Spectral Behavior of Lanthanides

During the past few months several interesting papers have come to our attention dealing with the spectral properties of the lanthanide elements and some of their potential applications.

DISPEL MISCONCEPTIONS

The cathodoluminescent properties of the trivalent lanthanides in \( \text{Y}_2\text{O}_3 \) were studied by Buchanan and co-workers, J. Appl. Phys. 39, 4342 (1968). They noted that their results indicate, contrary to extensive prejudices, that optimum activator concentrations in \( \text{Y}_2\text{O}_3 \) are quite large (1 to 10%). The reasons for these past prejudices and the advantages of \( \text{Y}_2\text{O}_3 \) as a host over other materials are discussed.

Buchanan and co-workers also show that ions at the beginning and end of the lanthanide series contrary to accepted opinions have luminescent efficiencies equal or greater than those for the ions in the middle of the series.

INFRARED QUANTUM COUNTER

An infrared quantum counter, as noted by Esterowitz and co-workers (Appl. Optics 7, 2053 (1968)), is the only quantum amplifier with photon gain that can approach a noise temperature of 0.00K. These researchers have investigated 165 different combinations of trivalent lanthanide ions in a variety of inorganic single crystal lattices.

Some of the best combinations of lanthanide ions and host crystal, and their output wavelengths were found to be \( \text{Pr}^3+ \) in \( \text{LaCl}_3 \) (0.645\( \mu \)), \( \text{Er}^3+ \) in \( \text{CdF}_2 \) (0.668\( \mu \)), \( \text{Tm}^3+ \) in \( \text{CaWO}_4 \) (0.385\( \mu \)), \( \text{Ho}^3+ \) in \( \text{LaF}_3 \) (0.538\( \mu \)), and \( \text{Er}^3+ \) in \( \text{LaF}_3 \) (0.546\( \mu \)).

(Continued on Page 4)

Diffusion

In two different papers Russian scientists have reported on the self-diffusion of yttrium and the chemical diffusion of zirconium in yttrium.

The self-diffusion results by Maskalets and co-workers (J. Metall. Metallurgy, Chist. Metal., No. 6, p. 189, Atomizdat, Moscow (1967); Metal Abstracts 1, No. 13-0770 (1968)) are the first such values reported for any rare-earth metals, as far as RIC News is aware. The temperature dependence of self-diffusion was given as \( D = 5.5 \times 10^{-6} \exp (-30800/RT) \) for the temperature range 1000-11750\( ^\circ \)C. The authors noted that in this temperature range volume diffusion is the dominant mechanism for transport of material and its activation energy is 25-30 kcal/mol.

The chemical diffusion of zirconium in yttrium was measured from 1000 to 1300\( ^\circ \)C, and the temperature dependence was determined to be \( D = 4 \times 10^{-3} \exp (-38000/RT) \). These studies were reported by Rogozin, Gert, and Babad-Zakhryapin in Izv. Akad. Nauk SSSR, Metally 1968 [3] 228. These authors also determined the chemical diffusion coefficients of molybdenum and niobium in yttrium at 1300\( ^\circ \)C to be \( 1.8 \times 10^{-8} \text{ cm}^2/\text{sec} \) and \( 1.4 \times 10^{-8} \text{ cm}^2/\text{sec} \), respectively.

(Continued on Page 2)
Lanthanum Compound
As Electrode Material

Considerable attention has been given in recent years to solid electrode voltammetry for use in electrochemical applications. Curran and Fletcher, *Anal. Chem.* 40, pp. 78, 180 and 1809 (1968), have used LaB₆ as an indicator electrode for anodic oxidation instead of mercury which is hampered by oxide formation. LaB₆ has high cathodic and anodic over-potential in aqueous solutions although the potential span is very short.

In the first study, a procedure was found for determining cathodic limit of the electrodes by reduction of water at high pH or reduction of hydrogen ion at low pH, and for the anodic limit by gross oxidation of LaB₆. The potential range was found to be 1 V. The second study involved application of LaB₆ as an indicator-electrode for acid-base titrations in aqueous solutions by using constant current potentiometry. The study demonstrated precision of a few parts per thousand of a hydrochloric acid with potassium hydroxide titration.

In the third study LaB₆ was used as an electrochemical generator of La(III) for titrations in determining Ni(II), Cu(II) and Zn(II). Constant current electro-oxidation of LaB₆ in pH-controlled solutions allows generation of known amounts of La³⁺, where EDTA can be used for determining these three metal ions with excellent accuracy.

**F r i c t i o n**

The influence of crystal structure and other properties on the friction and adhesion of some hexagonal metals have been studied by Buckley and Johnson, *Wear* 11, 405 (1968). A number of the hexagonal rare-earth metals were included in this study.

These authors found that the coefficient of friction was inversely proportional to the ratio of the interbasal planar spacing to the a lattice parameter. Thus the heavy lanthanide and yttrium metals which have the small ratios (~1.57) have coefficients of friction of about 0.7, while the light lanthanides which have large ratios (~1.61) have values of about 0.35 for this coefficient. Most of the other hexagonal metals have coefficients of friction between 0.35 and 0.7; titanium, however, is a notable exception with a coefficient of 1.2.

Buckley and Johnson also point out that in general body-centered and face-centered cubic metals have higher coefficients of friction than the hexagonal metals.

**T H E R M I C O N C O N V E R T E R S**

Interest in high-heat-resistant materials for use in thermionic converters led to the investigation of Y₂O₃. E. S. Keddy reports that 98.7% pure Y₂O₃ withstood 1000°C in vacuum, but disintegrated at 2000°C [U.S. Atomic Energy Comm. Report LA-3822-M (1968)]. A similar sample of Y₂O₃ failed at 1000°C after immersion in molten barium or lithium. Higher purity Y₂O₃ (99.5%) withstood all the above tests, although there was some surface attack by barium and lithium.

Impurities in Y₂O₃ affect heat resistance considerably and indicate that high-purity yttria must be used in high-temperature thermionic converters.

**Rare Earths Common in Body**

Since 1945, the determination of rare earths in the human body has been conducted by a team at the Technical University, Otaniemi, Finland. Results were negative until recent use of x-ray emission spectroscopy has proved their presence to be surprisingly common.

Yttrium was found (0.003% of the ash) in 61 out of 236 organ specimens of patients who died in Helsinki hospitals reports Erämet, Sihvonen and Forsén, *Ann. Med. Biol. Fenniae* 46, 179 (1968). Distribution varied and was high at 0.670% yttrium in one specimen.

**Describe Rare-Earth Metal Production**

The industrial methods used to produce rare-earth metals have been described in two articles during the past year. The fused salt electrolysis method was described by I. S. Hirschhorn, *J. Metals* 20, 19 (Mar. 1968), and the metallothermic method was discussed by J. L. Moriarty, *Jr. J. Metals* 20, 41 (Nov. 1968).

Moriarty is primarily concerned with the preparation of high purity rare-earth metals, whereas Hirschhorn emphasizes mischmetal and commercial grade metals.

**La Improves Ti**

The effect of lanthanum additions on the strength and plasticity of titanium between -196 to 800°C has been reported by Ul'yanov and Koptun in *Izv. Akad. Nauk SSSR* Metally 1967, 44117 (English translations - Russ. Metallurgy 1967, 44159). Alloys containing between 0.4 and 2.2 wt % La were examined. Ul'yanov and Koptun found that 1.8 wt % La was optimum with respect to the tensile strength; a 50% increase in strength was obtained for this addition.

Lanthanum additions also improved the ductility, especially below room temperature. A 1.0 wt % addition was found to be optimum with respect to ductility. At -196°C the ductility of the 1.0 wt % La alloy was increased by 100% over that of pure Ti.

It would appear that lanthanum is a beneficial alloying additive for titanium especially for low temperature service applications.

(Continued from Page 1)

**COOL CONTROL RODS**

A Dy₂O₃-Ni cermet developed at Douglas United Nuclear, Inc., may eliminate the need for water to cool nuclear reactor control rods. The cermet can withstand the heat of a reactor core, absorbs neutrons readily, and neither swells nor contracts under prolonged neutron bombardment.
Cobalt-RE Alloys By Electrolysis

A method for producing cobalt–rare earth alloys by electrolysis has been developed at the Reno Metallurgy Research Center of the U. S. Bureau of Mines. Morrice and co-workers reported on their process in J. Metals 21, 34 (Jan. 1969).

