3</sub> are also investigated. Several structural relations between the Ln<sub>2</sub>O<sub>3</sub> polymorphs, e.g., epitaxy, twinning or phase transitions, are studied by electron microscopy. The (LnO)<sub>n</sub><sup>+</sup> materials exhibit the largest nephelauxetic effect known and have large transition probabilities. As a consequence they are considered to be some of the best of the industrial rare earth phosphors.

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Iowa State University  
Ames, Iowa 50010

Other types of materials being investigated include garnets, aluminates, phosphates and members of the Ln<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, Ln<sub>2</sub>O<sub>3</sub>-LnCl<sub>3</sub>, and Ln<sub>2</sub>O<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O systems. By using Ce, Nd, Eu and Tb as structural probes, attempts are being made to understand the reasons for better quality phosphors from a structural viewpoint. The growth of garnet and spinel single crystals is also important in this regard.

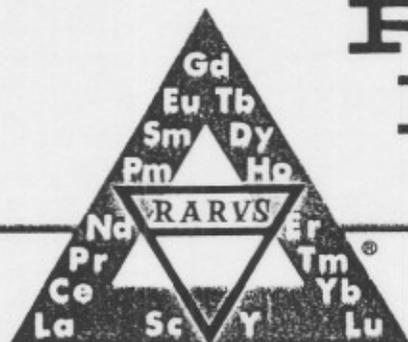
Special attention is given to the intense allowed 4f<sup>n-1</sup>5d↔4f<sup>n</sup> transitions of Ce<sup>3+</sup>, Tb<sup>3+</sup> and Eu<sup>2+</sup>. Energy transfer from rare earth to rare earth is also of interest in connection with structure.

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

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

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

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# RARE-EARTH INFORMATION CENTER NEWS

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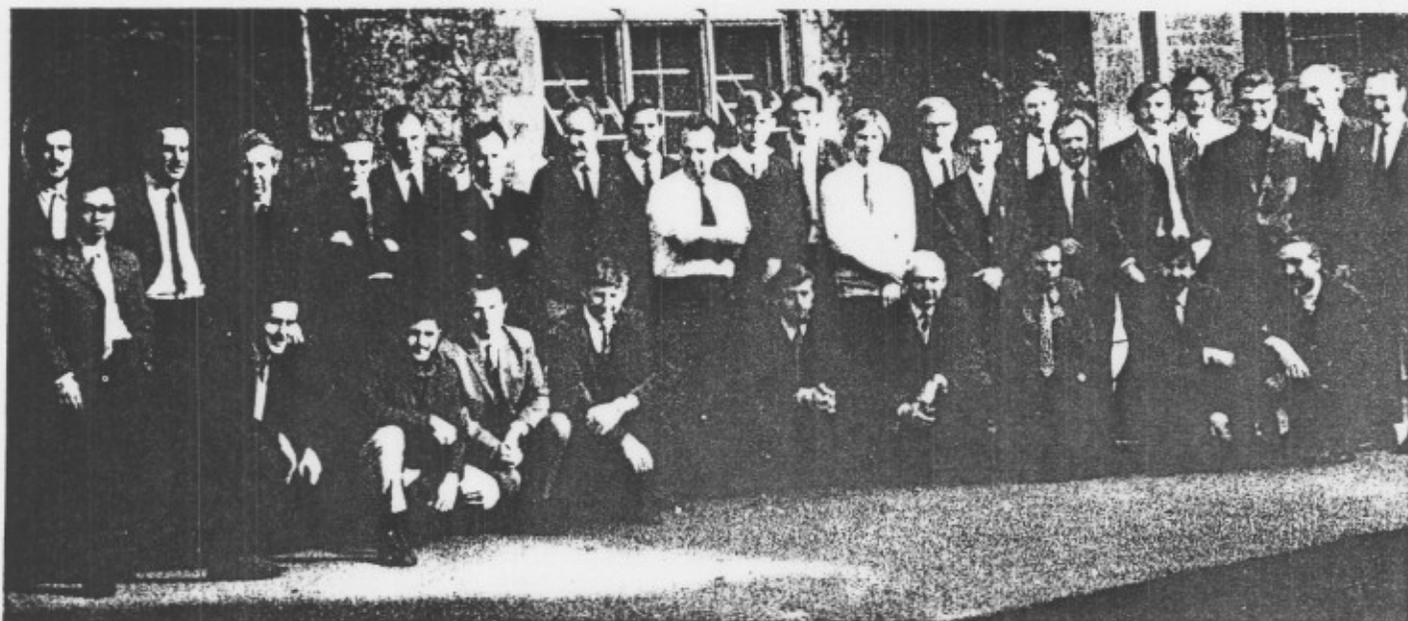
IOWA STATE UNIVERSITY / AMES, IOWA

