RARE-EARTH INFORMATION CENTER NEWS

ENERGY AND MINERAL RESOURCES RESEARCH INSTITUTE
IOWA STATE UNIVERSITY / AMES, IOWA

Volume IX | March 1, 1974 | No. 1

Experimentalists Gain on Theorists

The rare earth experimental physicists are slowly closing in on the elusive Fermi surfaces of the *trivalent* rare earth metals. The Fermi surface is important to scientists because it governs the nature of the transport properties of solids, in particular the electrical resistivity, thermal conductivity, Hall effect, magnetic susceptibility, etc. The most recent advance was reported in December by R. C. Young, R. G. Jordan and D. W. Jones [*Phys. Rev. Letters* 31, 1473-6 (1973)] who measured seven different frequencies in gadolinium metal—three in the basal plane and four along the c-axis. Until now the best that experimentalists were able to do was measure a single frequency in lutetium [J. A. Hoekstra and R. A. Phillips, *Phys. Rev. A* 4, 4184-6 (1971)].

The first of the Fermi surfaces was calculated by theorists about ten years ago, and subsequently they have been calculated for most of the rare earth metals. The results of Young and co-workers support the Fermi surface calculations in general, but there are some differences in the details. Furthermore, some of the observed low frequencies could not be explained because the band structure calculations had not been carried out in sufficient detail. But now, with some reliable data on hand, the theorists can go back to the computers and try to refine their calculations.

Two months prior to the Young, *et al.* paper, J.-P. Jan [*Phys. Rev. B* 8, 3590-4 (1973)] reported the first de Haas-van Alphen measurements of the Fermi surface of any rare earth intermetallic compound, YZn. In this case, he claims, no theoretical model can satisfactorily explain his observations.

Now it appears that the tortoise has moved ahead of the hare in the race.

The first Fermi surface measurements on any rare earth material were made in 1967 on *divalent* metallic ytterbium [*RIC News* III [1] 3 (1968)].

FLUORESCENT STANDARDS

Rare earth-doped glasses are promising standard reference materials for fluorescent spectroscopy according to R. Reisfeld, *J. Research NBS-A. Phys. Chem.* 76A, 613-35 (1972). Reisfeld studied absorption, excitation and fluorescent spectra, oscillator strength, and quantum efficiency of glasses doped with Gd^{3+}, Tb^{3+}, Eu^{3+}, Sm^{3+}, Tm^{3+}, and Ce^{3+}. Other variables investigated were concentration dependence, fluorescent lifetimes, quenching by surrounding medium, and stability.

Quantum efficiency from the lowest excited fluorescing levels approaches unity for Eu^{3+}, Gd^{3+}, Tb^{3+} and Sm^{3+}. Tm^{3+} fluoresces in some of the same regions as Tb^{3+} although its quantum efficiency is

(Continued on Page 4)

Explosive Explanation

Dr. Fred Holtzberg has offered a different explanation for the explosive behavior of Gd-doped SmS than that proposed by A. Jayaraman *et al.* and reported in *RIC News* VIII [4] p. 1. Holtzberg, of IBM's Thomas J. Watson Research Center, attributes the behavior to a phase separation rather than a phase transition.

In Holtzberg's model, both the black-colored phase and the gold-colored phase are initially present. Upon cooling, differential stresses are experienced in the crystal lattice which finally gives way to an explosive phase separation. Gold crystals collected after the explosive transition became black upon cooling and regained the gold color upon heating. Thermal cycling revealed no further deterioration in the crystals.

Holtzberg concludes that the explosion is the consequence of a change in the valence state of Sm, however, the actual mechanism of the reaction is phase separation, he explains. His results were presented at the Magnetism and Magnetic Materials Conference in Boston last November.

CONTRIBUTORS

Contributions have been received from Allied Chemical, Inc., Foote Mineral Co., and GTE Laboratories, Inc., all located in the U.S.A. and contributing for the second time, and from Rhone-Progil, France, a four-time contributor. Center supporters now total 31.

ACS Southwest Region Honors John Margrave


J. L. Margrave

The 1973 American Chemical Society (ACS) Southwest Regional Award, presented annually to an outstanding Houston area chemist, has been won by John L. Margrave. He is dean of advanced studies and research at Rice University, Houston, Tex., U.S.A.

Margrave's research, some involving rare earths, has been concentrated mainly on chemistry under extreme conditions (high and low temperatures and high pressure) and fluorine chemistry.

Rare Earths In the News

A RARE MEMORY

A rare earth ceramic developed by Sandia Laboratories promises to give computer holographic memory units a boost when the image storing device is applied to data processing. The ceramic, a thin, transparent, ferroelectric PLZT plate (7% La with a 65:35 ratio of lead titanate), deforms into thousands of microscopic depressions when light is projected through a photographic negative and a voltage applied to the PLZT. The depressions, some as deep as 1300 Å, vary according to the light intensity.

LASER CRYSTAL

Yttrium vanadate, a new laser crystal host for rare earth laser materials, is undergoing intensive investigation at the newly-formed Center for Laser Studies at the University of Southern California. The material is highly transmissive in the infrared regions (cut-off point is 5μ). It is being considered for optical ranging devices and systems.

Explain Enigma

H. W. de Wijn, A. M. van Diepen and K. H. J. Buschow have explained through a series of three papers the anomalous magnetic behavior of samarium in intermetallic compounds. Ever since the first measurements of the magnetic susceptibility of samarium metal about 17 years ago, scientists have been baffled by the fact that Sm does not follow a Curie-Weiss behavior above its magnetic ordering temperature—the only rare earth metal not to do so.

Although other scientists have thought the crystal field a Sm^{3+} ion sees in a compound is important, de Wijn, van Diepen and Buschow [*Phys. Rev. B* 7, 524-33 (1973)] show it is essential to include in one's calculations 1. the higher energy multiplet level (J = 7/2) in addition to the ground state multiplet (J = 5/2), and 2. sixth-order crystal field potentials in addition

(Continued on Page 3)

STAFF CHANGE


Betty Verkade

RIC is pleased to announce the addition of Ms. Betty Verkade to our staff. Ms. Verkade attended the University of Illinois and Iowa State University where she received her B.S. degree in chemistry. She has taught in both high school and college. She will be working half-time answering information inquiries and working on special reports which are becoming an increasing workload for the Center.

AT NEW SOUTH WALES

K. N. R. Taylor, formerly on the faculty of the University of Durham, England, has been appointed to a Chair in Physics at the University of New South Wales, Australia. Taylor is a co-author of the book, *Physics of Rare Earth Solids.* Also joining him at Sydney is R. G. Curry from Durham.

CEF Conference

A conference on Crystalline Electric Field Effects in Metals and Alloys, with the bulk of papers centered upon the rare earths, will be held in Montreal, Canada, June 26 through 29, 1974, inclusive. Both theoretical and experimental work will be extensively covered.

Invited speakers include Prof. P. Fulde, Institut Max von Laue-Paul Langevin, Germany; Prof. R. Orbach, University of California, U.S.A.; Dr. E. Bucher, Bell Telephone Laboratories, U.S.A.; Prof. H. W. de Wijn, Rijksuniversiteit, Holland; Prof. M. Zuckermann, McGill University, Canada; Prof. W. E. Wallace, University of Pittsburgh, U.S.A.; Dr. H. Heer, Institut fur Reaktorforschung, Switzerland; and Prof. D. Goodings, McMaster University, Canada.

Authors of contributed papers should forward an abstract, 100 words maximum, to the conference organizer before May 1, 1974. The time allowance for contributed papers will be 25 minutes maximum.

Prospective conferees should notify the organizer by March 31, 1974, or as near to that date as possible. The registration fee is $20 Cdn. Contact:

Dr. R. A. Devine
CEF Conference
Departement de Physique
Université de Montréal
D.P. 6128, Montréal 101
Canada

RIC Documents Available

IS-RIC-4 *Rare Earth Metals in Steels,* Nancy Kippenhan, Karl A. Gschneidner, Jr., March 1970.

IS-RIC-5 *Thermochemistry of the Rare Earth Carbides, Nitrides, and Sulfides for Steelmaking,* Karl A. Gschneidner, Jr., Nancy Kippenhan, August 1971.

IS-RIC-6 *Thermochemistry of the Rare Earths, Part I. Rare Earth Oxides, Part 2. Rare Earth Oxysulfides, Part 3. Rare Earth Compounds with B, Sn, Pb, P, As, Sb, Bi, Cu and Ag,* Karl A. Gschneidner, Jr., Nancy Kippenhan and O. Dale McMasters, August 1973.

Reports listed above are available without charge from the Rare-Earth Information Center, Energy and Mineral Resources Research Institute, Iowa State University, Ames, Iowa 50010 or from Molybdenum Corporation of America, Metallurgical Sales Service Office, No. 4 Gateway Center, Pittsburgh, PA 15222.