The method utilizes rare-earth oxides as seed materials to produce alloy products rich in rare-earth metals. Desired compositions can then be achieved by the addition of more cobalt.

The thermal-gradient cells used in the preparation of the alloys consisted of a graphite crucible to contain the electrolyte (usually LiF and the respective rare-earth fluoride), a graphite anode and a cobalt cathode. The authors report that, in general, all the alloy products were relatively low in impurities.

Cobalt alloys containing, individually La, Ce, Pr, Nd, Sm, Gd, Dy, Y, didymium mixture, and mixed yttrium - and cerium-group metals have been produced.

Lab Safety

Several recent studies have dealt with the biochemical hazards and exposure to radioactive $^{147}$Pm and neodymium lasers.

A report by C. V. Durham, U. S. Air Force Report APGC-TR-68-53 (June 1968) contains a brief discussion of laser systems and a more detailed review of the Nd-doped laser. More specifically, this report makes recommendations for safe operation of the laser. For example, special safety goggles with an optical density of over 16 at the Nd wavelength are required for all personnel within range of the laser. Serious corneal injury to the eye can occur from infrared and ultraviolet radiation.

Exposure to $^{147}$Pm has recently been of great concern. Studies have been primarily focused on the distribution in the body after exposure, ingestion, or inhalation of the isotope. Conner and Knapp, Health Physics 15, 166 (1968), studied the leaching effect that gastric juice has on $^{147}$Pm.

Howell and King, ibid., p. 174, described radiation protection problems encountered during preparation of $^{147}$Pm capsules. Both Bremstrahlung energy spectra and $\beta$-energy require strict contamination control such as inspection of rubber gloves damaged from ozone or high temperatures.

Palmer and co-workers, ibid., p. 187, were called upon to establish realistic exposure limits and to determine the dose from accidental exposures, uptake, retention, and localization of $^{147}$Pm. Internally deposited $^{147}$Pm was evaluated by using urinary and fecal excretion data.

The above studies with $^{147}$Pm resulted from investigation of potential accidental acute intakes and recognized safety hazards of the workers at Battelle-Northwest.

LaB$_6$-MHD Generator

The use of lanthanum hexaboride to increase the conductivity of the working fluid in a magnetohydrodynamic (MHD) generator was discussed by Honma and Nomura, Denki Shikenkho Ho 32, 507 (1968); Nucl. Sci. Abstracts 22, No. 47877 (1968). The increased conductivity of the gas is due to the favorable thermionic emission properties of LaB$_6$. The authors found that an electron density of $10^{14}$ cm$^{-3}$ is obtained with a powder density of $10^3$ cm$^{-3}$ for LaB$_6$ solid particles of 10-5 cm radius. (Note solid LaB$_6$ contains 102 formula units/cm$^3$).

The maximum conductivity was calculated to be 0.1 mho/cm for these conditions at 23000K with nitrogen gas.

The other transport values, e.g., viscosity and thermal conductivity, were also calculated, and it was found that these properties were not appreciably affected by the LaB$_6$ powder suspension in the gas.

NEW ARC LIGHT

During the past few years Sylvania has developed a new high pressure discharge light which is claimed to be the closest anyone has ever come to duplicating natural sunlight. This light, called Metalarc, contains primarily mercury, and scandium and sodium oxides. The mercury lines in the discharge give rise to blue and green light and the oxides to red, orange and yellow.

The lines in the spectrum are generally less than 20A apart and when thorium is included the spacing between lines becomes less than 5A. Minor amounts of other rare earths are added to improve the spectral characteristics of the light.

Metalarc is presently being used in several sports stadiums and indoor coliseums in the United States, including Charger Stadium in San Diego. The basic ideas of Metalarc are covered by United States patents 3,334,261 and 3,407,327.

TRANSMUTATION

A novel use of lanthanum has been developed by J. W. Denison, Jr. of Trak Microwave Corp., Tampa, Fla. The lanthanum is alloyed with nickel which is used as cathodes in vacuum radio tubes.

After the tube is manufactured it is irradiated by neutrons in an atomic pile, which transmutes the lanthanum to barium. When the new tube is used the barium, which (Continued on Page 4)}
TUNABLE PHONON DETECTOR

A tunable, acoustical phonon detector has been demonstrated by Sabisky and Anderson, *Appl. Phys. Letters* 13, 214 (1968), by using $\text{Tm}^{+2}$ ions in a $\text{CaF}_2$ host. The phonon detector is based on the optical detection of the spin population difference of an impurity ion ($\text{Tm}^{+2}$) through the spin-phonon interaction. The phonons were generated at $1.4^{\circ}\text{K}$ by a transducer using a few milliwatts of radio frequency power at $9.5\times10^9$ Hertz (cycles per second).

PHOSPHORS AND SCINTILLATORS

The application of lanthanide ions for radiation detection and measurement was discussed by Buchanan and Wickersheim, *IEEE Trans. Nucl. Sci.* NS-15, [3] 95 (1968). The luminescent properties of lanthanide phosphors fall into two groups: those which exhibit sharp line spectra due to $4f-4f$ transitions and those which exhibit broad-band spectra due to $5d-4f$ transitions of the activator ion or from emission of the host itself.

In the first category the efficiencies of the phosphors are high, but decay times range from micro- to milli-seconds. Materials which have these characteristics are being studied for imaging and energy conversion applications.

In the second category phosphors have decay times in the nano- to micro-seconds range, and thus these materials look quite attractive for scintillation counting applications. The stopping power of the host material is quite important in this application. $\text{Y}_2\text{O}_3$, a common host material, is too light but $\text{Gd}_2\text{O}_3$ and/or $\text{Lu}_2\text{O}_3$ should be effective hosts since their stopping powers are significantly higher than that of $\text{Y}_2\text{O}_3$.

PHOTOSENSITIVITY

$\text{Eu}^{+3}$ and $\text{Tb}^{+3}$ in fluid solutions emit fluorescence which in turn is absorbed by organic sensitizers present as non-associated solutes and can be measured quantitatively. These rare-earth ion probes were one of the topics presented by N. Filipescu at the 156th American Chemical Society Meeting in Atlantic City, N. J.

Rate constants for the transfer process in several organic carbonyl compounds were taken at varying lanthanide concentrations, viscosities and temperatures. Then treatment was extended to photochemical reactions. The photokinetic data were consistent with an inter-molecular (collisional) transfer.

RE-OPEN AUSTRALIAN TREATMENT PLANT

The South Australian Government's uranium treatment plant at Port Pirie, closed since 1962, will be re-opened as a result of the merger of two Australian firms which have purchased the plant from the Government.

Australian Ceramic Industries Pty. Ltd. and Field Group Research Pty. Ltd. will process both uranium and rare-earth oxides at the Port Pirie plant. Re-opening of the plant is expected to boost Australia's annual export earnings by millions of dollars.

The site taken over by the new company covers 80 acres including 70 acres of residue dams left over from previous operations. South Australian Minister of Mines R. C. DeGaris said the dams contain the world's largest known supply of scandium which has potential for a new type of light. (see story on page 3).

RE'S IN TOP 100

When Industrial Research Inc. named the 100 innovations it considered the most significant technical products for 1968, the rare-earth industry took a giant step forward.

Four of the 100 products named by Industrial Research Inc. were developed around the rare earths. The four products named which employed rare earths in their manufacture included three lasers, all of which employed Nd - one of which also utilized YAG as the host material - and a solid state lamp which converts infrared radiation to visible green light by means of a $\text{LaF}_3$ phosphor.

Rare Earthers, hold your heads high!

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paid at Ames, Iowa.
The Cleary Award of the Air Force Materials Laboratory (AFML) has been presented to Dr. Karl J. Strnat, John C. Olson and Capt. Gary I. Hoffer. They were honored for their work on magnetic materials which entailed a study of the anisotropic magnetic intermetallic compounds.

The Cleary Award was established in memory of Charles J. Cleary, a member of AFML for 25 years who was assistant chief of the Laboratory at his death in 1943.