Volume VII

September 1, 1972

No. 3

## Diversity Marks United Kingdom 4f Group



**MARCH MEETING**—Members of the British 4f group who posed for this group portrait at their March 1972 meeting. Standing from left are A. P. Young, Oxford; H. Fujimora, Loughborough; M. T. Hutchings, Harwell; B. Bleaney, Oxford; M. Whittaker, Metals Research, Ltd.; J. Crangle, Sheffield; J. Hunter, Durham; S. B. Palmer, Hull; J. Liesegang, La Trobe; K. N. R. Taylor, Durham; D. Melville, Southampton; F. A. Wedgwood, Harwell; K. Robinson, Oxford; P. Mattocks, Southampton; T. Egami, Sussex; I. R. Williams, Southampton; M. G. Hall, R. Levi and

R. Jordan, all of Birmingham; H. Zijlstra, Philips, Eindhoven; W. E. Gardner, Harwell; and J. P. Jakubovics, Oxford. Kneeling from left are D. E. G. Williams, Loughborough; A. Nayyar, Imperial College; K. E. Davies, Rare Earth Products, Ltd.; J. B. Forsyth, Harwell; R. D. Greenough, Hull; W. D. Corner, Durham; M. S. S. Brooks, Portsmouth; E. W. Lee, Southampton; and D. M. S. Bagguley, Oxford. Photo courtesy of D. W. Jones, a group member from the Centre for Materials Science, The University of Birmingham.

British research workers who are directly interested in the rare earth metals collaborate as a coordinated, loosely organized group supported by a small grant from the Science Research Council (U.K.). This financing arrangement has proved to be a flexible and outstandingly successful method of encouraging cooperative effort in a field rapidly growing in importance. The close interaction of individual researchers resulting from this project has given rise to a stimulating association in which new and creative ideas can be discussed and encouraged from the initial stages. In addition, the range of interests of cooperating members is sufficiently wide that together they can develop projects of potential value.

An essential feature of the group's activities is the annual meeting held each March in Oxford. At this meeting, general policy is determined, new experiments are proposed and current work is reviewed. On these occasions workers carrying out the actual physical measurements can discuss their problems among themselves, with their colleagues from

(Continued on page 4)

## RIC FINANCES

At the time this issue goes to press 20 producers, traders, mining companies and advanced technology corporations from all over the world have contributed or pledged to contribute to the support of RIC during the July 1972–June 1973 fiscal year. These companies are listed below. The number in parenthesis behind each contributor's name indicates the number of years that firm has supported RIC, including the current fiscal year.

(Continued on page 2)

## RIC Finances

(Continued from page 1)

- Cometals, Inc., U.S.A. (1)  
 Denison Mines, Ltd., Canada (1)  
 General Electric Co., High Intensity Quartz Department, U.S.A. (1)  
 General Electric Co., Phosphor Research Laboratory, U.S.A. (3)  
 Th. Goldschmidt AG, Germany (4)  
 W. R. Grace & Co., U.S.A. (5)  
 Indian Rare Earths, Ltd., India (4)  
 Leico Industries, Inc., U.S.A. (4)  
 A/S Megon & Co., Norway (4)  
 Michigan Chemical Corp., U.S.A. (3)  
 Mobil Research and Development Corp., U.S.A. (2)  
 Molybdenum Corporation of America, U.S.A. (5)  
 Rare Earth Products, Ltd., England (1)  
 Reactor Experiments, Inc., U.S.A. (3)  
 Ronson Metals Corp., U.S.A. (5)  
 Treibacher Chemische Werke, Austria (1)  
 United States Radium Corp., U.S.A. (3)

In addition to the above list of contributors, we (the staff) wish to acknowledge the Ames Laboratory of the U.S. Atomic Energy Commission and Iowa State University's Institute for Atomic Research for underwriting our indirect costs and paying a small fraction of direct costs.