RE Abstracts

Multi-Science Publishing Co., Ltd., undertook early in 1973 the publication of an interdisciplinary abstracting journal, *Rare Earth Bulletin*, edited by Dr. R. F. Kelleher, University of Nairobi, Nairobi, Kenya, and issued bimonthly with annual subject and author indices. Subscriptions are available from Multi-Science, The Old Mill, Dorset Place, London E15 1DJ, England at £30 (about $68 U.S.) per year postpaid.

Articles abstracted include not only those from the leading chemistry and physics journals, but also from those devoted to electronics, ceramics and glass, magnetics, crystallography, optics, mineralogy, earth sciences, textiles, nuclear physics, solid-state, metallurgy, mining, and materials science. Abstracts are organized into seven major divisions—Distribution and Extraction, Chemical Properties, Crystallography, Nuclear Properties, Solid State Properties, Mechanical Properties, and Applications.

MEETING

11th RARE EARTH CONFERENCE

The 11th Rare Earth Research Conference committee has established deadlines for those wishing to present papers. Abstracts, sufficiently detailed to permit evaluation, should be sent to Dr. Harry A. Eick, Department of Chemistry, Michigan State University, East Lansing, MI 48824, U.S.A., to reach him no later than April 1, 1974. Authors of accepted papers will be notified by May 1, completed papers are due by July 1.

Sessions are planned in the areas of crystal chemistry, metals and alloys, spectroscopy, intermetallics, magnetism and physics, shift reagents, organometallics, coordination chemistry, solid state science, and catalysis, and a general session.

Pittsburgh Award To Rare Earther

W. E. Wallace

W. E. Wallace, chairman, department of chemistry, University of Pittsburgh, has received the 1973 Pittsburgh Award presented annually by the Pittsburgh Section of the American Chemical Society.

The award recognized Wallace's contributions to chemistry and to the Pittsburgh academic community. He is best known to rare earthers for his work on magnetic properties and heat capacities of rare earth metals and alloys. This has led to a much better understanding of the physics and chemistry of rare earth solids, particularly their crystal fields.

Explain Enigma

(Continued from Page 2)

to the fourth-order ones. This enables them to explain theoretically both the Knight shift and magnetic susceptibility of $SmAl_2$ and $SmSn_3$. Furthermore, they note that in certain crystal fields the orbital angular quantum number, L, and the spin quantum number, S, combine additively (L + S) rather than subtractively (L-S) as other light lanthanides and thus behave as a heavy lanthanide.

In their other papers they explain the change in the easy direction of magnetization in $SmFe_2$ at 175°K [van Diepen, de Wijn and Buschow—*Phys. Rev. B* 8, 1125-9 (1973)] and the reduction in the magnetic moment on the Sm^{3+} ion in several intermetallic compounds [Buschow, van Diepen and de Wijn—*Phys. Rev. B* 8, 5134-8 (1973)]. Although the authors attempted no explanation of the magnetic susceptibility of metallic Sm, it is quite likely that an extension of their method will enable theorists to calculate the correct temperature variation of Sm in the elemental form.

New Laser System

J. Stone and C. A. Burras have reported on the operation of a new Nd-doped laser system, *Appl. Phys. Letters* 23, 388-9 (1973).

Fused silica (SiO_2) is used as a noncrystalline host material because it has a minimum transmission loss in the same wavelength range in which Nd lasing occurs.

The laser system has a clad optical fiber geometry and can be end-pumped for maximum pumping efficiency. Absorbed pump power thresholds of 1-2 mW have been achieved for cores 40 μm in diameter. The laser operates at room temperature.

Fused silica, because of its high melting point, low thermal expansion, strength, favorable transmission characteristics, and ease of fabrication, warrants more investigation as a laser host, say Stone and Burras. They estimate that lasers as short as 1 to 3 cm with diameters $\leqslant$ 15 μm could be made provided a suitable pumping device is developed.

RUSSIAN ACQUISITION

The Russian book: *Fizicheskie Svoistva Khalkogenidov Redkozemelnykh Elementov (Physical Properties of Chalcogenides of the Rare Earth Elements)* by A. V. Golubkov, E. V. Goncharova, V. P. Zhuze, G. M. Loginov, V. M. Sergeeva, and I. A. Smirnov (Izdalet'stvo Nauk, Leningrad, 1973) 304 pp., has been added to RIC's collection.

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Bernie Evans, W. H. Smith and Betty Verkade
Staff Writers

End of an Era

Kerr-McGee shut down its rare earth operations Dec. 31, 1973. Economic pressures involved in complying with the Environmental Protection Agency's pollution standards were cited by management as the overriding factor in the decision.

Kerr-McGee, a relative newcomer to the rare earth industry, in its 1970 merger with American Potash and Chemical Corporation (TRONA) inherited a long legacy of pioneering going back to Lindsay Light Co., founded in 1902. Lindsay manufactured incandescent gas mantles with thorium extracted from monazite ores. Although rare earths are 5-20 times more plentiful than thorium in monazite, most of them were discarded prior to World War I. Soon after, new uses were developed for rare earths and Lindsay became a leader in the production of salts and in developing new industrial applications. Over the years the name of the company changed to Lindsay Light and Chemical Co. (1935) and then to Lindsay Chemical Co. (1952) reflecting the changing emphasis in production. In 1955 Lindsay was first to commercially produce highly pure individual salts by ion exchange. Lindsay merged with TRONA in 1958.

We acknowledge with gratitude the active support Lindsay has given RIC for the past several years.

Reports Booklets Brochures

INITIATES MISCHMETAL BULLETINS

The Metals Division of Rare Earth Industries, Inc., has begun a series of technical bulletins devoted exclusively to mischmetal applications. The series is entitled RAREARTH 96® (with appropriate subtitles outlining specific applications).

Two bulletins have been issued so far: *Mischmetal in High Strength Low Alloy Steels,* and *Mischmetal in Vacuum Degassed Steel.* They are not numbered so requesters should order them by title.

To order the bulletins now available and to have your name placed on the permanent mailing list for the series, write to:

Rare Earth Industries, Inc.
Metals Division
P.O. Box 365, Route 168
West Pittsburg, PA 16160, U.S.A.

RECORD YEAR FOR R.E. DISCOVERY

In case there is no listing in the *Guinness Book of World Records,* we note that 1879 was a record year for the discovery of rare earth elements. Samarium, holmium, thulium and scandium were isolated that year by L. de Boisbaudran, P. T. Cleve and J. L. Soret (independently), P. T. Cleve and L. F. Nilson, respectively. There is a two-way tie for the second best year between 1843 (terbium and erbium) and 1885 (praseodymium and neodymium).

Rare Earth Use In Steelmaking

Rare earth usage in steelmaking was among the topics presented at the 31st Electric Furnace Conference held at Cincinnati, Ohio, Dec. 5-7, 1973.

Deoxidation, desulfurization, inclusion manipulation, rare earth recovery, and steel toughness and ductility were discussed with respect to rare earth additions in the manufacture of steel. Also, effects of the different methods of rare earth addition were examined.

Current trends in rare earth usage were discussed with a cost/quality emphasis. In Europe, the major innovation has been a switch from the use of rare earth silicides to mischmetal for steelmaking.

Garners Garnets

Although F. F. Y. Wang makes no claim to being comprehensive, he does cover a lot of area in the field of garnets in his recent article "Physical and Chemical Properties of Garnets", *Treatise on Materials Science and Technology* 2, 279-384 (1973).

The preparation and properties (primarily crystal data, phase equilibria, chemical, thermodynamic, magnetic and optical) of simple rare earth and substituted garnets are presented and discussed.

In the article, which contains more than 300 references, Wang attempts to illustrate the suitability of garnets as prototype compounds for materials science research.

Fluorescent Standards
(Continued from Page 1)

considerably lower. For this reason Tb^{3+} is preferred over Tm^{3+} as a standard reference material.

Reisfeld's investigations suggest that rare earth-doped glasses are particularly well suited as reference standards for compounds having narrow fluorescent emission spectra. For example, Eu^{3+} is an acceptable standard in the range λ = 600-700 nm, Gd^{3+} emits only in the ultraviolet region, Tb^{3+} is useful at λ = 480, 543, 587 and 624 nm, and low concentrations of Sm^{3+} are applicable at λ = 560, 602 and 640 nm.

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RARE-EARTH INFORMATION CENTER NEWS

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Materials Research Laboratory–

Rare Earth Research at Penn State

PENN STATE GROUP–In the back row from left are P. Provenzano, J. Blanks, E. Imperato, T. Besmann and Dr. L. Drafall. In the center row from left are Dr. K. E. Spear, D. Petsinger, Dr. W. B. White, Dr. G. J. McCarthy and N. Price. Kneeling in front from left to right are R. Johnston, S. Boldish, M. Davidson, T. Choy and C. Sipe.