The research specifically cited for the award was reported by the three in a paper, "Permanent Magnet Properties of YCo5 Powders," presented at the Sixth Rare Earth Research Conference in May of 1967. They have been granted a patent for a method of producing RCo5 magnets (U.S. Patent No. 3, 424, 578) and a second patent covering the products (magnets containing RCo5 alloys) is pending.

Dr. Strnat, principal investigator of the research, is an internationally recognized authority on magnetic materials and is credited with organizing the magnetic materials exploratory development program at AFML. Now a professor of electrical engineering at the University of Dayton, Strnat is organizing a magnetic materials laboratory at that institution.

Polarized Electron Beams

The use of Eu(Gd)S to produce polarized electron beams has been discussed by G. Obermair (Z. Physik 217, 91 [1968]). In this paper Obermair describes the theory of field emission from ferromagnetic solids in which the two spin sub-bands of the conduction band are split. He concludes that highly polarized beams (as high as 100%) are possible by using ferromagnetic Eu1-xGdxS with x = 0.055 as the optimum concentration of gadolinium.

Polarized electron beams (80% polarization) have been produced using ferromagnetic gadolinium metal (M. Hofmann, et al., Phys. Letters 25A, 270 [1967]). But the use of Eu(Gd)S should lead to much more highly polarized beams. Obermair also notes that field emission studies from ferromagnetic solids should also yield valuable information about the magnetic and band structures of these materials.

EXPANDS RE LINE

Molyco has added seven additional rare earths to its product line bringing to 15 the number of rare earths it offers for sale. The seven rare earths are Tb, Dy, Ho, Er, Tm, Yb and Lu. The addition of these elements to Molyco’s line was made possible through a cooperative marketing arrangement with Shin-Etsu Chemical Industry Co., Ltd. Shin-Etsu, Japan’s largest rare-earth producer, will separate Molyco’s raw material.

HOT LASER

A pulsed laser capable of heating materials to 20 million°F has been developed at Sandia Laboratories, Albuquerque, N.M. The laser incorporates four neodymium-doped glass rods. Discharging 50 joules of energy in 10 picosecond bursts, the laser’s output peaks to 5 x 1012 watts, the highest power yet generated by a pulsed laser, says Sandia’s Dr. Garth Gobeli.

UP RARE-EARTH STOCKPILE

In a revision of strategic stockpile objectives, the Government revised upward its stockpile objectives for rare earths. The new objective is for 6500 short dry tons, more than double the previous 3000-ton stockpile.

RE CHROMITE ELECTRODES

A new ceramic part for electrodes made of rare-earth chromite has been developed. Electrodes (Continued on Page 3)
Neutron Scattering and Rare Earth Research at ORNL

The Solid State Division of the Oak Ridge National Laboratory has two neutron scattering groups which are actively studying rare-earth metals, compounds, and alloys.

The neutron diffraction group consists of W.C. Koehler, J.W. Cable, H.R. Child, and R.M. Moon as permanent staff and one graduate student, A.H. Millhouse. This group had, with M.K. Wilkinson and E.O. Wollan, first determined the complex magnetic structures of the heavy rare-earth metals by elastic scattering from single crystals.

As part of a long-range program of study of the magnetic properties of the rare earths a number of alloy systems have subsequently been investigated. Most recently, the magnetic structures of single crystal specimens in the Er-Dy, Er-Tb, Er-Gd, Er-Ho, and Dy-Ho systems have been determined. Conclusions relating to the nature of the exchange interactions and the origin of the anisotropy of the rare earths have been derived from these studies.

Recently, a large single crystal specimen of low capture cross section $^{160}\text{Gd}$ has been grown and the group is currently investigating the form factor of metallic Gd by means of its new polarized neutron facility at the High Flux Isotope Reactor (HFIR). The group is also studying, in collaboration with members of the neutron spectrometry group, the spin wave scattering from Gd.

The neutron spectrometry group, consisting of H.G. Smith, H.A. Mook, R.M. Nicklow, M.K. Wilkinson, with guest scientist J.C.G. Houmann and graduate student J.G. Traylor, is concerned with measurements of the inelastic scattering of neutrons from solids. Its rare earth-related projects include the determination of the phonon dispersion relations of Ho, Tb, and $^{160}\text{Gd}$, and the magnon dispersion relations in the spiral regions of Ho, and Tb. This work is being done at (Continued on Page 4)

Crystal Growing Methods Reviewed

New crystal growing devices and growth techniques developed over the past two years are summarized in *J. Cryst. Growth* 3, 4, 60-807 (1968). This issue comprises the Proceedings of the Second International Conference on Crystal Growth, Birmingham, U.K., July 15-19, 1968. Those papers devoted to rare-earth materials are briefly described.

Neodymium-doped calcium and yttrium aluminum garnet single crystals for solid state lasers which exhibit linear optical effects were grown by the Czochralski method. Their performance in the laser cavity varied and depended on structural defects.

A hollow cathode floating-zone melting process was also used to grow yttrium aluminum garnet and yttrium aluminide crystals. The latter compound is metastable and crystallizes incongruently from the 1 Y$_2$O$_3$/1 Al$_2$O$_3$ melt. Addition of 10% Nd$_2$O$_3$ eliminates this. Yttrium aluminum garnet has nearly optimum properties for a laser host material. The limiting factor is the difficulty of preparing crystals with activator ions such as neodymium. Experiments to increase concentrations of these activators were conducted.

Yttrium iron garnet films were grown from molten salt solutions. Crack-free films 0.5 to 1000 m thick were grown on gadolinium garnet substrates. An imperfect substrate surface tended to cause film cracking and line broadening.

Some additional compounds investigated were EuTe, EuSe and EuS grown by chemical transport and sublimation, and PrP by reaction with iodine in a closed system.

Lanthanum hexaboride is of interest for its thermoemissive properties. It was prepared in a very small crystal form by two methods: vapor-phase and liquid-phase crystallization. Its electro-optical properties were also measured.

Single crystals of Gd, Tb, Dy, Ho, and Er metals were prepared by three methods: (1) RF induction floating zone technique under high purity argon, (2) recrystallization in the solid state, and (3) by DC solid state electrolysis.

Other topics included the growth of mixed cation iron garnets from flux in yttrium gallium and yttrium calcium silicate systems, and growth of Ce$_2$O$_3$ and La$_2$O$_3$ by an arc transfer process.

Binary rare-earth oxide solid solution crystals such as La$_2$O$_3$-Er$_2$O$_3$ were grown by the Verneuil method.

REFRACTORY PrP

The highest melting point ever observed for a rare-earth compound was reported by K.E. Mironov in a description of his method of preparing PrP [*J. Cryst. Growth* 3, 4, 150 (1968)]. The melting point reported by Mironov was 2850°C.

The next highest reported melting point is that of Yb$_6$, 2800°C. Next in line are ScN and YN which melt at 2550°C; Lu$_2$O$_3$ at 2490°C, the highest melting oxide; CeS at 2450°C; and GdC$_2$ and YC$_2$ at 2415°C.

Although PrP's high melting point makes it a potentially attractive refractory material, other data reported earlier indicate that its high temperature applications may be limited. For example, K.A. Gingerich found that PrP has a phosphous partial vapor pressure of 10-5 to 10-9 atm. between 820 and 1275°C (*J. Am. Chem. Soc.* 87, 1660, [1965]). Furthermore Mironov and co-workers found that PrP will oxidize in air above 700°C (*Doklad. Akad. Nauk SSSR* 176, 841 [1967]; English translation, *Doklady Chem.* 176, 873 [1967]).
Faculty Award
To LeRoy Eyring

Dr. LeRoy Eyring, chairman of the chemistry department, Arizona State University (ASU), Tempe, Ariz., has received the ASU Alumni Association's Faculty Achievement Award for 1969.

In naming Eyring as the 1969 recipient, the Alumni Association cited his achievements in solid state chemistry research, his worldwide reputation as an authority on rare-earth oxides, and his ability, as department chairman, to stimulate and encourage the research and teaching excellence of the faculty.

