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RARVS

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Nobel Rare Earther

Louis Néel

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

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

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

Pacemaker Development Tied to Rare Earths

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

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

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

Those *f* Electrons

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

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

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

(Continued on Page 4)

Michigan State University–

Rare Earth Chemistry Group

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

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

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

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

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

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☆ Reports ☆

☆ Booklets ☆

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TYPPI OY-FINLAND

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

High Temperature Oxides

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

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

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

Analytical Volume

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

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

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

High Purity RE Review

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

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

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

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

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

MEETING

DURHAM RE CONFERENCE

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

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

8 More Firms Support RIC

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

Elettrochimica Italiana Delle Terre Rare, Italy.

General Electric Company, U.S.A.

International Energy Company, U.S.A.

Lunex Company, U.S.A.

Philipp Brothers, U.S.A

Rare Earth Corporation of Australia, Ltd., Australia.

Sel-Rex Corporation, U.S.A.

Shin-Etsu Chemical Industry Company, Ltd., Japan.

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

Inert Refractories

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

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

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

THE AGE OF DISCOVERY

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

Rare Earths In the News

ERBIUM SINGLE CRYSTAL

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

SPEEDY X-RAY

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

La HI TEMP ALLOY

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

YTTRIUM BOOSTS TEMP LIMIT

NASA's Lewis Research Center reports that small amounts of yttrium, and tantalum or hafnium added to Fe-Cr-Ni alloys impart increased high temperature oxidation resistance to these superalloys up to 1260° C. A 10-mil thick foil of Fe-25Cr-4Al-0.5Ta-0.08Y subjected to this temperature for 800 hours exhibited a weight loss of less than 3.5 mg/cm^2. This, NASA reports, is a 60° C temperature advantage over commercially available superalloys.

RE Technology

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

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

Duwez Named ASM Fellow

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

To RESA Governing Board

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

(Continued from Page 1)

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

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