Rare earth research at Pennsylvania State University's Materials Research Laboratory spans two decades. Early work, initiated by Prof. Rustum Roy, director of the Materials Research Laboratory, was concerned with crystal chemistry, phase relations and defects in oxide and halide systems. Current research is focused on rare earth oxides, borides and sulfides.

Dr. G. J. McCarthy directs a variety of projects on rare earth oxides. R-M-O systems are being studied for phase relations (M=Mo, W, Nb), applications to catalysis (M=Mn, Co), and systematic crystal chemistry and x-ray powder diffraction standards (M=1st row transition metals). He is collaborating with Prof. J. E. Greedan of McMaster University on synthesis, stability and magnetic properties of ternary and quaternary oxides containing Eu^{2+}. Another project is concerned with fixation of commercial power reactor radioactive wastes of which the rare earths are the most abundant cationic species. Group members include graduate students R. Johnston and T. Choy, and technical assistants M. Davidson, N. Price and C. Sipe.

(Continued on Page 4)

Scandium Handbook

A dramatic increase in the literature dealing with scandium and its differences in behavior and crystallochemical properties as compared with the rare earths are given as reasons for the compilation of *GMELINS Handbook of Inorganic Chemistry, System No. 39 Rare Earth Elements, Part A2, Scandium,* I. Kubach, W. Muller, eds. (GMELIN–Institute for Inorganic Chemistry, Max Planck Society for the Advancement of Science, Weinheim, Germany, 1973) 181 pp. The price is DM 254 (~ $94).

The handbook begins with a brief history. Scandium's abundance in stars, meteorites, and lunar rocks is covered in cosmochemistry. The geochemistry of scandium deals with its crystallochemistry and abundance in the earth, water and atmosphere. The scandium-bearing minerals are extensively reviewed and finally the recovery of scandium, location of mineral deposits, possible applications, and the costs involved are discussed.

The handbook, published in German, features both German and English tables of contents and English headings and subheadings in the margins.

RARE EARTH INDUSTRIES PROMOTES LEON LUYCKX

Leon Luyckx has been named manager of product and market development for Rare Earth Industries, Inc., West Pittsburg, Pa. Just prior to his appointment, Luyckx had been a metallurgical consultant to the firm.

Iowa State Honors Pioneer Rare Earther


F. H. Spedding

Iowa State University on May 6, 1974, honored one of its most distinguished scientists when in formal ceremonies it renamed one of the major Ames Laboratory buildings the Frank H. Spedding Hall. Spedding is the founder of Iowa State's Energy and Mineral Resources Research Institute and the Atomic Energy Commission's Ames Laboratory which is located on the ISU campus. Now professor emeritus, Spedding directed a World War II project at Iowa State which resulted in the production of more than 2 million pounds of uranium metal. He has won acclaim for his work on the chemistry and metallurgy of the rare earths which spans four decades.

RIC SUMMARY

The Center's activities were summarized at a recent U.S. Government sponsored meeting on Materials Information and Data Centers. A limited number of copies of the summary were produced and they are available free to *RIC News* subscribers while the supply lasts. Included is a list of all the Center's industrial contributors since 1968.

New Plant for Ronson

Ronson Metals Corp. has announced the start-up of its new mischmetal production plant at Newark, N.J. Vice President I. S. Hirschhorn says the added capacity of the new plant gives Ronson the largest capacity for mischmetal production in the United States. Incorporated in the new facility are electrolytic cells of the most modern design coupled with the latest material handling and ingot casting equipment.

RIC-DD Airmail Rate Change

Due to recent changes in postage rates, RIC has revised the airmail rate schedule for RIC-DD documents. The new schedule is as follows:

Airmail Rate Schedule - U.S. $

Rate	A	B	C
U.S., Canada, Mexico	.40	1.10	1.70
Central, South America	1.20	3.00	4.60
Elsewhere	1.50	3.60	5.70

RIC-DD documents are priced to include the cost of first-class surface mail. Documents will be sent by airmail upon payment of the appropriate airmail schedule for each document in addition to its stated price.

The five additional documents listed below have been placed in the RIC Document Depository.

RIC-DD-8 State Functions for Many-Electron Atoms. Eigenfunctions of L^2 and S^2 for One- and Two-Open Shell Configurations by J. Karwowski and S. Fraga (1974) 71 pp. (U.S. $7.10)[Airmail Rate B]

RIC-DD-9 State Functions for Many-Electron Atoms. Eigenfunctions of J^2 and S^2 for p^N, d^N, and f^N Configurations, by J. Karwowski and S. Fraga (1974) 69 pp. (U.S. $6.90)[Airmail Rate B]

RIC-DD-10 State Functions for Many-Electron Atoms. Eigenfunctions of J^2 and S^2 for f^6 Configurations, by J. Karwowski and S. Fraga (1974) 92 pp. (U.S. $9.20)[Airmail Rate B]

RIC-DD-11 State Functions for Many-Electron Atoms. Eigenfunctions of J^2 and S^2 for f^7 Configurations, by J. Karwowski and S. Fraga (1974) 114 pp. (U.S. $11.40)[Airmail Rate C]

RIC-DD-12 Matrix Elements for Many-Electron Atoms. Spin-Orbit Interaction for One-Open Shell Configurations, by J. Karwowski and S. Fraga (1974) 107 pp. (U.S. $10.70)[Airmail Rate C]

THERMODYNAMIC BOOK

Termokhimiya Soedinenii Redkozemel'nykh i Aktinoidnykh Elementov (Thermochemistry of Compounds of Rare Earth and Actinide Elements) by G. A. Krestov (Atomizdat, Moscow, 1972) 253 pp., has been translated into English by the U.S. Joint Publications Research Service (AEC-tr-7505) and is available for $7.60 from the National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22151.

The book emphasizes oxides, halides and aqueous solutions. In

(Continued on Page 3)

New Magnet Alloy

J. P. Heinrich, H. Garrett and R. P. Allen report a breakthrough in the synthesis of the first 2:17 alloy to exhibit useful permanent magnet properties, *J. Appl. Phys.* 45, 1873-4 (1974). It had been demonstrated earlier that $Sm_2(Co, Fe)_{17}$ alloys had potential permanent-magnet properties which were even better than those of $SmCo_5$. The difficulty involved in achieving that potential was that most 2:17 alloys prepared previously had low coercive forces. A method of preparing $Sm_2(Co_{0.7}Fe_{0.3})_{17}$ is described which results in values of 5600 Oe for $_mH_c$ and 12 MG Oe for $(BH)_{max}$. The authors believe that even though there is still a large gap between the theoretical and actual properties obtained, their alloy already competes favorably with several existing commercial permanent magnet materials in that it has a higher energy product and lower production cost.

MORE CAPTURED

More of the shifty Lanthanide gang have been captured in print by A. F. Cockerill, G. L. O. Davies, R. C. Hardin and D. M. Rackham in "Lanthanide Shift Reagents for Nuclear Magnetic Resonance Spectroscopy", *Chemical Reviews* 73, 553-88 (1973).

This review covers theory, experimental procedures, data evaluation, application of lanthanide shift reagents (LSR) to mono- and polyfunctional molecules, their limitations, and recommended procedures for the use of LSR.

Reprints are not available from the authors but can be purchased from the Journals Department, American Chemical Society, 1155 16th Street N.W., Washington, D.C. 20036. Price $4.00 each; send cash or check with order.

ERRATA

IS-RIC-6, Thermochemistry of the Rare Earths:

On page 26 the value for $-\Delta G_f^\circ$ for Praseodymium Sesquioxide (Pr_2O_3) at 1600°K which reads 331.076 SHOULD READ 326

RE in Cloud Nine

Recent research directed by S. Drapatz has finally put a rare earth in "Cloud Nine" as evidenced by a paper entitled "Experiments with Europium-Vapour Clouds in the Upper Atmosphere" presented at the 16th Plenary Meeting and Specialized Symposia of the Committee on Space Research, May 23-June 6, 1973 at Constance, W. Germany, *Space Research* XIV (Academie Verlag, Berlin, 1974) pp. 233-40.

The purpose of the study was to determine the feasibility of using europium-vapor clouds to measure the magnitude and direction of electric fields in the upper atmosphere. Eu is theoretically applicable because of its low ionization potential, low evaporation temperature, short photoionization time scale, resonance lines of both atom and ion in the visible spectral range, and low abundance in the solar photosphere.

An artificial cloud is made by detonating an explosive charge in the upper atmosphere. Europium in the charge lining is vaporized, some in the ground state and some in an ionized state. The original cloud is soon divided into two clouds as the neutral cloud drifts along with the wind while the charged (ionized) cloud aligns itself with the electric fields.

Fluorescence spectra obtained in these studies have illuminated various atomic and molecular properties of europium, some of which could not be detected in laboratory situations. These observations include transition probabilities, photoionization cross sections, comparison of chemical reactivity of atoms in the ground and excited states, and the lifetimes, radiative transitions and oxidation processes of metastable states.