In the past few years we have been attempting to increase industrial contributions to cover all of our direct costs. We are proud to note that many of our faithful benefactors have made substantial increases (as much as 80%). Furthermore, many other companies have responded favorably to our plea for help and have joined the

(Continued on page 4)

## M<sup>3</sup> Conference

D. Graham, Jr. and J. J. Rhyne, eds. (American Institute of Physics, New York, 1972) \$17.50. The proceedings were formerly published in the March issue of the *Journal of Applied Physics*.

Many topics of interest to rare earths were discussed at the meeting. Invited papers covered 1. technologies for memory hierarchy, 2. permanent magnet materials and applications, 3. magnetic recording, 4. bubble domain physics and materials, and 5. magnetic levitation of high-speed trains and magnetic filtration. Magneto-optics and spectroscopy of the rare earth garnets, NMR of intra-rare earth alloys, magnetic oxides, critical phenomena, and magnetic structure of various rare earth compounds were topics of contributed papers.

## NASA Honors Haskin

Prof. Larry Haskin, University of Wisconsin, has received the National Aeronautics and Space Administration (NASA) Exceptional Scientific Achievement



Haskin

Medal for developing rare earth chemistry for studying igneous processes on earth and the application of these techniques to lunar samples resulting in a better understanding of the geochemistry of the moon.

For the past two years Dr. Haskin has served on NASA's 12-member Lunar Sample Analysis Planning Team, which advises NASA on maintaining the scientific integrity of lunar samples and on their allocation to investigators.

## Dura Earths

introduced by Alloy Metals Inc. The lanthanum addition enhances wettability and provides both a gettering and grain refining action. The two alloys, available in either powder or tape form, are said to be applicable to join many different base metals from very thin foils to thick sections and to be ideal for wide gap brazing. Cost savings are realized because they can be used where more costly gold and silver alloys have been traditional.

### CERIUM DECOLORIZERS

Flint glass container plants are rapidly embracing a cerium decolorizing process first introduced in mid-1970. About 25% of the U.S. plants have adopted the cerium system that reduces glass decolorizing costs by as much as 50%. The new system eliminates completely the usage of arsenic and substantially reduces the amounts of selenium, cobalt and other costly decolorants. As with most rare earth uses, a little goes a long way; about 0.01% cerium is utilized in the decolorizing process.

### MORE MAGNETS

Researchers at the University of Dayton have discovered that a series of Sm (or Pr) - Co com-

(Continued on page 3)

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 Nancy Kippenhan and W.H. Smith  
 Staff Writers

## Magnetism Review

J. J. Rhyne and T. R. McGuire have emphasized current experimental results in relation to available theory in their review of the magnetic properties of rare earth elements, alloys and compounds, *IEEE Trans. Magnetics* MAG-8, 105-130 (1972).

Bulk magnetic measurements and related transport phenomena are discussed for a variety of materials including the rare earth metals, intra-rare earth alloys, ionic compounds such as the pnictides, chalcogenides and halogens, solid solution systems including magnetic semiconducting and insulating compounds, intermetallic compounds, and bubble domain materials. Tables present crystal structures, magnetic ordering temperatures, magnetic transition temperatures and paramagnetic Curie points for the materials discussed.

The authors give an over-all view of rare earth compounds, classifying them according to structure and magnetic properties. Topics covered include exchange interactions, magnetization processes, crystal field effects, magnetostriction, spin structures and their field dependence, optical effects and the effect of magnetic order on specific heat, resistivity, Hall effect, thermal conductivity and other properties.

### Rare Earths in the News

(Continued from page 2)

pounds doped with Fe-R<sub>2</sub> (Co<sub>1-x</sub>Fe<sub>x</sub>)<sub>1.7</sub>—have energy products exceeding 60 MG and Curie temperatures greater than 600°C. These materials appear to be more promising as permanent magnets than the familiar RCo<sub>5</sub> compounds.

### AUTO EXHAUST CATALYST

Nd<sub>1-x</sub>Pb<sub>x</sub>MnO<sub>3</sub>, PrCoO<sub>3</sub> and similar compounds may be promising substitutes for platinum catalysts in the treatment of auto exhaust. Results announced by Bell Laboratories show that the RE compounds were more active than the commercial Pt catalyst in the conversion of CO to CO<sub>2</sub> and compared favorably in lifetime.

## SCANDIUM COORDINATION CHEMISTRY

Most of the work on the coordination chemistry of scandium has been reported only during the last few years. The earlier lack of attention was caused by the difficulty of obtaining pure scandium. G. A. Melson and R. W. Stotz have thoroughly reviewed the research in this area in *Coord. Chem. Rev.* 7, 133-160 (1971).