A member of the ASU faculty since 1961, Dr. Eyring in his eight years as chemistry department chairman has built the chemistry department into one of the strongest in the ASU College of Liberal Arts. His was one of the first two departments at ASU to qualify to offer doctor of philosophy degree programs.

Dr. Eyring has been active in the field of rare-earth research for about 20 years and has lectured extensively in Europe and the United States. He was chairman of the Third Rare Earth Research Conference in 1964.

Dr. Eyring has published more than 40 papers in scientific journals and is the editor of three review volumes dealing with the rare earths and with high temperature chemistry.

He is only the sixth ASU faculty member ever named for a Faculty Achievement Citation.

(Continued from Page 1)

prepared with the new ceramic are electrically conductive from ambient temperature up to their melting temperature. The inventor is M. Foëx of the French Atomic Energy Commission.

Transparent RE Oxides

Transparent Y₂O₃ has been obtained by pressure forging techniques, Spriggs and Atterman, p. 701 in Ceramic Structure, Fulbrath and Pask, eds., Wiley, New York (1968). Several other desired properties resulting from this technique include enhanced densification rates, controlled porosity or full density, composite fabrication, pressure bonding single and polycrystalline ceramic materials together, and oriented microstructure.

Single-phase Y₂O₃ has shown crack-free, dense, and highly transparent properties after press-forging as compared to the opaque sample which is obtained from conventional pressure-sintering. Microstructures showed elongated grains perpendicular to direction of pressure and x-ray texture studies revealed preferred orientation in pressure-forged samples. Other materials of interest to which the technique was successfully applied were lanthanum, samaria and ceria.

Stone is Grace V.P.

R.L. Stone, head of W.R. Grace & Co.'s rare-earth department, has been named a vice president of the firm's Davison Chemical Division, the parent division of Grace's rare-earth department.

RE Industry Reappraisal

The rare-earth industry, which experts (including RIC News) predicted would have its greatest year in 1968, is currently the subject of intensive review as prognosticators try to figure out what happened. More accurately, they are trying to figure out why it happened.

One of the big markets for rare earths, the color television industry, did not come through as it had expected. Color television sales of 5 million sets in 1967 were supposed to climb to 7 million sets in '68, but leveled off at 5.6 million sets.

Some say that the industry is in the same position it was prior to the color television boom—waiting for a research “find” to create new markets. Despite the current lag in rare-earth demand, the industry is still considered a growth industry.

This optimism stems from the flexibility of the industry itself. Many producers are looking toward specialized markets and are tailoring production accordingly.

Another reason for optimism stems from the problem of rare-earth separation—you cannot separate one without separating them all. In producing one or several rare earths for a specific market, you cannot help but increase the availability of the rest of the series. This ready availability of many rare earths not presently used extensively is expected to attract other manufacturers to them.

For a worldwide review of the rare-earth industry see Industrial Metals No. 14, Nov. 1968, pp. 9-27, and No. 16, pp. 35 and 36, where supplemental discussions of Japan's and India's rare-earth industry appear. India's rare-earth industry is also reviewed in Nuclear News 12, April 1969, pp. 22 and 24. The United States industry was featured in Chemical and Engineering News 47, No. 13, Mar. 24, 1969.

NEUTRON FILTER

Scandium is aiding researchers at Idaho Nuclear in their investigation of the nuclear properties of structural and fuel materials that will be used in the fast breeder reactors.

(Continued on Page 4)
NEW BOOKS

SPECTRA AND ENERGY LEVELS

There are two valuable chapters in this book which one might not expect to find in a volume such as this. They are “Crystals Available for Study” and “Experimental Procedure.” In addition to these two, there are twelve more chapters: “Introduction”, “Historical”, “The Rare Earths”, “Spectra and Levels of the Free Ions”, “The Crystal Field”, “Crystal Symmetry and Structure of the Spectrum”, “Intensities, Selection and Polarization Rules”, “Comparison with Empirical Data”, “Zeeman Effect and Magnetic Properties”, “Divalent Rare Earth Ions in Crystals”, “Review of the Empirical Data”, and “Line Structure.”

The book is well illustrated and contains many tables, some of which may be as long as 6, 11 or 30 pages. The original literature is well documented with more than 650 references. Author and subject indexes are also included.

This 400+ page volume should be of value to those of us who are working on the spectra, optical behaviors, magnetic properties, NMR, EPR and other solid state properties, especially those involving the crystalline environment of these elements and their ions.

SCAN DEUM

There is much interest these days in the physical behavior of scandium and scandium-rich alloys as evidenced by the number of papers presented on this topic (six) at the American Physical Society Meeting in Philadelphia, March 24-27, 1969. Most of the work, both theoretical and experimental, is being carried out at the Argonne National Labo-

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International Conference

In early May the French National Center for Scientific Research sponsored and served as hosts for a six-day meeting on the rare earths. Furthermore, their gracious financial assistance enabled a number of non-French scientists to attend the Conference who otherwise might not have participated. Of the 200 persons attending the Conference, most came from Western Europe, but there were also scientists from Canada, Hungary, Romania, the U.S.A. and the U.S.S.R.

The first three days (May 5-7) of the meeting were spent in Paris, where the Conference dealt with the metallurgy, chemistry and optical behavior of the rare earths (a complete list of the papers presented at the Conference follows this story). The last half of the Conference (May 8-10) was held in Grenoble, where the emphasis was on solid state physics.

The Paris portion of the Conference was organized by Dr. F. Trombe and his co-workers and the Grenoble portion by Dr. E.F. Bertaut and his co-workers. Both groups are to be commended for the excellent Conference and their kind hospitality.

The keynote speaker at the Conference was Dr. F.H. Spedding, Iowa State University, Ames, Iowa, who spoke on 'The Preparation, Handling and Properties of "Pure" Rare Earth Metals.'

All attendees were given a copy of the abstracts of the papers presented at the Conference. Furthermore, the Conference Proceedings will be published in two volumes, one for the Paris half and the other for the Grenoble half. As soon as these volumes are published RIC News will announce their availability.

Fifteen Firms Support RIC

The publication of RIC News for at least another year, and the resumption of RIC's inquiry answering function have been assured through a broadened base of financial support from 15 of the world's leading rare-earth producers.

Begun as a U.S. Atomic Energy Commission information center in 1966, RIC faced extinction when the AEC was forced to withdraw its support of the Center in 1968. However, grants to Iowa State University's Institute for Atomic Research from five American rare-earth companies made it possible to continue publication of RIC News.

The original five Industrial supporters of RIC have been joined by 10 more companies representing seven countries, including the U.S., for support of the Center through July 1970.

Financial support for RIC now comes from American Metallurgical Products Co., USA; American Potash & Chemical Corp., a subsidiary of Kerr-McGee, USA; Elettrochimica Italiana delle Terre Rare, Italy; Th. Goldschmidt A.G., Germany; W.R. Grace & Co., USA; Indian Rare Earths, Ltd., India; Leico Industries, Inc., USA; Michigan Chemical Corp., USA; Molybdenum Corporation of America, USA; Pechiney-Saint Gobain, France; Research Chemicals Division, Nuclear Corporation of America, USA; Ronson Metals Corp., USA; Shin-Etsu Chemical Industry (Continued on Page 7)
International Conference Program

PARIS SESSIONS

1. General Metallurgy


F. Parthé: Quelques principes structureaux des composés ternaires métalliques des terres rares.


G. Schiffermacher, G. Maich and F. Trombe: Préparation des métaux des terres rares par réduction métalthermique de leurs oxydes.

2. Oxides and Ternary Oxides


S. Anderson: The change of oxide structures by unionation.

G. Hoppe: Die ternären Oxyde der seltenen Erden mit Alkalimetallen.

H. Bäringhausen: The crystal structure of CeO.

M. Gomis and A. Wainw: Étude des composés TIO2 (étant une terre rare) obtenue par haute pression et à haute température.


R. Rouanet: Diagrammes de solubilité et diagrammes des phases de haute température des systèmes formés par la zircon avec les sesquioxys des lanthanides.

3. Metals and Alloys

K.H. Buschow: Rare Earth Cobalt intermetallic compounds.