Thermodynamic Book

(Continued from Page 2)

addition to experimental data the author presents methods of estimating thermodynamic properties from interionic distances and crystal chemical radii.

Get the Lead Out

Rare earths may soon be taking the hard knocks – in gasoline, that is. The U.S. Environmental Protection Agency's imperative to "get the lead out" (of gasoline) has prompted researchers to investigate lanthanide anti-knock compounds, according to a report in *Chem. & Eng. News* 52, 27-8 (Mar. 25, 1974). A group led by Dr. R. E. Sievers demonstrated encouraging results in simulated tests using supercharged and conventional engines. Data from road tests being conducted are not yet available, but preliminary indications are favorable.

Cerium compounds – particularly cerium (2, 2, 6, 6- tetramethyl -3, 5-heptane-dionate)$_4$ or Ce (thd)$_4$ – appear to be the most promising. The cerium chelate not only raises the octane rating of the fuel, but the CeO_2 combustion product may also serve to reduce smog-forming hydrocarbon emissions by catalysis. Further enhancement of the already favorable cost picture of these compounds is likely through the substitution of mischmetal for pure cerium.

CONTRIBUTORS

Contributions received from six more rare earth firms during the last three months bring the total number of Center supporters to 37 for FY 1974. Additional financial support came from:

British Flint and Cerium Manufacturers, United Kingdom (2),*

Companhia Industrial Fluminense, Brazil (2),

Hitachi Magnetics Corp., (formerly General Electric Co., Magnetic Materials Product Section), U.S.A. (2),

Lim Fong Seng Sdn. Bhd., Malaysia (3),

Shinetsu Chemical Industry Co., Ltd., Japan (5), and

Westinghouse Electric Corp., U.S.A. (2).

*Indicates years in support of RIC including present fiscal year.

It's Pm Time

Promethium, the mercurial recluse of the 4*f* family which until 1945 eluded scientific sleuths, has at last emerged from its obscure shadows. Researchers, primarily at Hanford and Battelle-Northwest Laboratories, though hampered as recently as 1965 by inadequate supplies of the relatively short-lived radioactive material, have uncovered a substantial portion of the element's characteristic habits. Because many of these results have not been published or are available only in U.S. Atomic Energy Commission documents, E. J. Wheelwright has published a comprehensive review, *Promethium Technology* (American Nuclear Society, Hinsdale, Il., 1973) 395 pp., $20.25 for ANS members, $22.50 for non-members.

Scientists and engineers will find extensive information on a range of subjects including historical perspectives, recovery techniques, and purification schemes. Six of the 15 chapters are devoted to promethium's unique radiochemical properties and their biological implications. Analytical chemistry, preparation and properties of the sesquioxide and the metal, and a review of current applications complete the discussion. The brief outline and summary preceding each chapter is especially helpful as well as the author index which indicates both those cited in the text and those included in the list of references after each chapter.

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K. A. Gschneidner, Jr. . . . . Editor
Bernie Evans, W. H. Smith and Betty Verka
Staff Writers

RE Proceedings

The proceedings of the Seventh Russian Conference on Rare Earth Metals, Moscow, Sept. 12-17, 1972, E. M. Savitskii, ed., has been published as *Rare Earth Metals, Alloys and Compounds [Redkozemelnye Metally Splavy i Soedineniya]* (Izdatel'stvo Nauk, Moscow, 1973) 355 pp. The cost is 1R, 81K (approximately $2.00 U.S.)

The total of 86 papers, written in Russian (67), English (14) or French (5), cover general properties, magnetic materials, alloys, refractory compounds and miscellaneous applications. RIC will provide free a copy of the table of contents in English (except for the papers published in French). The proceedings may be purchased through a commercial firm dealing with Russian publications.

LETTER

To the Editor:

With reference to the news item "Explain Enigma" which appeared on page 2 of the March 1974 *RIC News* we wish to point out that the anomalous *behaviour* of the Knight shift in $SmSn_3$ and $SmAl_2$ arises due to the admixture of excited (J=7/2) state into ground (J=5/2) state of Sm^{3+} by crystal fields as shown by Malik and Vijayaraghavan [*J. Phys. (Paris)* 32, Cl-1028 (1971) and *Phys. Letters* 34A, 67 (1971)]. The inclusion of sixth degree terms in the crystal potential is only necessary for fitting the experimental results and does not change the features first shown by us. To date the only noncubic Sm compound in which Knight shift behaviour has been found to be anomalous is SmF_3 [Malik, Vijayaraghavan and Bernier, *J. Mag. Resonance* 8, 161 (1972)] and this has also been explained on the basis of mixing of levels by crystal fields of lower symmetry.

Yours sincerely,

R. Vijayaraghavan

Rare Earth Research at Penn State

(Continued from Page 1)

Phase equilibria, crystal chemistry, property correlations, and chemical vapor deposition synthesis studies on rare earth-boride systems are being conducted by the research group directed by K. E. Spear. A major goal of this program is to help develop an understanding of the chemical bonding and properties of these borides through empirical correlations of carefully measured properties, and to relate these observations to the fundamental properties of the elements. An extensive review and analysis of R-B systems has been carried out and is to be published as a book chapter.

Experimental research is directed toward filling in the gaps in phase equilibria and related synthesis data for R-B systems. Three graduate students are conducting their Ph.D. research on projects within this program. T. M. Besmann is studying the chemical vapor deposition of metal borides, an extremely complex kinetic and thermodynamic problem. E. G. Imperato is completing a detailed phase equilibria study of the Er-B system, which includes examining the homogeneity ranges and defect structures of the phases. J. H. Blanks has begun his research on a phase equilibria study of the Gd-B system. Other recently accomplished research includes phase equilibria studies of the Sm-B and Dy-B systems and studies of the fascinating RB_{66} phases. D. W. Petsinger, an undergraduate technician, assists in all of the experimental studies.

Prof. W. B. White heads up research in rare earth-containing chalcogenides including the synthesis and crystal growth of compounds suitable for use in high power laser windows, and infrared and Raman spectra of these compounds. He also has worked on the luminescence of rare earth-activated phosphors in a number of studies over the last ten years. His group consists of Dr. L. Drafall, who is completing a post doctoral project on ternary sulfides, and doctoral candidates P. L. Provenzano and S. I. Boldish.

MEETING

PERMANENT MAGNET WORKSHOP

A workshop on Rare Earth-Cobalt Permanent Magnets will be held Oct. 13-16, 1974, at the University of Dayton. The meeting was set for the week after the 11th Rare Earth Research Conference (Oct. 7-10, 1974) to make it convenient for foreign visitors to attend both.

Topics to be covered, in addition to the Introduction and Preview, are Raw Materials, Magnet Alloys, Magnet Manufacture, Special Topics in Magnet Production, Magnet Properties and Magnetic Processing, and Device Applications. A "satellite" symposium on the general topic Magnetic Crystal Anisotropy and Coercivity of Rare Earth-Transition Metal Intermetallics will be held the day following the close of the formal workshop.

Prospective conferees may obtain additional information from Prof. K. J. Strnat, Magnetics Laboratory, KL-365, School of Engineering, University of Dayton, 300 College Park, Dayton, Ohio 45469, U.S.A.

Rare-Earth Information Center
Energy and Mineral Resources Research Institute
Iowa State University
Ames, Iowa 50010

RARE-EARTH INFORMATION CENTER NEWS

ENERGY AND MINERAL RESOURCES RESEARCH INSTITUTE
IOWA STATE UNIVERSITY / AMES, IOWA

Volume IX | September 1, 1974 | No. 3

RARE EARTHS GROW

Having been in the rare earth field since mid-1952 it has been with interest, excitement and pleasure, and occasionally some misgivings, that I have witnessed the growth of the research activity and industry during these 22 years. I am not writing to cite the landmarks of accomplishments since the 1950's—these will be duly noted upon their anniversary dates in future issues of this newsletter—but rather to look to the future, especially the growth of consumption and uses of rare earth materials.

Since 1967, despite several valleys and peaks, the usage of rare earths has increased by very nearly 20% per year—truly a phenomenal growth rate. With acceptance of rare earth additions to glass (decolorizing) and steels (as a desulfuring agent) this growth rate would be expected to be maintained for the next few years. And with continued research and potential applications such as auto exhaust catalysts and antiknock gasoline additives, an average 20% growth rate for the next decade is not at all inconceivable.

Stopping for a moment to reflect, we quickly realize that after a number of years growing by 20% per annum, even a small quantity will expand to a very large one. In 1973 about 15,000 tons of rare earth oxide equivalent were consumed in the United States alone. Generally it is thought that the remainder of the world consumes an equal amount. The most recent information on rare earth world-wide resources indicated 18.7 millions of tons of oxide deposit have been identified (J. W. Adams and M. H. Staatz, *U.S. Geol. Survey Prof. Paper No. 820*, pp. 547-56, U.S. Government Printing Office, Washington, D.C., 1973). A quick mathematical calculation indicates that in the year 2008 disaster will strike and no longer will there be any rare earths around—except for a few precious vials some scientists had the foresight to hide on the laboratory shelf or in a desk drawer.