In this review the coordination chemistry is discussed according to the nature of the donor ligand—neutral oxygen donor ligand, β-diketonates, carboxylates, alcoholates, hydroxyscandates, ammonia, primary, secondary and tertiary amines, complexes with both oxygen and nitrogen donor ligands, halide complexes and other miscellaneous complexes. The preparation and stability of the complexes as well as spectral and crystal data defining the coordination and stoichiometry of the complexes are presented. The authors point out the unusual scandium species such as some eight-coordinate complexes and one of the few paramagnetic compounds, Sc (bipyridyl)<sub>3</sub>. In comparing the scandium complexes with the corresponding lanthanide complexes, the authors note that the size of the Sc ion is important in determining the stoichiometry and relative stability of the species formed.

The next few years, say the authors, will see a large increase in the number of scandium complexes synthesized including species containing Sc in oxidation states other than three and organoscandium compounds. However, physical measurements and structural characterization of existing species are still needed to resolve questions of stereochemistry, mode of bonding and stability.

### CORRECTION

The form on p. 3 of some issues of the March *RIC News* listed the year of the 10th RE Conference as 1972 instead of 1973.

## Sc Film Tuners

Scandium thin film targets are reported to be useful in tuning the primary beam of an ion microprobe, J. W. Guthrie and R. S. Blewer, *Rev. Sci. Instr.* 43, 654-655 (1972).

Spatial uniformity of the primary beam of an ion microprobe is important for surface and thin film analysis. Thin films of scandium metal, prepared by vacuum sublimation of Sc onto a polished sapphire substrate, show an immediate and striking color change when bombarded by energetic ions. The colored area, which reveals the position, shape and size of the beam and its current density uniformity, is much brighter and sharper than that of fluorescing KBr, commonly used as a tuning sample. Moreover, the spots or tracks resulting from various tuning parameter changes remain undegraded after the beam is removed allowing a photographic record to be made.

## La Stimulates Crystal Growth

The growth of thinner elongated SiC crystals is enhanced by the presence of La<sub>2</sub>O<sub>3</sub>. The growth rate increases in the longitudinal direction and decreases in the transverse direction, according to G. Verspui, W. F. Knippenberg and G. A. Bootsma, *J. Crystal Growth* 12, 97-105 (1972).

The effect was found to be dependent on the temperature and amount of La<sub>2</sub>O<sub>3</sub> present. The critical temperature for a few grams of La<sub>2</sub>O<sub>3</sub> was 2450°C. Below this temperature normal, platelike crystal growth occurred and above this temperature no growth occurred.

*Other rare earths in the form of oxides, chlorides, carbides or silicides also changed the growth mode of SiC.*

## Welcome New RIC Subscribers

During the past few months we have made a massive mailing to scientists and engineers who have published work on rare earth materials. As a result our *RIC News* family has grown from about 1800 to 2400—welcome aboard. We hope our new readers will find the *RIC News* informative, interesting and useful. You can help make it timely by sending us information about new developments you are involved in, and even sending a contribution to our feature "Rare Earthers Around the World."

Reprints of your publications are essential to keep us informed and to help us answer information inquiries. If you need some help let us know—we will do what we can to assist you.

### RIC SYMBOL

Many of our new readers, and even some of our old ones, may be intrigued by the RIC symbol. It is apparent that the rare earths are arranged in the two arms of the triangle in descending order according to the number of unpaired  $4f$  electrons. The remainder of the symbol may not be as obvious, so we have reprinted the following from the first issue of the *RIC News*, May 1, 1966:

No doubt you alchemy buffs may be wondering, "Is the history of the discovery of the rare earths, as recorded in our texts, wrong? Did the alchemists know about these 'unusual soils' centuries before Lt. Arrhenius' discovery in 1787?" No, we at RIC must confess we did not make a new find in the history of the discovery of the rare earths.

*The truth is*, we took poetic license and combined the alchemist's symbol for earth, "terra," (an inverted equilateral triangle with a cross bar) with the Latin word for rare (*rarus*) to generate the symbol we have incorporated into our letterhead and brochure.

### U. K. $4f$ Group

(Continued from page 1)

theoretical physics, and with the teams whose effort is directed towards the production of high purity materials and good quality crystals. The personal contacts established at these meetings and the freedom of discussion encouraged by their informal atmosphere has enabled the separate research teams, from widely different locations in the United Kingdom, to work together with mutual understanding and sympathy. These meetings have also provided opportunities for visiting colleagues from abroad to meet with their friends in the United Kingdom. Two recent and welcome guests from the United States were Professors Sam Legvold and S. H. Liu from Iowa State University.