R. Lemaire and D. Paccard: Structures cristallines du composé TbNi.

G. Buzzing, M.L. Fornaini and F. Merko: Rare earth-zirconium compounds close to the 1:4 composition.

A. Palenzona and E. Franceschi: The crystal structure of RE2T1 compounds.

A. Olesse: Sur la structure électronique du cérium dans ses composés intermétalliques binaires.

C.E. Lindin: The structural characteristics of the samarium-type phase in rare earth alloy systems.

A. Lendei and A. Palenzona: Binary phase diagram of ytterbium with Cu, Ag, Au.


N. Boulet: New crystallographic studies of samarium in microscope electronique.


C.K. Jefjorgon: Les déviations de trivalence dans les groupes f et le paramètre (f-A).

G. Busch, E. Kaft and P. Wachtler: Syntheses, crystal growth and physical properties of some rare earth nitride phases.


A. Laplace and R. Lorenzelli: Étude de monocarboxydes d'europium et d'ytterbium. Structure cristalline et valence des ions métalliques.

J.S. Anderson and A.N. Bagshaw: Thermodynamic studies of lanthanum, cerium and neodymium carbides.

G. Lellé: Etude par rayons X et par diffraction neutronique des carbhydrures et sulfhydrures d'yttrium.


D.A. Johnson and J.T. Corbet: The relative stability of the rare earth metal diiodides.

5. Optical Properties of Oxides and Salts


J.P. Briffaut: Cramp cristallin au site de Eu3+ dans un système d'orthovonadates.

C. Bonelle and R.C. Karnailaia: Étude par spectroscopie X des distributions d3 de gadolinium et d'eupéric dans le métal et l'oxide.


S. Natanson: Luminescence phenomena in rare earth activated lanthanum oxychlorides.

*Invited speaker
MEETING
8TH RARE EARTH CONFERENCE
The Committee for the 8th Rare Earth Research Conference has issued a call for abstracts from participants intending to present papers at the April 19-22, 1970 meeting. The deadline for abstracts is Oct. 15, 1969, according to T.A. Henrie, chairman.

Thirteen sessions will be held in five meeting periods are planned. Topics to be covered are solid state reactions, chemistry, physics, metallurgy, geology, and industrial processes.

Abstracts and requests for information about the Conference should be addressed to:
T.A. Henrie, Chairman
8th Rare Earth Research Conference
% U.S. Bureau of Mines
Reno, Nevada 89505 U.S.A.

Letters
To the Editor:
A recent item in RIC News entitled “Transparent RE Oxides” (Vol. IV, No. 2, p. 3) implies that preparation of transparent Y$_2$O$_3$ by press forging is a new achievement. I would like to call your attention to the paper by R.A. Lefever and John Matsko, “Transparent Yttrium Oxide Ceramics,” Mat. Res. Bulletin 2, 865 (1967), in which the preparation of completely transparent glasses of Y$_2$O$_3$ by vacuum press forging is described. The procedure involves a single vacuum hot isostatic pressing operation requiring temperatures and pressures on the order of only 950° C and 10,000 psi, respectively...

R.A. Lefever
Sandia Laboratories
Albuquerque, N.M. 87115

Rare Earth Goofs
Vol. IV, No. 2 June 1969.

If you had trouble finding the source material for our “Reappraisal” story, it’s because we couldn’t find it ourselves in the references listed. The worldwide review was contained in Industrial Minerals No. 4 in Industrial Metals as reported. Also, the review of India’s RE industry begins on page 23 instead of on page 22 in Nuclear News, Vol. 12.
2. Neutron Diffraction


C. Becle and R. Lemaire: Propriétés magnétiques et structures magnétiques des composés magnétiques de type Pr2MFe14C2 et Pr2ZnFe12C2. 

K. Tanaka and A. Fujita: Propriétés magnétiques et structures magnétiques des composés magnétiques de type CeMFe12C2.

H.B. Hickmott, R.J. Roe and W.A. James: The Ho-Fe binary system and related magnetic properties.


A.D. Woods, M.W. Stringfellow, T.M. Holdren and B.M. Powell: Exchange and crystal field interactions in 3d and 4f elements and the origin of antiferromagnetic ordering.

F. Bertaut, R. Scherrer and F. Tchou: Ordre magnétique de la terre rare dans les gruits.


G. Bocelli et F. Levy: Distortion tetragonale et trigonale du réseau de certains composés trivalent des terres rares.

M. Mercier et P. Bauer: Mesures magnétoélectriques sur quelques cations, amines et ferri oxides ferrites.

G. Lee, M. Mercier et P. Bauer: Mesures de l'effet magnétoélectrique sur les gruits aux basses températures.


E.F. Westrum Jr.: Thermal and Electronic Behavior of the Rare Earth Hexaborides from Cyanogen Calorimetry.


S. Hufner: Optical investigations of magnetic rare earth oxides with the garnet and perovskite structure.

G.M. Klaun, G.K. Sheny and B.D. Dunlap: Repulsive interactions in Er2O3 and Yb2O3 between 20K and 15K.


F.D. Jones: Pr141 and Tm169 Nuclear Magnetic Resonances in Van Vleck Intermetallic Paramagnets.

3. Resistivity, Kondo Effect

A. Blundin: Interactions d'échange dans les métaux et alliages de terres rares.

J.J. Rhine: Anomalous Hall effect in rare earth metals.


H.H. Hill et R.O. Elliott: Virtual bound states in plutonium: the Kondo effect in LaPu and PrPu alloys.


M. Methfessel: Magnetic, electric and optical properties of rare earth chalcogenides.

B. Coqblin: Considerations théoriques sur les changements de valence de terres rares.

C. Ch. Schüller: Optical properties of rare-earth metals.

Rare-Earth Halides


Halogen and oxyhalogen complexes of lanthanides and actinides including yttrium and scandium are extensively reviewed. The first chapter presents an overall picture of halide chemistry and its special problems. Fluorides, chlorides, bromides and iodides and their respective oxyhalides are dealt with in four succeeding chapters each of which are subdivided by valence states. Preparation, chemical and physical properties, structures, and halogeno-complexes are discussed. Differences and similarities between the lanthanide and actinide series are presented in parallel.

Thermochemical data, infrared vibrational frequencies and mixed halides of trivalent and tetravalent uranium are listed in separate appendices for convenient location. Literature coverage through the end of 1967 is provided.

Chelates Point to Novel Separation

Thermodynamic properties have recently been reported on a series of remarkably volatile and thermally stable lanthanide chelates, J. Am. Chem. Soc., 91, 3476 (1969).

J.E. Sjöv and co-workers at the Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio, have found large differences in the vapor pressures, heats of vaporization, and heats of sublimation of the lanthanide chelates of 2, 6, 6-tetram ethyl-3, 5-heptandione, H(thd). Their findings corroborate the trend detected earlier by gas chromatography and reported by Eisenbraut and Sievers in 1965. Complexes of the higher atomic number lanthanides are more volatile than those of the lighter, larger ones; this is an effect of the lanthanide contraction.

Vapor pressure as a function of temperature was measured for 13 lanthanide complexes. The differences were large enough to permit novel separation of these elements. A recent patent of Eisenbraut and Sievers (U.S. Patent 3,429,904) describes the use of the tetra-methylheptanedionato complexes to separate cleanly and purify lanthanide mixtures by fractional sublimation. For example Eu(thd)3, Yb(thd)3, and Tm(thd)3 sublime at temperatures about 100°C lower than those required for La(thd)3, Pr(thd)3, and Nd(thd)3. A thermal gradient fractional sublimation apparatus is used to effect separation.
Rare Earths
In the News

NORWEGIAN RE PRODUCER
The Metal Extractor Group of Norway, MEGON, was formed in April of this year by ten Norwegian industrial firms to produce rare earths (primarily yttrium oxide) and other metals and materials from various Norwegian ore sources.

CANADIAN YTTRIUM OXIDE
Denison Mines has announced that it is resuming production of yttrium oxide from tailings of the uranium mining operation. This material is being shipped to MolyCorp for further processing.

1000 WATT Nd LASER
Sylvania has announced it will be producing a 1000 watt CW Nd-doped yttrium aluminium garnet laser. Delivery on the first models is scheduled for January 1972.