Although we do not subscribe to the "Club of Rome" doomsday philosophy, one should realize that the world's supply of rare earths are finite. In reality the "2008 disaster" will never occur in such a sudden manner since supply and demand will cause a slower growth rate in the 1990's. Furthermore, recovery and secondary usage of rare earths will be an important segment of the industry; new sources of rare earths will continue to be discovered and known resources will be better evaluated (from 1970 to 1974 the known resources have increased by 83%). These factors and competition from other materials will push back the day of reckoning well into or beyond the 21st century.

National Academy Elects Margrave

John L. Margrave

Rare Earther John L. Margrave, Rice University, has been elected to the National Academy of Sciences. He was one of 95 Americans newly elected to membership in February of this year. Election to the Academy recognizes distinguished and continuing achievements in original research and is one of the highest honors that can be accorded an American scientist or engineer.

M AND M--ANDM

The proceedings of the 19th Annual Conference on Magnetism and Magnetic Materials, held in Boston, Nov. 13-16, 1973, are now available in a two-volume set as the **AIP Conference Proceedings No. 18, Magnetism and Magnetic Materials**–1973, C. D. Graham, Jr. and J. J. Rhyne, eds. (American Institute of Physics, New York, 1974). The cost is $25.00.

Well over a third of the 300+ papers and abstracts presented deal with rare earth metals, alloys, compounds and amorphous systems. Among the topics discussed are the preparation, investigation and application of bubble devices, optical properties, magnetic properties, critical phenomena, spin waves, theory and applications.

Most of the papers dealt with rare earth garnets for bubble devices and rare earth-cobalt permanent magnets.

MEETING

11TH RE CONFERENCE PROGRAM

The 11th Rare Earth Research Conference committee has rounded up a galaxy of rare earth stars as invited speakers to illuminate the extensive technical sessions planned for the four-day conference to be held Oct. 7-10, 1974, at Traverse City, Michigan.

Astronaut Harrison H. Schmitt, the first scientist-astronaut on the moon, will give the plenary address on the opening day of the conference. His topic, quite naturally, will be Lunar Geology.

Also planned for the opening day will be a special Frank H. Spedding Symposium to honor the founder and first director of the U.S. Atomic Energy Commission's Ames Laboratory. Spedding, one of the foremost of modern rare earth researchers, will conclude the special symposium with a talk entitled Some Remarks on the Rare Earths by a Fifty-Year Student of the Subject.

A complete listing of invited speakers and their topics appears below. The presenters' names are in boldface type.

PLENARY ADDRESS, *Lunar Geology,* Astronaut **Harrison H. Schmitt.**

Electronic Band Structures of the Rare Earth Metals–A Review of Concepts and Results, **H. L. Davis,** Oak Ridge National Laboratory, U.S.A.

Energy Bands, Fermi Surface, and Magnetic Ordering of Rare Earths, **S. H. Liu,** Iowa State University, U.S.A.

Rare Earth Containing Catalysts for Auto Emission Control, **D. W. Johnson,** Bell Laboratories, U.S.A.

Lanthanide Binding Sites on Antibodies and Active Antibody Fragments, **R. A. Dwek, J. A. Knott, A. C. McLaughlin, E. M. Press, N. C. Price, R. Myatt, R. E. Richards, and A. I. White,** University of Oxford, England.

Studies of the Calcium Binding Sites of Porcine and Bovine Trypsin Using Lanthanides as Probes, **J. Reuben, M. Epstein, A. Levitzki,** Weizmann Institute of Science, Israel.

New Developments on the Use of Lanthanide Ions for Structural Probes, **A. V. Xavier,** Instituto Superior Technico, Portugal, and University of Oxford, England.

†Review of Ion-Exchange Technology Used for the Purification of the Individual Rare Earths, **E. J. Wheelwright,** Battelle Pacific Northwest Laboratory, USA.

†Impure Rare Earth Metals, **D. W. Jones and D. A. Hukin,** University of Oxford, England.

†A Part of the Birth and Evolution of Rare Earth Magnetism, **J. J. Rhyne,** Naval Ordnance Laboratory, USA.

†Zeeman Effect for Rare-Earth Ions in Ethylsulfate Crystals, **R. H. Good,** The Pennsylvania State University, USA.

†Some Remarks on the Rare Earths by a Fifty-Year Student of the Subject, **F. H. Spedding,** Ames Laboratory, USAEC, USA.

Uranocene and Related Chemistry, **A. Streitweiser, Jr.,** University of California, USA.

The Structure and Bonding of 4f and 5f π Sandwich Organometallic Compounds, **K. N. Raymond, E. C. Baker, and G. W. Halstead,** University of California, USA.

New Directions in f-Element Compounds: Sigma-Bonded Organometallic Derivatives, **M. Tsutsui, N. Ely and A. Gebala,** Texas A&M University, USA.

Influence of Alloying on the Magnetic Properties of Rare Earth-d Transition Metal Systems, **W E. Wallace,** University of Pittsburgh, USA.

Neutron Crystal Field Spectroscopy in Metallic Rare-Earth Systems, **A. Furrer,** Institut fur Reaktorforschung, Switzerland.

The Rare Earth Lasers, **M. Weber,** Lawrence Livermore Laboratory, University of California, USA.

Spectroscopy of 5f-Systems: Actinides versus Lanthanides, **R. Pappolardo,** GTE Laboratories Incorporated, USA.

Hydrogen in Rare Earth Intermetallics, **K. H. J. Buschow, F. A. Kuijpers, and A. R. Miedema,** Philips Research Laboratories, The Netherlands.

Lanthanide Complexes Derived from Ligands With Non-Oxygen Donor Groups, **T. Moeller,** Arizona State University, USA.

Electronic Structure, Magnetic Exchange and Conductivity in the Magnetic Compounds EuS, GdS and GdP, **G. Guntherodt and P. Wachter,** ETH, Switzerland.

Electronic Phase Transitions in Rare Earth Monochalcogenides Under Pressure and Alloying, **A. Jayaraman,** Bell Laboratories, USA.

Optical Absorption in SmSe and SmTe Under Pressure, **K. Vedam and J. L. Kirk,** The Pennsylvania State University, USA.

Volatile and Organic-Soluble Rare Earth Chelates: From NMR Shift Reagents to Fuel Additives, **R. E. Sievers, J. A. Cunningham, and W. E. Rhine,** ARL-LJ, Aero Space Research Laboratory, Wright Patterson Airforce Base, USA.

NMR Shift Reagents, **R. E. Davis,** University of Texas, USA.

Crystal Chemistry and Chemical Bonding in Ternary Sulfides, **W. B. White,** Pennsylvania State University, USA.

Composes Ln-IIIb-S et Ln-IVb-S, **J. Flahaut, G. Collin, M. Guittard, S. Jaulmes, M. Julien, P. Laruelle, A. Mazurier, D. Messin, and A. Michele,** Laboratoire de Chimie Minerale Structurale, France.

Etude Structurale Des Composes Ternaires Formes Par Les Terres Rares Avec Le Soufre Et Un Second Non Metal, **J. Flahaut, P. Laruelle, C. Dagron, C. Adolphe, J. Etienne, G. Ghemard, O. Loye, N. Rysanek, N. Savigny, and F. Thevet,** Laboratoire de Chimie Minerale Structurale, France.

Crystal Structures and Magnetic Properties of Compounds Type $La_2Fe_2S_5$, **J. Flahaut, F. Besrest, G. Collin and O. Gorochov,** Laboratoire de Chimie Minerale Structurale, associe au CNRS, Universite Rene Descartes, Paris, France, and **R. Plumier,** Centre D;Etudes Nucleaires de Saclay, France.

Magnetoelastic and Related Properties of Rare Earth-Fe_2 Intermetallic Compounds, **A. E. Clark,** Naval Ordnance Laboratory, USA.

Some Aspects of Luminescence and Energy Transfer in Rare Earth Crystals, **J. van der Ziel,** Bell Laboratories, USA.