## ACS Award to Mooney

Richard W. Mooney, vice president and general manager of GTE Sylvania's Chemical and Metallurgical Division, has won the 1972 Eugene C. Sullivan Award

presented by the Corning Section of the American Chemical Society. Dr. Mooney was cited for his outstanding achievements in chemistry and industry.

Mooney's research has included work in lamp phosphors and fundamental process variables involved in phosphor manufacture, including those of the rare earth series.



Mooney

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## Improved IR Quantum Counter

Measurements conducted on oxygen-fired  $\text{CdF}_2:\text{Er}^{+3}$  indicate that this material could be used to construct an uncooled infrared counter having a minimum detection power of  $3.6 \times 10^{-14}$  W at  $1.53 \mu\text{m}$ , which is appreciably better than the currently available detectors sensitive at this wavelength. These results were reported by N. E. Byer, T. C. Ensign and W. M. Mulaire, *Appl. Phys. Letters* 20, 286-288 (1972).

The green radiative efficiency of  $\text{CdF}_2$  single crystals doped with 0.1 mol%  $\text{ErF}_3$  was increased from 1.9 to 52% by selective generation of trigonal ( $C_{3v}$ ) symmetry at the Er ions by oxygen compensation. This was accomplished by firing at  $800^\circ\text{C}$  for 20 h in dry oxygen.

### RIC Finances

(Continued from page 2)

RIC family of supporters. These actions have brought us closer to our goal—but we still have not reached it.

*Perhaps you can help us reach our goal. Many companies have funds to support professional and scientific activities, while others consider their contributions to RIC as part of their advertising expenses. If you think your company can help, please write us—we will be glad to pursue the matter further. Contributions to the Center range from about \$100 to well over \$1000—any contribution large or small is deeply appreciated.*



# RARE-EARTH INFORMATION CENTER NEWS

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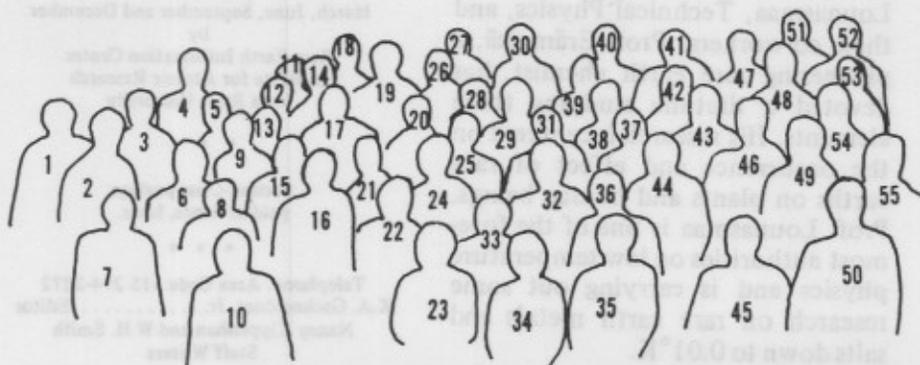
No. 4

## NATO Holds RE Advanced Study Institute



NATO Advanced Study Institute participants posed for this group photo. Please refer to the key below to match names with faces. 1. D. A. Hukin, 2. B. Gaudernack, 3. D. W. Jones, 4. J. van Ooyen, 5. K. E. Davies, 6. M. Steinberg, 7. J. Khaladji, 8. S. Larach, 9. J. E. Whitley, 10. E. Andersen, 11. J. E. Mathers, 12. R. E. Shrader, 13. F. Molnar, 14. E. Herrmann, 15. R. A. G. de Carvalho, 16. R. Ámli, 17. M. Ødegård, 18. A. Kvalheim, 19. A. Bjune, 20. H. Ståblein, 21. J. M. P. Cabral, 22. K. A. Gschneidner, 23. B. Grøttum, 24. W. L. Griffin, 25. B. E. Danielsen, 26. O. N. Carlson, 27. D. E. Stijfhoorn, 28. J. Lausch, 29. H. A. Das,

