RARE-EARTH INFORMATION CENTER NEWS

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Giant Magnetostrictions

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

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

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

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

Rare Earths Are Fluorescent Probes

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

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

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

Cresson Award to Van Vleck

Van Vleck

Harvard University's John H. Van Vleck has received one of two Elliot Cresson Medals awarded for 1971 by the Franklin Institute. Established in 1848, the Cresson award is the oldest of the Franklin Institute's awards.

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

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

27 Firms Back RIC

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

Rare Earths In the News

Y_2O_3-AlN COMPOSITE

A dense, high strength, fiber-reinforced product has been produced by K. Komeya and H. Inoue by sintering 25 wt % Y_2O_3 with AlN at 1700°C [*Trans. Brit. Ceram. Soc.* 70, 107-113 (1971)]. The reaction product consisted of $Y_3Al_5O_{12}$, and possibly $Y_4Al_2O_9$, and well-developed, randomly oriented AlN fibers.

SPACE SHUTTLE

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

ORE ANALYZERS

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

HELICOPTER PARTS

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

FREE

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

Ferroelectric Molybdates

Considerable disagreement exists in the literature on the structure of gadolinium molybdate. This question as well as the physical properties and possible uses of $Gd_2(MoO_4)_3$ are considered by L. A. Drobyshev, A. Z. Rabinovich and Yu. N. Venevtsev in their review of rare earth molybdates, *Izv. Akad. Nauk SSSR, Ser. Fiz.* 34, 2528-2540 (1970); Eng. transl., *Bull. Acad. Sci. USSR-Phys. Ser.* 34, 2250-2261 (1970).

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

The coexistence of ferroelectric properties and laser activity in single crystals of $Gd_2(MoO_4)_3$:Nd suggest that this compound could be used to obtain internally modulated laser radiation. The authors also suggest that the rare earth molybdates could find application in light and color gates controlled by low voltages or relatively small mechanical stresses, optical pressure sensors, controlled pyroelectric sensors and memory devices.

Distorted Nuclei

Recent measurements of the $E4$ moments in ^{152}Sm and ^{154}Sm suggest a departure of about 10% from a purely ellipsoidal shape for the nuclei, F. S. Stephens, R. M. Diamond and J. de Boer, *Phys. Rev. Letters* 27, 1151-1154 (1971).

The $E4$ transition moments between the ground state and the 4+ rotational state in the Sm nuclei were determined from Coulomb excitation experiments with 10-12 MeV ^4He projectiles. The $E4$ moment is of interest because it results from the intrinsic shape of the nucleus and can give detailed information about that shape.

The experimental data were subjected to quantum mechanical corrections. The resulting β_4 values for the nuclear charge distribution were about twice those obtained for the nuclear field from α, α' measurements above the Coulomb barrier, and also larger than expected on the basis of present calculations of nuclear shapes. Assuming that the nucleus is a rigid, uniformly-charged rotor, the large $E4$ moment indicates a large hexadecapole deformation.

The authors described the exact meaning of the β_4 values as an open and interesting problem, and indicated that more experiments were necessary.

LETTER

To the Editor:

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

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

10th Rare Earth Research Conference

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

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

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

(Detach)

10TH RARE EARTH RESEARCH CONFERENCE

Carefree, Arizona, U.S.A. April 30-May 3, 1973

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

Plan to attend. ☐ Yes ☐ No Plan to present paper. ☐ Yes ☐ No

(Please type or print)

Special interest area (s). _____

_____

Name _____

Address _____

_____

_____

Previous RE Conference Proceedings

ASM-AEC Symposium on Rare Earths, Chicago, Illinois, November, 1959.
The Rare Earths, F. H. Spedding and A. H. Daane, eds., John Wiley and Sons, Inc., New York (1961). Reprinted and available from R. E. Krieger Publishing Co., Inc., P. O. Box 542, Huntington, NY 11743; $16.50.