ULTRAVIOLET Nd-DOPED LASERS
The use of a frequency doubler and a special output mirror which is reflective to 1.06 μ but transmits 0.53 μ enables quadrupling the frequency of Nd lasers to 0.265 μ. The Nd-doped glass laser which is manufactured by Korad, has an average energy of 5 mJoules, and is particularly useful for initiation of photochemical reactions and the study of living tissues.

Rare Moon Dust

"To all scientists this is a very, very exciting time," claimed a geologist at the Lunar Receiving Laboratory as he opened the first samples from the moon. Soon to share his excitement are the 142 principal investigators from the U.S. and eight foreign countries who will be receiving nearly 50 pounds of lunar material as the two-month quarantine period nears an end.

Speculation on the presence and concentration of rare earths runs high. A number of the principal investigators will be using highly sophisticated techniques to seek out traces of the rare earths including mass spectrometry, neutron activation, and emission spectroscopy.

Among the principal investigators involved in the search for rare earths are: P.W. Gast, Lamont Geological Observatory; L.A. Haskin, University of Wisconsin; A.W. Helz, U.S. Geological Survey; T.P. Kohman, Carnegie Institute of Technology; V.R. Murthy, University of Minnesota; G.W. Reed, Argonne National Laboratory; and R.A. Schmitt, Oregon State University.

The preliminary findings of these studies will be presented in Houston by the principal investigators three months after they receive their samples about September 20

Not So Refractory PrP

In striking contrast to the high melting point of praseodymium monophosphide, 2850 ± 50°C, reported in the last issue of RIC News, the 2400°C melting point for non-stoichiometric PrP observed by E. Franchesch and G.L. Olcese, J. Phys. Chem. Solids 30, 903 (1969). This reported melting point places PrP as about the eighth highest melting rare-earth compound.

Non-stoichiometry in PrP was determined by evaluating the variation of the lattice constant and density with composition. Quasi-stoichiometric phases occurred in the composition range PrP to PrP0.85. The magnetic properties of these phases showed that the effective valency of Pr was approximately 3.3, and that PrP could not be regarded as a simple ionic compound.

Metamagnetic Eu3O4

A Russian team headed by A.A. Samakhalov has measured the magnetic properties of Eu3O4 single crystals (Zh. Eksp. Teor. Fiz. 54, 1341 [1968]). They conclude that Eu3O4 is metamagnetic with a strong magneto-crystalline anisotropy and not a ferromagnet as proposed in earlier studies which had examined only polycrystalline samples. A metamagnetic material is one which is antiferromagnetic at low applied magnetic fields, but becomes ferromagnetic when the field is high enough to change the spin alignment.

They believe that the magnetic structure of Eu3O4 consists of ferromagnetic linear chains with antiferromagnetic coupling between chains. Neutron diffraction studies, however, are needed to confirm this proposed structure.

OXIDE ELECTROLYTES

A double cell containing two combinations of oxides (ZrO2-CaO, ThO2-Y2O3) to measure emf values over a wider range of oxygen pressures than has heretofore been possible is described by Tretyakov and Muan in J. Electrochem. Soc. 116, 331 (1969).

The ZrO2-CaO electrolyte permits cell operation at high oxygen pressure, and the ThO2-Y2O3 electrolyte at very low oxygen pressures. The electrolyte compositions are 85 m/o ZrO2-15 m/o CaO and 92 m/o ThO2-8 m/o Y2O3. The cell is described and its behavior and operating conditions are discussed.

ROMANIAN MAGNETISM

A comprehensive review of the rare-earth elements has just come to RIC News' attention. This book, Magnetismul Pliniintuirilor Rare [Magnetism of the Rare Earths] by I. Pop, was published by Editura Academiei Republicii Socialiste Romania, Bucharest (1968).

The first chapter is concerned with basic definitions and behaviors, the magnetic properties of ionic compounds of the rare earths, magnetic resonance phenomena, energy levels, and crystal field effects. The next three chapters deal exclusively with the magnetic behaviors of the metals, alloys and intermetallic compounds, and ferrites. The fifth and last chapter is on applications.

This 416-page book with almost 700 references costs 28 Lei (approx. $4.60).
INTERNATIONAL HAPPENINGS

RE's in Grenoble, Zürich and Moscow

While in Europe during and after the French International Rare Earth Conference the Editor took the opportunity to visit several laboratories which are conducting research on rare earths.

In Grenoble the Conference was held at the Nuclear Center, and the conference had an opportunity to visit some of the laboratories there. Unfortunately, because of the lack of time I saw only their crystal growing laboratory. This laboratory is probably one of the largest of its kind in the world. They grow a variety of materials, including rare-earth garnets and aluminates, by a number of different techniques. Of course, the Nuclear Center, under the direction of L. Néel, and the National Center for Scientific Research’s laboratories, under E.F. Bertaut, are well known for the excellent studies on the magnetic properties and x-ray and neutron crystallography of rare-earth materials.

After the Conference, I traveled by train from Grenoble to Zürich. In Zürich I visited the Institute of Solid State Physics of the Swiss Federal Institute of Technology which is headed by Dr. G. Busch. Dr. Busch’s group is doing a great deal of work on the rare-earth non-metallic compounds RX, where X is N, P, As, Sb or Bi and R is a trivalent lanthanide, and EuX where X is O, S, Se or Te. They are primarily interested in semi-conducting ferromagnets and are studying magnetic and optical properties, crystal structures and photocemission. They have recently found that they can obtain polarized electrons (35% polarization) from photo-emission of EuS (see Solid State Comm. 7, 775, 1969). A great deal of effort is also being spent on preparing high-purity samples and on better characterization of their materials for solid state studies.

After my visit to Zürich I traveled to Moscow to visit Professor E.M. Savitskii and his research group, the Laboratory of Rare Metals and Alloys in the Institute of Metallurgy of A.A. Baikov of the Academy of Sciences of USSR.

Again, the shortage of time prevented my spending more than a day there. Professor Savitskii has five groups working under his supervision. Only one of these groups deals exclusively with the rare earths. The rare-earth group is primarily concerned with the determination of rare-earth alloy phase diagrams. Presently, those of La, Ce, Pr, Nd, Gd, and Sc with a variety of other metals including other rare earths are of greatest interest. Other groups which deal with thermionic emission, super-conductivity, and rhenum alloy chemistry only indirectly or occasionally work with the rare earths. A great deal of their work is directed toward finding technological applications, especially in electronic and electrical areas.

RARE EARTHERS on the move

Dr. Therald Moeller (RE complexes), professor of chemistry at the University of Illinois, will become chairman of the Department of Chemistry at Arizona State University, Tempe, in September. Moeller replaces Dr. LeRoy Eyring (RE oxides), chairman of the Arizona State Chemistry Department for the past 8 years, who returns to research and teaching.

At the AEC’s Ames Laboratory, Iowa State University, Ames, Dr. V.A. Fassel (RE analytical spectroscopy) has been named deputy director to replace Dr. Morton Smutz (RE liquid extraction). Smutz is now associate dean and director of research in the College of Engineering, University of Florida, Gainesville. A member of the Ames Laboratory staff since 1942, Fassel is also a professor of chemistry at Iowa State University.

Alloy Advances
SUPERALLOYS

The addition of lanthanum, cerium or yttrium to superalloys used for marine turbine applications has proved to be beneficial in increasing the high temperature corrosion resistance of these alloys. Lanthanum or cerium is added to the nickel-based superalloys and yttrium to the cobalt-based alloys. Without the 0.1 to 0.2% rare-earth addition the corrosion rate may be as much as ten times more severe.

MAGNESIUM

The American producers of mischmetal for alloy additions to magnesium expect an increase in output during the next few years, because of the interest shown by U.S. foundries for a magnesium-zinc-rare earth-zirconium alloy (ZE41) for a casting alloy. Although this alloy has been widely used in Europe for many years, it is just becoming popular in America.

The improved castability, lower reject rate and better welding efficiency of ZE41 over the standard casting alloys (magnesium-aluminum-zinc alloys) has all but turned the tide in its favor, even though the costs are slightly higher.