†Spedding Symposium paper

RIC-DD Acquisitions

RIC-DD-13 Matrix Elements for Many-Electron Atoms. Electrostatic Interaction Energies for Two-Open-Shell Configurations, by J. Karwowski and S. Fraga (1974) 354 pp. (U.S. $35.40) [Airmail Rate C]

RIC Automates Retrieval System

In a continuing effort to improve its service, RIC is changing its information storage and retrieval system. Heretofore a punched card system was used, but with approximately 800 items being added yearly this method proved cumbersome and inefficient. A computer system, developed within the past year with assistance of Ames Laboratory and Iowa State University computer personnel, became operational March 5, 1974. All new articles, reports and books are indexed and retrieved by both author(s) and key word(s). We are also re-indexing all items received by the Center prior to August 1973. It is expected to take about two years to incorporate the entire literature file into the computer system. A typical printout is shown below.

```
Doc. I.D. No. → 973004690
Author(s) → STALINSKI;B          KLETOWSKI;Z          HENKIE;Z
Title → ELECTRICAL RESISTIVITY OF RESN3 SINGLE CRYSTALS (RE = LA, CE
        PR AND ND)
Reference → PHYS. STAT. SOLIDI (A) 19, K165-8 (1973)
Key Words → 1973          LASN3          CESN3          PRSN3
            NDSN3         SINGLE-CRYSTAL NEEL-TEMP      MAG-TRANS-TEMP
            RESISTIVITY   RES-RESISTIVITYT<10           T<298
```

A description of this system can be found in "Operation and Maintenance of the Rare-Earth Information Center's Information Retrieval System (RICIRS)", by J R. Jordan, R. P. Sun, and C. G. Maple. IS-3388 (July 1974). Copies are available free from the Center.

Rare Earths In the News

ARC LAMP

A new, high-efficiency arc lamp which uses a unique combination of cerium, cesium and samarium iodides has been developed by Westinghouse Electric Corp. The new lamp, said by Westinghouse to produce 60% more light per watt of input power than fluorescent lamps of comparable whiteness, has exhibited a luminous efficiency of 130 lumens per watt.

AMORPHOUS SUPERCONDUCTOR

Dr. Pol Duwez, California Institute of Technology, and two of his students, W. L. Johnson and Sui-Joe Poon, have announced the development of an amorphous superconductor made from a gold-lanthanum alloy. The alloy was prepared as a thin film (0.005 mm thick) by splat cooling.

TUBULAR RESISTOR

The French Atomic Energy Commission has announced the development of a doped lanthanum chromite material (called PYROX) for heating resistors or electrodes for use at high temperatures in oxidizing environments. Temperatures up to 1850°C can be attained with low power consumption when the material is used as a tubular resistor. It is also said that a controlled degree of oxidation of the component being treated can be achieved.

Anisotropic Metals On Review

Among the approximately 60 metallic elements, about one half have electrical conductivities which are anisotropic, including 16 of the 17 rare earths. Although research was, for some time, directed primarily at the simpler cubic, isotropic elements, renewed interest in non-cubic structures in the past decade has produced substantial results.

In a recent review [*Adv. Phys.* 23, 315-433 (1974)], C. M. Hurd surveys the isothermal galvanomagnetic properties of the anisotropic metals—electrical resistance, magnetoresistance and Hall effects—with particular emphasis on those elements exhibiting low field intrinsic anisotropy. The heavy rare earths are among the most complicated anisotropic metals, yet their galvanomagnetic properties have been the most thoroughly researched. The rare earther should thus find a wealth of information in this article.

A brief illustrated review of the various non-cubic atomic arrangements and their relationships to observed galvanomagnetic phenomena provides the non-specialist with a basic understanding for experimental purposes. Practical definitions and experimental approaches are outlined for each galvanomagnetic effect.

A guide to the recent literature contains 375 references and covers essentially the last decade, 1964 to 1974, with some earlier authors cited for completeness. Supplementary information is included for each of the metals to help the reader determine the relevance and value of a particular reference.

USEFUL POISON

J. D. Noden reports on a recent study undertaken to develop a burnable poison material suitable for use in a High Temperature Reactor (HTR) with a prismatic core [*Nucl. Eng. Inter.* 18, 641-6 (1973)].

The general requirements for HTR's narrowed the choice of materials to boron carbide and gadolinium oxide. Gadolinium oxide was chosen in the form of a Gd_2O_3/Al_2O_3 ceramic because of its superior irradiation stability.

Analysis of chemical properties revealed an inertness toward graphite and gaseous impurities at high temperatures to the extent that no cladding is necessary. Physical and mechanical studies showed excellent dimensional stability under irradiation with no surface cracking, spalling or powdering. Design form and fabrication methods are also described.

LETTER

To the Editor:

In an article entitled *Explain Enigma* in the March 1974 *RIC News* you state that it is quite likely that an extension of the crystal field methods of S. K. Malik and R. Vijayaraghaven [*Phys. Lett.* 34A, 67 (1971)] and H. W. deWijn, A. M. van Diepen and K. H. J. Buschow [*Phys. Rev.* B7, 524 (1973)] will enable the unusual temperature dependence of the paramagnetic susceptibility of elemental samarium to be understood.

This is not the case.

It has been predicted [A. M. Stewart, *Phys. Rev.* B6, 1985 (1972)] and confirmed by the neutron diffraction experiments of W. C. Koehler and R. M. Moon [*Phys. Rev. Lett.* 29, 1468 (1972)] that effects due to the magnetization of the conduction electrons in samarium are of importance and comparable to those due to crystal fields. Therefore it will be essential to take these effects into account in an analysis of the susceptibility.

Yours Sincerely,
A. M. Stewart
The University of New South Wales
Kensington, N.S.W. Australia

ERRATA

IS-RIC-6, Thermochemistry of the Rare Earths–Parts 1, 2 and 3:

Page 16, line 4: monoclinic SHOULD READ cubic

Page 30: The value for $-\Delta G_f^o$ for Europium Sesquioxide, C-form, cubic (Eu_2O_3) at 900°K which reads 332.378 SHOULD READ 330.038 and at 1000°K 320.652 SHOULD READ 323.252.

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K. A. Gschneidner, Jr. ..... Editor
Bernie Evans, W. H. Smith and Betty Verkade
Staff Writers

Coercivity Not Needed

Highly coercive methods will not be needed to generate interest in a new book entitled **Rare Earth Permanent Magnets**, by E. A. Nesbitt and J. H. Wernick (Academic Press, Inc., New York, 1973) 208 pp., $12.50. This monograph provides good reading for materials scientists, engineers and students interested in permanent magnet research and development.

Elementary aspects of permanent magnetism, rare earth elements, their alloys with iron, copper and cobalt, and magnetic properties of these compounds are discussed in the first three chapters. The preparation and properties of cast permanent magnets (Ch. 4) and permanent magnets based on powders (Ch. 5) are presented. Finally, the relatively new rare earth permanent magnets are compared with established permanent magnet materials. Subject and author indexes are included.

FY 1975 Support

Contributions are being received for Fiscal Year 1975 from RIC's financial supporters, many of them substantially over individual firm's previous year's support. So far 19 firms have sent checks or made their 1975 pledges.

It appears our suggestion that contributors consider increasing their support to RIC by the same rate as their rare earth product volume was not at all unreasonable. Under this contribution formula, our support could be considered a barometer of the rare earth industry in general and we're glad the outlook is so bright for so many of you.

Contributions so far have come from:

American Metallurgical Products Co., U.S.A. (6)*
Atomergic Chemetals Co., U.S.A. (3)
Brown, Boveri & Company, Limited, Switzerland (3)
Companhia Brasileira De Technologia Nuclear Usina Santo Amaro, Brasil (3)
Foote Mineral Company, U.S.A. (3)
Th. Goldschmidt AG, Germany (6)
W. R. Grace & Co., U.S.A. (7)
GTE Laboratories, Inc., U.S.A. (3)
GTE Sylvania, U.S.A. (3)
Kolon Trading Co., Inc., U.S.A. (2)
Leico Industries, Inc., U.S.A. (6)
Lunex Company, U.S.A. (5)
A/S Megon & Co., Norway (6)
Molybdenum Corporation of America, U.S.A. (7)
Reactor Experiments, Inc., U.S.A. (5)
Ronson Metals Corporation, U.S.A. (7)
Treibacher Chemische Werke, Austria (3)
United States Radium Corporation, U.S.A. (5)
Wako Bussan Co., Ltd., Japan (6)

*years in support of RIC including present fiscal year.

Phase Data for RE-Co Magnets

Researchers concerned with the general metallurgical behavior of rare earth-cobalt magnet materials or the properties to be expected of a particular mixed rare earth-cobalt alloy will find a convenient source of information in a recent review by A. E. Ray [*Cobalt*, 13-20 (1974)].

Ten rare earth-cobalt phase equilibria investigations have been reported since 1966 when RCo_5 alloys were first identified as possible permanent magnet materials. From these and 39 additional references, Ray has compiled the phase diagrams of all of the six technologically important rare earths—Y, La through Nd, and Sm.

RE's Shed Light On X-Ray Anomaly

The anomalous line-like structures, which have hindered identification of valence band density states in lanthanum, may be part of the continuum spectrum according to R. J. Liefeld, A. F. Burr and M. B. Chamberlain, *Phys. Rev. A* 9, 316-22 (1974). Examination of a sequence of M-series x-ray spectra for closely spaced electron-excitation energies reveals energy-dependent structures characteristic of a classical scattering resonance. They occur in the vicinity of the M_5 and M_4 inner levels and display intensities which correspond to the statistical weights of these levels.