First Rare Earth Research Conference, Lake Arrowhead, California, October, 1960
Rare Earth Research, E. V. Kleber, ed., Macmillan Co., 60 Fifth Avenue, New York, NY 10011. Price unknown.

Second Rare Earth Research Conference, Glenwood Springs, Colorado, September 24-27, 1961
Rare Earth Research, J. F. Nachman, C. E. Lundin, eds., Gordon and Breach Science Publishers, Inc., 150 Fifth Avenue, New York, NY 10011. Ref. $24.50/prof. $18.50 (1968-69 price).

Third Rare Earth Research Conference, Clearwater, Florida, April 21-24, 1963
Rare Earth Research II, K. S. Vorres, ed., Gordon and Breach Science Publishers, Inc., 150 Fifth Avenue, New York, NY 10011. Ref. $34.50/prof. $15.60 (1968-69 price).

Fourth Rare Earth Research Conference, Phoenix, Arizona, April 22-25, 1964
Rare Earth Research III, L. Eyring, ed., Gordon and Breach Science Publishers, Inc., 150 Fifth Avenue, New York, NY 10011. Ref. $44.50/prof. $22.50 (1968-69 price).

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

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

$6.00 each book.

Symposium co-sponsored by the Division of Inorganic Chemistry and The Division of Nuclear Chemistry and Technology, 152nd ACS meeting, New York, New York, September 13-14, 1966
Advances in Chemistry Series No. 71 Lanthanide/Actinide Chemistry, P. R. Fields and T. Moeller, symposium chairmen. Available from special issue sales, American Chemical Society, 1155 16th Street N.W. Washington, DC 20036 USA. $11.00.

Proceedings of the 6th Rare Earth Research Conference, Gatlinburg, Tennessee, May 3-5, 1967, CONF-670501. Available from the National Technical Information Service, Springfield, VA 22151, USA. $6.00.

Proceedings of the 7th Rare Earth Research Conference, Coronado, California, October 28-30, 1968, Sessions A-H CONF-681020-(Vol. 1) and Sessions I-M, CONF-681020-(Vol. 2). Available from the National Technical Information Service, Springfield, VA 22151, USA., $6.00 each volume.

French International Rare Earth Conference, May 5-10, 1969, Paris and Grenoble, France
Les Éléments des Terres Rares, Tome I and Tome II, Bureau 3A-Service de Presse, Centre National de la Recherche Scientifique, 15 Quai Anatole France, Paris 7^{e}, France. Tome I-price unknown, Tome II-107.50 F.

Proceedings of the 8th Rare Earth Research Conference, Reno, Nevada, April 19-22, 1970, available from Dr. R. Lindstrom, Reno Metallurgy Research Center, U.S. Bureau of Mines, Reno, NV, 89505, USA, $17.00.

Conference on Rare Earths and Actinides, University of Durham, Durham City, England, July 5-7, 1971
Conference Digest No. 3, Rare Earths and Actinides, Durham 1971, Institute of Physics, London, England (1971). Available from Dawsons of Pall Mall, Cannon House, Folkestone, Kent, England. £5 (except £3.50 for members of the Institute of Physics).

Proceedings of the 9th Rare Earth Research Conference, Blacksburg, Virginia, October 10-14, 1971, available from Dr. Alan Clifford, Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA, $20.00.

REnaissance

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

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

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

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

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Reviews Neutron Activation Analysis

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

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

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

4*f* BONDING

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

The 4*f* concentration in the valence band was estimated to vary from 0.7 of an electron per atom for the light lanthanides (La, Ce, Pr, ...) to 0.1 or less for the heavy lanthanides (. . . Er, Tm, Yb, Lu). In making these calculations, the energies of the electronic configurations of the neutral lanthanide atoms (see accompanying story on Electronic Configurations, p. 6) were essential in determining the fractional number of 4*f* electrons in the valence band. According to the author, this dual electron model explains the crystal structure sequence found in these metals, their melting points and heats of sublimation, and it is the only model which is capable of explaining all three of these properties.

CORROSION

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

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

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

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