30. I. Hundere, 31. L. A. Haskin, 32. V. A. Fassel, 33. M. Tecotzky, 34. M. R. Grade, 35. M. Bonnevie-Svendsen, 36. P. N. Yocom, 37. E. Steignes, 38. P. Möller, 39. A. Follo, 40. R. Conzemius, 41. G. Chr. Faye, 42. I. Alstad, 43. J. Haaland, 44. E. L. DeKalb, 45. M. Centincelik, 46. G. Blasse, 47. O. B. Michelsen, 48. M. Skarestad, 49. A. Rannestad, 50. Y. Khan, 51. E. Østgaard, 52. N. Gjelsvik, 53. T. Danielsen, 54. A. C. Pappas, and 55. D. J. Hobbs (Photo courtesy of Institutt for Atomenergi, Kjeller, Norway)



*Greetings of the Season  
from RRC*



## Rare Earth Glue

The role of rare earth additions in reducing the oxidation rate of high temperature alloys, such as Fe-25% Cr-4% Al, has been investigated by J. K. Tien and F. S. Pettit, *Met. Trans.* 3, 1587-1599 (1972). Although the rare earths, specifically Y or Sc, increase the initial oxidation rates by providing faster diffusion paths for oxygen, they promote the adhesion of the oxide scale to the metal body and prevent spallation of the oxide.

Tien and Pettit found that spallation of the scale is caused by distribution of small voids at the oxide-substrate interface, but those alloys which contained Y or Sc were free of voids. They suggest that Y or Sc either form vacancy complexes with excess vacancies or provide internal oxide boundaries for the condensation of excess vacancies. In either case the rare earths prevent the formation of vacancies at the oxide-substrate interface, and thus eliminate spallation of the protective oxide coating.

## Russian RE Meeting

On September 12-17, 1972, the 7th Russian Conference on Rare Earth Metals was held in Moscow. A number of non-Russian scientists were invited to attend. A combination of individual papers and the reporter system (one person summarizing the results of several papers) was used throughout the Conference. Of the 92 presentations about 20 were by non-Russian scientists.

Seven topics were covered in the conference: 1. magnetism, 2. superconductors and semiconductors, 3. electronic and lighting materials, 4. alloys, 5. refractories, 6. catalysis, and 7. rare earths in agriculture, biology and medicine. An English translation of the program listing the titles of all papers is available free from RIC.

*Availability of the conference proceedings will be published by RIC after the volume is issued.*

Editor Reports—

# Scandinavian RE Research

SCANDINAVIA 1972

The editor was fortunate to have attended the NATO Advanced Study Institute on "Analysis and Application of Rare Earth Materials" at Kjeller, Norway (near Oslo) in late summer and to visit four other laboratories in Finland, Sweden and Denmark. The wonderful kindness and generous help of my gracious hosts, and nearly perfect weather made my first journey to the Scandinavian countries a delightful and memorable one. The scientific and technical research being carried out at these laboratories is impressive, and the visits were scientifically quite profitable.

### NATO CONFERENCE

My first port-of-call was the Institutt for Atomenergi, Kjeller, Norway, at which the week-long Study Institute was held. A total of 28 invited tutorial-type lectures were presented by experts from Europe, the Near East, and America. In addition, all 66 of the participants had an opportunity to interact with the various experts during three panel discussions and breaks between papers. As the conference title implies, almost all analytical techniques, and all major and some of the exciting on-the-horizon applications were discussed. *The Advanced Study Institute plans to publish in early 1973 all of the papers presented at the Conference. The availability of this Conference proceedings will be announced in the RIC News.*

### FINLAND

Two 40-minute flights, with an intermediate stop at Stockholm, took me from Oslo to Helsinki. There I visited the Helsinki University of Technology in the Helsinki suburb of Otaniemi. In particular, I visited with Professors O. Erämetsä, Inorganic Chemistry, and O. Lounasmaa, Technical Physics, and their co-workers. Prof. Erämetsä, a pioneering rare earth chemist, has devoted a lifetime studying these elements. His research is centered on the occurrence and effect of rare earths on plants and human beings. Prof. Lounasmaa is one of the foremost authorities on low temperature physics and is carrying out some research on rare earth metals and salts down to 0.01°K.

### SWEDEN

The Institute of Physics at the University of Uppsala was my next stop. Although only a little rare earth research is being done at this Institute, a number of interesting investigations in physics are being pursued, such as solid state physics and electron spectroscopy. The only work involving the rare earths are angular correlation studies under the direction of Dr. Erik Karlsson.