To explain these phenomena, the authors suggest the existence of an intermediate negative-ion bound state involving an excited $3d$ electron and a captured incident electron initially in bound orbitals around the $3d$ vacancy. Decaying radiatively, the $3d$ electron reverts to its original state and the captured electron occupies a $4f$ orbital above the Fermi level. It is predicted that a similar mechanism should be operative whenever an inner quantum level is being filled, *viz.* the transition metals, lanthanides and actinides. Wave function calculations and an examination of cerium spectra are said to support this interpretation [M. B. Chamberlain, A. F. Burr and R. J. Liefeld, *Phys. Rev. A* 9, 663-7 (1947)].

These observations are relevant to a variety of other spectral studies including appearance-potential and continuum-limit spectroscopies.

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RARE-EARTH INFORMATION CENTER NEWS

ENERGY AND MINERAL RESOURCES RESEARCH INSTITUTE
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Experimentalists Gain on Theorists

The rare earth experimental physicists are slowly closing in on the elusive Fermi surfaces of the *trivalent* rare earth metals. The Fermi surface is important to scientists because it governs the nature of the transport properties of solids, in particular the electrical resistivity, thermal conductivity, Hall effect, magnetic susceptibility, etc. The most recent advance was reported in December by R. C. Young, R. G. Jordan and D. W. Jones [*Phys. Rev. Letters* **31**, 1473-6 (1973)] who measured seven different frequencies in gadolinium metal–three in the basal plane and four along the c-axis. Until now the best that experimentalists were able to do was measure a single frequency in lutetium [J. A. Hoekstra and R. A. Phillips, *Phys. Rev. A* **4**, 4184-6 (1971)].

The first of the Fermi surfaces was calculated by theorists about ten years ago, and subsequently they have been calculated for most of the rare earth metals. The results of Young and co-workers support the Fermi surface calculations in general, but there are some differences in the details. Furthermore, some of the observed low frequencies could not be explained because the band structure calculations had not been carried out in sufficient detail. But now, with some reliable data on hand, the theorists can go back to the computers and try to refine their calculations.

Two months prior to the Young, *et al.* paper, J.-P. Jan [*Phys. Rev. B* 8, 3590-4 (1973)] reported the first de Haas-van Alphen measurements of the Fermi surface of any rare earth intermetallic compound, YZn. In this case, he claims, no theoretical model can satisfactorily explain his observations.

Now it appears that the tortoise has moved ahead of the hare in the race.

The first Fermi surface measurements on any rare earth material were made in 1967 on *divalent* metallic ytterbium [*RIC News* **III** [1] 3 (1968)].

FLUORESCENT STANDARDS

Rare earth-doped glasses are promising standard reference materials for fluorescent spectroscopy according to R. Reisfeld, *J. Research NBS-A. Phys. Chem.* **76A**, 613-35 (1972). Reisfeld studied absorption, excitation and fluorescent spectra, oscillator strength, and quantum efficiency of glasses doped with Gd^{3+}, Tb^{3+}, Eu^{3+}, Sm^{3+}, Tm^{3+}, and Ce^{3+}. Other variables investigated were concentration dependence, fluorescent lifetimes, quenching by surrounding medium, and stability.

Quantum efficiency from the lowest excited fluorescing levels approaches unity for Eu^{3+}, Gd^{3+}, Tb^{3+} and Sm^{3+}. Tm^{3+} fluoresces in some of the same regions as Tb^{3+} although its quantum efficiency is

(Continued on Page 4)

Explosive Explanation

Dr. Fred Holtzberg has offered a different explanation for the explosive behavior of Gd-doped SmS than that proposed by A. Jayaraman *et al.* and reported in *RIC News* **VIII** [4] p. 1. Holtzberg, of IBM's Thomas J. Watson Research Center, attributes the behavior to a phase separation rather than a phase transition.

In Holtzberg's model, both the black-colored phase and the gold-colored phase are initially present. Upon cooling, differential stresses are experienced in the crystal lattice which finally gives way to an explosive phase separation. Gold crystals collected after the explosive transition became black upon cooling and regained the gold color upon heating. Thermal cycling revealed no further deterioration in the crystals.

Holtzberg concludes that the explosion is the consequence of a change in the valence state of Sm, however, the actual mechanism of the reaction is phase separation, he explains. His results were presented at the Magnetism and Magnetic Materials Conference in Boston last November.

CONTRIBUTORS

Contributions have been received from Allied Chemical, Inc., Foote Mineral Co., and GTE Laboratories, Inc., all located in the U.S.A. and contributing for the second time, and from Rhone-Progil, France, a four-time contributor. Center supporters now total 31.

ACS Southwest Region Honors John Margrave


J. L. Margrave

The 1973 American Chemical Society (ACS) Southwest Regional Award, presented annually to an outstanding Houston area chemist, has been won by John L. Margrave. He is dean of advanced studies and research at Rice University, Houston, Tex., U.S.A.

Margrave's research, some involving rare earths, has been concentrated mainly on chemistry under extreme conditions (high and low temperatures and high pressure) and fluorine chemistry.

Rare Earths In the News

A RARE MEMORY

A rare earth ceramic developed by Sandia Laboratories promises to give computer holographic memory units a boost when the image storing device is applied to data processing. The ceramic, a thin, transparent, ferroelectric PLZT plate (7% La with a 65:35 ratio of lead titanate), deforms into thousands of microscopic depressions when light is projected through a photographic negative and a voltage applied to the PLZT. The depressions, some as deep as 1300 Å, vary according to the light intensity.

LASER CRYSTAL

Yttrium vanadate, a new laser crystal host for rare earth laser materials, is undergoing intensive investigation at the newly-formed Center for Laser Studies at the University of Southern California. The material is highly transmissive in the infrared regions (cut-off point is 5μ). It is being considered for optical ranging devices and systems.

Explain Enigma

H. W. de Wijn, A. M. van Diepen and K. H. J. Buschow have explained through a series of three papers the anomalous magnetic behavior of samarium in intermetallic compounds. Ever since the first measurements of the magnetic susceptibility of samarium metal about 17 years ago, scientists have been baffled by the fact that Sm does not follow a Curie-Weiss behavior above its magnetic ordering temperature—the only rare earth metal not to do so.

Although other scientists have thought the crystal field a Sm^{3+} ion sees in a compound is important, de Wijn, van Diepen and Buschow [*Phys. Rev. B* 7, 524-33 (1973)] show it is essential to include in one's calculations 1. the higher energy multiplet level (J = 7/2) in addition to the ground state multiplet (J = 5/2), and 2. sixth-order crystal field potentials in addition

(Continued on Page 3)

STAFF CHANGE


Betty Verkade

RIC is pleased to announce the addition of Ms. Betty Verkade to our staff. Ms. Verkade attended the University of Illinois and Iowa State University where she received her B.S. degree in chemistry. She has taught in both high school and college. She will be working half-time answering information inquiries and working on special reports which are becoming an increasing workload for the Center.

AT NEW SOUTH WALES

K. N. R. Taylor, formerly on the faculty of the University of Durham, England, has been appointed to a Chair in Physics at the University of New South Wales, Australia. Taylor is a co-author of the book, *Physics of Rare Earth Solids.* Also joining him at Sydney is R. G. Curry from Durham.

CEF Conference

A conference on Crystalline Electric Field Effects in Metals and Alloys, with the bulk of papers centered upon the rare earths, will be held in Montreal, Canada, June 26 through 29, 1974, inclusive. Both theoretical and experimental work will be extensively covered.

Invited speakers include Prof. P. Fulde, Institut Max von Laue-Paul Langevin, Germany; Prof. R. Orbach, University of California, U.S.A.; Dr. E. Bucher, Bell Telephone Laboratories, U.S.A.; Prof. H. W. de Wijn, Rijksuniversiteit, Holland; Prof. M. Zuckermann, McGill University, Canada; Prof. W. E. Wallace, University of Pittsburgh, U.S.A.; Dr. H. Heer, Institut fur Reaktorforschung, Switzerland; and Prof. D. Goodings, McMaster University, Canada.

Authors of contributed papers should forward an abstract, 100 words maximum, to the conference organizer before May 1, 1974. The time allowance for contributed papers will be 25 minutes maximum.

Prospective conferees should notify the organizer by March 31, 1974, or as near to that date as possible. The registration fee is $20 Cdn. Contact:

Dr. R. A. Devine
CEF Conference
Departement de Physique
Université de Montréal
D.P. 6128, Montréal 101
Canada

RIC Documents Available

IS-RIC-4 *Rare Earth Metals in Steels,* Nancy Kippenhan, Karl A. Gschneidner, Jr., March 1970.

IS-RIC-5 *Thermochemistry of the Rare Earth Carbides, Nitrides, and Sulfides for Steelmaking,* Karl A. Gschneidner, Jr., Nancy Kippenhan, August 1971.