COPPER

The addition of 2 vol% Y2O3 to OFHC (oxygen-free high-conductivity) copper as a fine dispersion increases the strength by a factor of 5 over hard-drawn OFHC copper without altering the electrical conductivity. Although many applications require high-strength-high-conductivity copper, the use of Y2O3 in these materials will be given serious competition from Al2O3.

Reviews "Terres Rares"

A review, Les Éléments Des Terres Rares, by J. Flahaut has been published by Masson et Cie, Editeurs, Paris (1969) 165 pp. Topics covered are general properties, history of the periodic classification, natural abundance, extraction and separation procedures, preparation and properties of the metals, compounds, and the uses and applications.
GT&E Laboratories — 
LUMINESCENT MATERIALS GROUP

LUMINESCENT MATERIALS GROUP - In the front row from left are Brian O'Reilly, Frank Avella, Lily Ho, Frank Palilla, Richard Klein and Victor Attaurin. Pictured in the center row from left are Vincent Meyer, Thomas Biono, Robert Amster, Majis Tomkus, Thomas Peters and Samuel Natanson. In the back row from left are Tatsuki Yoshitake, Ojars Sovers, Rene Simon and Gleb Gashurov.

Luminescent materials research at the Bayside Research Center of the General Telephone & Electronics Laboratories located at Bayside, New York, covers all aspects of luminescence in inorganic solids. This program, under the direction of Frank C. Palilla, emphasizes research on rare-earth phosphors because of their tractability to theoretical investigations and because of their importance in color TV and lighting applications.

The basic studies cover the gamut of excitation, energy transfer and emission processes in inorganic phosphor systems. Examination of the response of phosphors to various excitation modes helps to identify the processes by which energy is absorbed or lost, and thereby to determine the ultimate radiant efficiencies obtainable.

Studies of the lifetimes of excited states clarify the host-activator and activator-other atom interactions involved in energy transport. In addition, precise spectroscopic studies of intensities and positions of the discrete emission characteristics observed with rare-earth activators in selected hosts are used to describe quantitatively the internal crystalline field experienced by the activator.

Concomitantly, exploratory synthesis research is carried out in a search for materials with high luminescence response throughout the visible spectral range. Emphasis is placed on the coupling of visibly emitting lanthanide ion activators (Ce, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb) to hosts containing rare-earth cations (Y, La, Gd, Lu). The significant features of the latter are that they are optically inert and they easily accommodate the former.

The experimental phosphors resulting from this research are evaluated for commercial use, and significant new developments are promptly transferred to the Chemical and Metallurgical, Lighting, and Electronic Components Divisions of Sylvania Electric Products Inc., a subsidiary of General Telephone &

Support RIC (Continued from Page 1)
Co., Ltd., Japan; Typpi Oy, Finland; and Wako Bussan Co., Ltd., Japan.

The first industrial support of RIC came from these companies: American Potash, Grace, Molybdenum Research Chemicals, and Ronson.

The resumption of RIC's inquiry answering service is a direct result of increased industrial support for Fiscal Year 1970. A half-time staff member has been added to provide this and other services (see story on Page 2). Despite RIC's curtailed activities, information requests are running 50% ahead of a year ago.

Although it appears that the Center will be operating at a near normal level through July 1970, its future is still uncertain. With little likelihood of Federal support, RIC's programs will depend on financial aid from additional companies in the rare-earth business.

The Center needs grants totalling $10,000 annually in addition to the support provided by Iowa State University to meet minimum objectives. To date about 60% of the needed funds have been received or pledged. If your firm would like to join our present benefactors in supporting RIC, contact Director K.A. Gschneidner, Jr.

"A continuing commitment on the part of rare-earth users and producers will enable the Center to plan farther into the future," according to Gschneidner. "Until then, we must necessarily operate on a year-to-year basis," he concluded.

Vol. IV, No. 3 September 1, 1969

published in
March, June, September and December
by
Rare-Earth Information Center
Institute for Atomic Research
Iowa State University

Second-Class postage paid at Ames, Iowa.

Telephone: Area Code 515 294-2272
K.A. Gschneidner, Jr. . . . . . . . Editor
Charl Bertrand, Nancy Kippenhan and W.H. Smith
Staff Writers
GEOCHEMICAL PROSPECTING

The occurrence of trace elements such as cobalt, europium, and scandium in ocean floor samples may be useful in determining origins of undersea sediments. Texas A and M University's Activation Analysis Research Laboratory is developing methods which use these elements in "geochanical prospecting" on the ocean floor. Although work is now limited to analyses of five major elements - silicon, oxygen, aluminum, magnesium, and iron.

MAGNETISM IN TECHNOLOGY

In an invited paper presented at the 14th Annual Magnetism Conference, I. S. Jacobs discusses the "Role of Magnetism in Technology." [His complete talk is published in the March, 1969, issue of J. Appl. Phys., 40, 917]. Jacobs notes that magnetism has an economic impact of over 1% on the gross national product of America, and presumably a similar percentage in other technologically advanced countries. The magnetism market, research, history, and esoteric role of magnetism are all discussed.

In addition to Jacob's paper, this issue of J. Appl. Phys. contains about 75 more papers dealing directly or indirectly with rare-earth materials.

RARE-EARTH INFORMATION CENTER
Institute for Atomic Research
Iowa State University
Ames, Iowa 50010

Thermocouple Insulator

Yttrium oxide was found to be better than BeO and as good as ThO2 for thermocouple insulators at temperatures between 1800 and 2000°C using tungsten/25% (or 3%) rhenium-tungsten thermocouple wires and Ta, Mo, Re, W, and Nb. Their work was found to be Y2O3 insulated thermocouples maintained their calibration for more than one month at 2000°C.


Publications Available

[Continued from Page 7]

Electronics Corporation. An example of such a development is the YVO4: Eu phosphors which have had a major impact in the lighting, television and rare-earth chemical industries.

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I | 1
II | 8
III | 4

Luminescent Materials Group
(Continued from Page 7)

Second-Class postage paid at Ames, Iowa.
AIME Alloy Theory Conference

Eight papers on the “Alloy Theory of the Rare-Earth Metals” were presented at the Fall Meeting of the Metallurgical Society of the Amer. Inst. of Mining Met. and Pet. Engr. The first paper, “Band Structures” by J. O. Dimmock, Massachusetts Institute of Technology, discussed the theoretical calculations of the electronic structures of the rare-earth metals. Several different methods for calculating the band structures were discussed and the usefulness and limitations of each were summarized.

“Transport and Magnetic Properties” by Sam Leybold, Iowa State University, dealt with rare-earth metal single crystals. The influence of the magnetic structures and band overlap on some of the properties were clearly demonstrated in several instances.

The results of neutron inelastic scattering experiments being carried out in several different laboratories were summarized by S. K. Sinha of Iowa State University in his talk, “Neutron Scattering.” He noted that the phonon dispersion curves for the normal hexagonal rare-earth metals were similar to one another and that the number of 4f electrons does not affect these curves. Furthermore, he pointed out that they have strong long-range forces within the basal plane but not between layers.

The results of “Mossbauer and Nuclear Magnetic Resonance” studies on the rare-earths was reviewed by G. M. Kalvius, Argonne National Laboratory. The similarities and differences between these two techniques were briefly summarized. The experimental difficulties in using these techniques to study rare earths and some of the significant and important results were noted.

C. C. Koch, Oak Ridge National Laboratory, spoke on “Solid Solution Intra-Rare-Earth Alloys.” The results from different laboratories were summarized, and several diverse explanations dealing with the existence of the various phases observed in these alloys were discussed.

“Solid Solutions with Non-Rare-Earth Metals” was presented by K. A. Schneidner, Jr., Iowa State University. He stated that information gleaned from these studies has shed new light on the factors which influence the formation of solid solution alloys.

Hugo Steinfink, University of Texas, delivered a paper entitled “Crystal Chemistry of Semi-Metallic-Rare-Earth Compounds.” The major portion of his talk was concerned with the sulfides, selenides, and tellurides, especially the R3X4-R3X2 region in the rare-earth(R)-chalcojenide(X) systems.