### DENMARK

In Denmark I visited the neutron physics group at the Danish Atomic Energy Commission's Research Establishment Risø, about an hour's drive from Copenhagen. Neutron scattering and theoretical work on rare earth materials under the direction of Dr. H. Bjerrum-Møller deals primarily with praseodymium metal. While at Risø I renewed my acquaintance with a former colleague from Iowa State, Dr. A. R. Mackintosh, director of the Research Establishment Risø.

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Nancy Kippenhan and W.H. Smith  
Staff Writers

## MEETING

### RARE EARTH METAL PHYSICS

A Europhysics Study Conference on the physics of rare earth metals will be held at the LO-Højskole, Elsinore, Denmark, Aug. 29-Sept. 1, 1973. Sponsored by the Metals and Magnetism Sections of the EPS and by the Danish Atomic Energy Commission, its formal program will consist entirely of invited review papers with attendance limited to 100 persons. However, there will be an opportunity for the informal presentation of recent research.

The conference fee, including meals and accommodations, will be approximately \$125. For additional information and a registration form, contact the conference secretary, J. C. G. Houmann, Physics Department, Danish Atomic Energy Commission, Research Establishment Risø, DK-4000 Roskilde, Denmark.

### How is Your RCo<sub>5</sub>?

Do you have a problem obtaining pure RCo<sub>5</sub> phases? According to F. A. J. den Broeder and K. H. J. Buschow, *J. Less-Common Metals* 29, 65-71 (1972) and Buschow, *ibid.*, 283-288, the RCo<sub>5</sub> phases do not exist at room temperature under equilibrium conditions.

The RCo<sub>5</sub> compounds were found to undergo a eutectoid decomposition forming R<sub>2</sub>Co<sub>7</sub> and R<sub>2</sub>Co<sub>17</sub>. The eutectoid temperature increases across the lanthanide series from 600°C for the first four, to 750°C for SmCo<sub>5</sub> and then to ~1350°C at thulium, the point at which the eutectoid and melting temperatures appear to coincide.

The eutectoid decomposition of the RCo<sub>5</sub> phase results in a diminished coercive force. Fortunately, by rapid cooling from above the eutectoid temperature, the RCo<sub>5</sub> phase may be retained without decomposition. Thus, RCo<sub>5</sub> magnets can be manufactured by maintaining proper conditions.

## LOW TEMPERATURE THERMOMETER

Cerium magnesium nitrate (CMN) has a new competitor in low temperature thermometry. J. C. Doran, U. Urich, and W. P. Wolf concluded from a recent investigation that CDP, trisodium tris-(pyridine-2,6-dicarboxylato) cerate (III) pentadecahydrate, is at least as good as CMN for millikelvin thermometry, and it has the additional advantage of smaller demagnetizing corrections because of its weak volume susceptibility, *Phys. Rev. Letters* 28, 103-106 (1972). On the basis of their results the authors stated that a detailed study of the low temperature properties of CDP is now called for.

## Before Fermi

As fantastic and incredible as it may seem, there is now evidence that the first nuclear chain reaction did not occur at Stagg Field on Dec. 2, 1942, but in an African uranium deposit 1.7 billion years ago.

The rare earth elements Ce, Nd, Sm and Eu—known fission products of uranium—were found in uranium ore, unusually depleted in <sup>235</sup>U, from the Oklo mines in Gabon. Dr. Francis Perrin, former high commissioner of the French Atomic Energy Commission, presented his evidence for nature's first reactor at an October meeting of the French Academy of Science. The deposit would have contained 3% <sup>235</sup>U 1.7 billion years ago, enough to support sustained fission. Dr. Perrin proposed that water filtering through the deposit acted as a moderator; when the heat from the reaction became too intense, the water vaporized and halted the chain reaction until the deposit cooled sufficiently for the steam to condense. He estimates that the fossil pile at Oklo functioned intermittently for anywhere from several hundred million to more than a billion years.

## Rare Earths In the News

### JOINT RE PRODUCTION VENTURE

Molybdenum Corp. of America and Aluminum Co. of America have embarked on a joint venture to produce mischmetal and pure rare earth metals by electrolytic reduction of the oxides.

### TWO IN TOP 100

Rare earths were again among *Industrial Research's* 100 most significant products of the year. A repetitively pulsed miniature YAG laser for use in alarm systems, tool alignment and educational kits, and an inexpensive solid state gas sensor employing a LaF<sub>3</sub> electrolyte (see story on p.4) were among those cited.