IS-RIC-6 *Thermochemistry of the Rare Earths, Part 1. Rare Earth Oxides, Part 2. Rare Earth Oxysulfides, Part 3. Rare Earth Compounds with B, Sn, Pb, P, As, Sb, Bi, Cu and Ag,* Karl A. Gschneidner, Jr., Nancy Kippenhan and O. Dale McMasters, August 1973.

Reports listed above are available without charge from the Rare-Earth Information Center, Energy and Mineral Resources Research Institute, Iowa State University, Ames, Iowa 50010 or from Molybdenum Corporation of America, Metallurgical Sales Service Office, No. 4 Gateway Center, Pittsburgh, PA 15222.

RE Abstracts

Multi-Science Publishing Co., Ltd., undertook early in 1973 the publication of an interdisciplinary abstracting journal, *Rare Earth Bulletin,* edited by Dr. R. F. Kelleher, University of Nairobi, Nairobi, Kenya, and issued bimonthly with annual subject and author indices. Subscriptions are available from Multi-Science, The Old Mill, Dorset Place, London E15 1DJ, England at £30 (about $68 U.S.) per year postpaid.

Articles abstracted include not only those from the leading chemistry and physics journals, but also from those devoted to electronics, ceramics and glass, magnetics, crystallography, optics, mineralogy, earth sciences, textiles, nuclear physics, solid-state, metallurgy, mining, and materials science. Abstracts are organized into seven major divisions—Distribution and Extraction, Chemical Properties, Crystallography, Nuclear Properties, Solid State Properties, Mechanical Properties, and Applications.

MEETING

11th RARE EARTH CONFERENCE

The 11th Rare Earth Research Conference committee has established deadlines for those wishing to present papers. Abstracts, sufficiently detailed to permit evaluation, should be sent to Dr. Harry A. Eick, Department of Chemistry, Michigan State University, East Lansing, MI 48824, U.S.A., to reach him no later than April 1, 1974. Authors of accepted papers will be notified by May 1, completed papers are due by July 1.

Sessions are planned in the areas of crystal chemistry, metals and alloys, spectroscopy, intermetallics, magnetism and physics, shift reagents, organometallics, coordination chemistry, solid state science, and catalysis, and a general session.

Pittsburgh Award To Rare Earther

W. E. Wallace

W. E. Wallace, chairman, department of chemistry, University of Pittsburgh, has received the 1973 Pittsburgh Award presented annually by the Pittsburgh Section of the American Chemical Society.

The award recognized Wallace's contributions to chemistry and to the Pittsburgh academic community. He is best known to rare earthers for his work on magnetic properties and heat capacities of rare earth metals and alloys. This has led to a much better understanding of the physics and chemistry of rare earth solids, particularly their crystal fields.

Explain Enigma

(Continued from Page 2)

to the fourth-order ones. This enables them to explain theoretically both the Knight shift and magnetic susceptibility of $SmAl_2$ and $SmSn_3$. Furthermore, they note that in certain crystal fields the orbital angular quantum number, L, and the spin quantum number, S, combine additively (L + S) rather than subtractively (L-S) as other light lanthanides and thus behave as a heavy lanthanide.

In their other papers they explain the change in the easy direction of magnetization in $SmFe_2$ at 175°K [van Diepen, de Wijn and Buschow—*Phys. Rev. B* 8, 1125-9 (1973)] and the reduction in the magnetic moment on the Sm^{3+} ion in several intermetallic compounds [Buschow, van Diepen and de Wijn—*Phys. Rev. B* 8, 5134-8 (1973)]. Although the authors attempted no explanation of the magnetic susceptibility of metallic Sm, it is quite likely that an extension of their method will enable theorists to calculate the correct temperature variation of Sm in the elemental form.

New Laser System

J. Stone and C. A. Burras have reported on the operation of a new Nd-doped laser system, *Appl. Phys. Letters* 23, 388-9 (1973).

Fused silica (SiO_2) is used as a noncrystalline host material because it has a minimum transmission loss in the same wavelength range in which Nd lasing occurs.

The laser system has a clad optical fiber geometry and can be end-pumped for maximum pumping efficiency. Absorbed pump power thresholds of 1-2 mW have been achieved for cores 40 μm in diameter. The laser operates at room temperature.

Fused silica, because of its high melting point, low thermal expansion, strength, favorable transmission characteristics, and ease of fabrication, warrants more investigation as a laser host, say Stone and Burras. They estimate that lasers as short as 1 to 3 cm with diameters ≤ 15 μm could be made provided a suitable pumping device is developed.

RUSSIAN ACQUISITION

The Russian book: *Fizicheskie Svoistva Khalkogenidov Redkozemelnykh Elementov (Physical Properties of Chalcogenides of the Rare Earth Elements)* by A. V. Golubkov, E. V. Goncharova, V. P. Zhuze, G. M. Loginov, V. M. Sergeeva, and I. A. Smirnov (Izdalet'stvo Nauk, Leningrad, 1973) 304 pp., has been added to RIC's collection.

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Staff Writers

End of an Era

Kerr-McGee shut down its rare earth operations Dec. 31, 1973. Economic pressures involved in complying with the Environmental Protection Agency's pollution standards were cited by management as the overriding factor in the decision.

Kerr-McGee, a relative newcomer to the rare earth industry, in its 1970 merger with American Potash and Chemical Corporation (TRONA) inherited a long legacy of pioneering going back to Lindsay Light Co., founded in 1902. Lindsay manufactured incandescent gas mantles with thorium extracted from monazite ores. Although rare earths are 5-20 times more plentiful than thorium in monazite, most of them were discarded prior to World War I. Soon after, new uses were developed for rare earths and Lindsay became a leader in the production of salts and in developing new industrial applications. Over the years the name of the company changed to Lindsay Light and Chemical Co. (1935) and then to Lindsay Chemical Co. (1952) reflecting the changing emphasis in production. In 1955 Lindsay was first to commercially produce highly pure individual salts by ion exchange. Lindsay merged with TRONA in 1958.

We acknowledge with gratitude the active support Lindsay has given RIC for the past several years.

Fluorescent Standards

(Continued from Page 1)

considerably lower. For this reason Tb^{3+} is preferred over Tm^{3+} as a standard reference material.

Reisfeld's investigations suggest that rare earth-doped glasses are particularly well suited as reference standards for compounds having narrow fluorescent emission spectra. For example, Eu^{3+} is an acceptable standard in the range λ = 600-700 nm, Gd^{3+} emits only in the ultraviolet region, Tb^{3+} is useful at λ = 480, 543, 587 and 624 nm, and low concentrations of Sm^{3+} are applicable at λ = 560, 602 and 640 nm.

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INITIATES MISCHMETAL BULLETINS

The Metals Division of Rare Earth Industries, Inc., has begun a series of technical bulletins devoted exclusively to mischmetal applications. The series is entitled RAREARTH 96® (with appropriate subtitles outlining specific applications).

Two bulletins have been issued so far: *Mischmetal in High Strength Low Alloy Steels,* and *Mischmetal in Vacuum Degassed Steel.* They are not numbered so requesters should order them by title.

To order the bulletins now available and to have your name placed on the permanent mailing list for the series, write to:

Rare Earth Industries, Inc.
Metals Division
P.O. Box 365, Route 168
West Pittsburg, PA 16160, U.S.A.

RECORD YEAR FOR R.E. DISCOVERY

In case there is no listing in the *Guinness Book of World Records,* we note that 1879 was a record year for the discovery of rare earth elements. Samarium, holmium, thulium and scandium were isolated that year by L. de Boisbaudran, P. T. Cleve and J. L. Soret (independently), P. T. Cleve and L. F. Nilson, respectively. There is a two-way tie for the second best year between 1843 (terbium and erbium) and 1885 (praseodymium and neodymium).

Rare Earth Use In Steelmaking

Rare earth usage in steelmaking was among the topics presented at the 31st Electric Furnace Conference held at Cincinnati, Ohio, Dec. 5-7, 1973.

Deoxidation, desulfurization, inclusion manipulation, rare earth recovery, and steel toughness and ductility were discussed with respect to rare earth additions in the manufacture of steel. Also, effects of the different methods of rare earth addition were examined.

Current trends in rare earth usage were discussed with a cost/quality emphasis. In Europe, the major innovation has been a switch from the use of rare earth silicides to mischmetal for steelmaking.

Garners Garnets

Although F. F. Y. Wang makes no claim to being comprehensive, he does cover a lot of area in the field of garnets in his recent article "Physical and Chemical Properties of Garnets", *Treatise on Materials Science and Technology* 2, 279-384 (1973).

The preparation and properties (primarily crystal data, phase equilibria, chemical, thermodynamic, magnetic and optical) of simple rare earth and substituted garnets are presented and discussed.

In the article, which contains more than 300 references, Wang attempts to illustrate the suitability of garnets as prototype compounds for materials science research.

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