The final paper was presented by W. B. Pearson, University of (Continued on Page 4)
More RIC Support

Two more rare-earth producers, Forskningsgruppen for Sjeldne Jordarter (Rare Earth Research Group) of Oslo, Norway and Nippon Yttrium Company, Ltd. of Tokyo have joined the other 15 leading companies which are now supporting RIC.

Rare Earth Pioneer,
Spedding, is Honored

Rare-earth pioneer Frank H. Spedding has been honored for his scientific contributions by both the Society for Applied Spectroscopy and the Franklin Institute of Philadelphia.

The Franklin Institute awarded Spedding its Francis J. Clamer medal for his “many important contributions to the science of extractive metallurgy . . . and for his pioneering contributions to rare-earth metallurgy.” The Society for Applied Spectroscopy named Spedding to honorary membership citing him for his continuing studies on the nature of solids by means of spectroscopy, with major work on rare-earth compounds.

Bell Bubbles

The recent announcement by Bell Laboratories of a bubble domain memory device may lead to an increased use of individual rare earths. The development involves the control of very small magnetic cylindrical domains (bubbles) moving through a thin single crystal of a rare-earth orthoferrite.

The device is capable of performing a variety of tasks: logic, memory, switching and counting, all in one crystal. A cubic inch of these crystals could store 15 million bits of information with a power consumption of a few tenths of a watt. The space and power savings each are of the order of 105 over present devices.

To date the most promising materials are orthoferrites containing samarium, terbium, dysprosium and thulium.

REactive in Certain Media

The Spex Mixer/Mill pictured at right was demolished and a technician was injured as a result of an explosion which occurred when an attempt was made to grind 20 g of samarium powder in approximately 20 cc of Freon 113 (1,1,2-trichlorotrifluoroethane). It was reported that detonation was almost instantaneous. Subsequent investigation revealed that the explosion was caused by the generation of fresh metal surface in the presence of the chlorinated halocarbon as a result of the grinding operation. It is thought that other RE’s will react in the same manner when ground in the presence of chlorinated halocarbons.

RIC has just published 25 Years of Rare Earths—A Bibliography of Rare-Earth Research Papers and Reports Published by the Ames Laboratory from Its Founding to Its 25th Anniversary, by Joan E. Smith, Charla C. Bertrand, and Karl Gschneider, Jr., August 1968, 241 pages.

This report is divided into three sections: papers published in journals, conference proceedings, and books; university theses and U. S. Atomic Energy Commission reports; and patents on rare-earth processes. Subject, materials, and author indexes are included. To obtain a copy, order USAEC Report IS-RIC-2 from the Clearinghouse for Federal and Scientific Technical Information, Springfield, Virginia 22151, U. S. A.; the price is $3.00.

Trademark Protection
For RIC Symbol

The United States Patent Office has granted trademark protection to the U. S. Atomic Energy Commission for the symbol used by the Rare Earth Information Center. The trademark is only the second granted to the AEC.

RIC’s trademark which appears on all RIC publications consists of a large triangle enclosing a smaller, inverted triangle. The chemical symbols for the rare earths are printed in the outer triangle from the apex down according to decreasing number of unpaired d electrons. The inner triangle with the cross bar is the chemist’s symbol for earth, and this combined with the Latin word for rare (rarus) gives “rare earth.”

In addition to using the trademark on the heading of RIC News, the Center uses it on brochures concerning the Center, and on the covers of its technical reports. And that, sharp-eyed readers, is why the ® appears next to the symbol on this issue.

Magnetic Review


The chapters on rare earths cover work on magnetic moment, paramagnetic susceptibility, ordering temperature and structure, exchange mechanism, and anisotropy for the metals, alloys, and compounds.
Superconducting Rare Earths

Recently, scientists at the University of California's Los Alamos Scientific Laboratory reported the preparation of a new high-temperature yttrium-thorium sesquicarbide superconductor. Krupka, Giorgi, Krikorian, and Szklarz state in their *J. Less-Common Metals* (19, 113, 1969) paper that the maximum temperature, 170 K, was found for an alloy of the composition Y₀.7Th₀.3C₁.55.

This compound has the body-centered cubic Pu₂C₃-type structure and must be prepared by high-pressure high-temperature techniques.

Does this study open the door to a new class of high-temperature superconductors much like the class based on the cubic W₃O(β-W) type structure? We at RIC believe it does—but only time will tell.

Review
(Continued from Page 2) pounds. There are additional references to rare-earth work under the chapters on theory, dilute systems, nuclear magnetism, and magnetoelastic phenomena. A material index by chemical symbols is included.

The digest is published annually, surveying the literature, books, and conferences of the preceding year; the price of the 1968 volume is $13.00.
Rare Earths
In the News

RONSON ACQUISITION

Ronson Corporation has acquired British Flint & Cerium Manufacturers, Ltd., which now becomes a division of Ronson Products, Ltd. The mischmetal manufactured by British Flint & Cerium will be primarily used in the United Kingdom for lighter flints and alloy additives.

LANTHANUM ELECTRON GUN

A patent for an improved electron gun which utilizes LaB₆ as the cathode from which electrons are emitted has been granted to the International Business Machines Corporation. The improved gun is the invention of Dr. Alec N. Broers. The gun is said to have five times the "brightness" of those made with the usual tungsten hairpin-shaped filaments.

Kanpur

(Continued from Page 3)

haviour of the e-electrons. Detailed studies on ortho-chromites, -manganites, and ferrites have been completed and presently cobaltites, nickelites and titanites are being examined.

4. Optical spectra of rare-earth ions doped in CaF₂ are being examined to understand the defect equilibria and energetics.

5. Infrared spectra and thermal decompositions of a number of rare-earth compounds (carbonates, nitrates, nitrates, acetates, formates etc.) have been investigated to establish the reaction modes and the nature of metal-anion bonding. Heavier rare-earth compounds generally decompose at lower temperatures due to the greater covalency of the metal-oxygen bonds; in these compounds distinct bands are seen in the infrared spectra due to the metal-oxygen stretching vibrations.

Rare Earthly Goofs


In the story on the June 1969 issue of Goldschmidt Informiert, articles 3, 4 and 5 were written by W. Bungardt and not by W. Brugger as reported.

AIME

(Continued from Page 1)

Waterloo (Canada) on "Crystal Chemistry of Metallic-Rare-Earth Compounds." He noted that the rare-earth-metallic compounds form most of the common-type structures found for metallic compounds, except in the cases where the large size of the rare-earth metal atom prevents their formation—such as sigma and related phases.

The papers presented at this symposium will not be published as a conference proceedings. However, most of the information presented at the conference has been or will be published in the usual journals.

Service

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In keeping with our previous tradition, all information inquiries and our new services are kept confidential unless otherwise directed by the requester. For further information, write the Director of RIC, Dr. Karl A. Gschneidner, Jr.

RE Lubricants

CeF₃ and LaF₃ have been found to be effective in reducing metallic wear in air or argon atmospheres at temperatures up to 1000°C, according to H. E. Slaney of National Aeronautics and Space Administration's (NASA) Lewis Research Center, Cleveland, NASA TN D-5301, July 1969.

During wear experiments the fluoride particles coalesced and flowed plastically in the contact areas forming a thin adherent film on Inconel sliding surfaces used in the study. Friction coefficients ranged from 0.1 to 0.4 and were fairly constant over a large temperature range. CeF₃ and LaF₃ were also found to be useful in lubricating nickel-base superalloys.

The lubricating properties of CeF₃ and LaF₃ combined with their chemical stability and high melting points make them attractive lubricants for special applications such as power transmission devices, especially at high temperatures.

The oxides of La and Ce were also investigated under the same conditions and found to be poor lubricants below 700°C, although there was some indication that they might have lubricating ability at very high temperatures (see RIC News Vol II, No. 4, p. 2, December 1967).

TROMBE NAMED TO C.N.R.S. BOARD

Felix Trombe, formerly director of the Rare Earth Laboratory of the French National Center for Scientific Research (C.N.R.S.), has been named to a three-year term as president of the Laboratory's board of directors. His appointment was effective in October 1969.

J. Loriers has succeeded Prof. Trombe as director of the Rare Earth Laboratory, and P. Caro has been appointed assistant director. Prof. Trombe will continue his research interests in rare-earth metallurgy in his new post with C.N.R.S.