### Rare, Earthly Goofs

*RIC News*, Vol. VII, No. 3, Sept. 1972: The continuation on p. 3 of the item entitled More Magnets in the "Rare Earths in the News" feature should have read, "...have potential energy products exceeding 60 MG Oe..."

## More Contributions

RIC is now receiving support from 28 rare earth companies as a result of contributions from eight more firms since the September issue of *RIC News* went to press. The following companies have made contributions to RIC for the 1973 Fiscal Year; the number in parenthesis behind each contributor's name indicates the total number of years that firm has helped fund RIC.

American Metallurgical Products, Co., USA (4)

American Rare Earth & Foil, Inc., USA (1)

Lunex Company, USA (3)

Rare Earth Industries, Inc., USA (2)

Research Chemicals, USA (5)

Rhone-Progil (formerly Pechiney-Saint Gobain), France (3)

Santoku Metal Industry Co., Ltd., Japan (3)

Shin-Etsu Chemical Industry Co., Ltd., Japan (4)

## Lutetium Discoverer



Georges Urbain (1872-1938)

*(Editor's note: This is the first of a series of articles commemorating the centennial of those scientists who made great contributions to the field of rare earths.)*

Georges Urbain's unquenchable thirst for truth led him at age 23 into a field in which some of the greatest chemists had become badly confused. Rare earths as a field of research may have seemed the most purely technical of all lines open to him, but Urbain deplored the fact that so few chemists were engaged in research on the rare earths despite the attraction of the unknown.

Urbain's 25 years of research on the rare earths included more than 200,000 fractionations—work which was of tremendous importance to the development of rare earth research. By effecting the rigorous separation of Sm, Eu, Gd, Tb, Dy and Ho, Urbain cleared up the confusion which existed in the chemistry of the yttrium series, and, moreover, discovered lutetium in 1907, a previously unknown element in what had been formerly known as ytterbium. The importance of following separations by both physical and chemical means was emphasized by Urbain who used phosphorescent spectra and the coefficients of magnetization of the rare earths to monitor their separation.

Besides his work on the rare earths, Urbain was also known for the discovery of element 72, celtium, in 1922, which was discovered the same year by Hevesy and Coster and named hafnium, and for his contributions to the study of cathode phosphorescence. Deeply interested in philosophy, Urbain also had a taste for the arts and was a talented pianist, composer, musicographer, painter and sculptor.

As Professor of General Chemistry at the Sorbonne, Urbain conducted a series of brilliant lectures which were immensely popular with the students. Urbain was also a Member of the Institute of France, Director of the Institute de Chimie de Paris, Co-director of Institute de Biologie Physico-Chimique and a Member of the International Committee on Atomic Weights.

## First X-Ray Laser Employs Neodymium

Pulses of infrared light from a neodymium-glass laser stimulated lasing action in what is believed to be the first x-ray laser. A University of Utah team produced a collimated beam of x-rays by shining the Nd laser light onto a sandwich consisting of a weak copper sulfate solution in gelatin between two microscope cover glasses. The experiment is not reproducible in that x-rays are produced only about 10% of the time.

X-ray lasers have far-reaching applications. Such lasers could be

incorporated into x-ray microscopes capable of observing the electronic structure of matter or could be used for heating and diagnostics in plasma physics.

The preliminary x-ray laser experiments were reported by E. M. Eyring, F. W. Cagle and J. G. Kapros, *Proc. Natl. Acad. Sci.* 69, 1744-1745 (1972).

## LaF<sub>3</sub> Gas Sensor

A LaF<sub>3</sub> thin film has been incorporated into a solid state sensor for the selective specific measurement of a variety of gases. The device, only a fraction of a square millimeter in area, consists of a gas-permeable membrane, a noble metal grid cathode, a film of the LaF<sub>3</sub> electrolyte as thin as 1000 Å and a metal anode, such as bismuth, which reacts with fluorine and the gas being measured to form a sink for the charge-carrying ions. A variety of gases (oxygen, carbon dioxide, sulfur dioxide and the nitrogen oxides) can be measured over a wide temperature range. Moreover, the low cost (\$1) of the LaF<sub>3</sub> gas sensor opens up the possibility of disposable sensors.

B. C. LaRoy, A. C. Lilly and C. O. Tiller of the Philip Morris, Inc., Research Center are responsible for the development of this probe.

## 25 With Fifteen

W. R. Grace & Co. is celebrating its 25th year in the rare earth industry as a producer of rare earth materials and polishing products.

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