RARE-EARTH INFORMATION CENTER NEWS

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ARIZONA STATE UNIVERSITY

Solid State Chemistry Group

The program of research at Arizona State University, Tempe, on the solid state chemistry of the rare-earth oxides is a continuing effort, considering these as a model system with proximate relevance to the general problems of solid state chemistry, particularly in relation to the question of gross nonstoichiometry.

ARIZONA GROUP — Standing from left are Dr. LeRoy Eyring, James O. Sawyer, Volker Scherer, Michael S. Jenkins and Gary R. Weber. Seated from left are Joyce M. Warmkessel, Joseph A. Houg, Rheal P. Turcotte and G. Duane Stone.

Of greatest interest in the present studies are the oxides of the rare-earth elements exhibiting higher oxidation states (Ce, Pr and Tb) which are among the most complex of oxide systems.

The following specific kinds of studies are being conducted:

1. *Tensimetric Studies*

Tensimetric investigations have been productive of detailed information about the ranges of thermodynamic stability of the several phases in the rare-earth oxide systems, as well as giving a wealth of information about the mode of transformation between phases.

2. *Growth of Single Crystals of Rare-Earth Oxides of Intermediate Composition*

Single crystals are necessary for x-ray and neutron diffraction studies leading to complete structural determinations. They are also necessary for definitive kinetic and equilibrium studies as well as diffusion and electrical property measurements.

3. *Heterogeneous Isotopic Exchange of Oxygen*

Material transport in oxides is of interest and has not been appreciably studied for the rare earths. Indirect evidence has led to the conclusion that oxygen transport is very rapid in these oxides and that the metal atoms are relatively

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Rare Earths In the News

STARTS PRODUCTION

Molybdenum Corporation of America has begun production of cerium concentrate at its $225,000 plant at Mountain Pass, Calif. Molycorp also announced the start of production of La_2O_3, Pr_6O_{11} and Nd_2O_3 at its Louviers, Colo. separation plant. The raw materials, which come from Molycorp's Mountain Pass, Calif. plant, will be separated by liquid-liquid ion exchange techniques. Annual production for the three oxides is estimated at 350, 30 and 100 tons, respectively.

BRITISH FIRMS ANNOUNCE MERGER

Two British firms, Thorium, Ltd., and Johnson, Matthey & Co., Ltd., have merged to form a new company, Rare Earth Products, Ltd. The new company brings together Thorium's interest in rare earths in metallic form and the Johnson Matthey interst in rare-earth compounds and metals.

Pm-W METAL CERAMIC

A Pm-W metal ceramic (cermet) is being developed at Douglas Aircraft's Richland, Wash. laboratories as a radioactive heat source for a high temperature power system that will convert heat directly into electrical or mechanical energy. Already the Pm-W cermet has withstood temperatures in excess of 2000°C for more than 1000 hours, Douglas reports.

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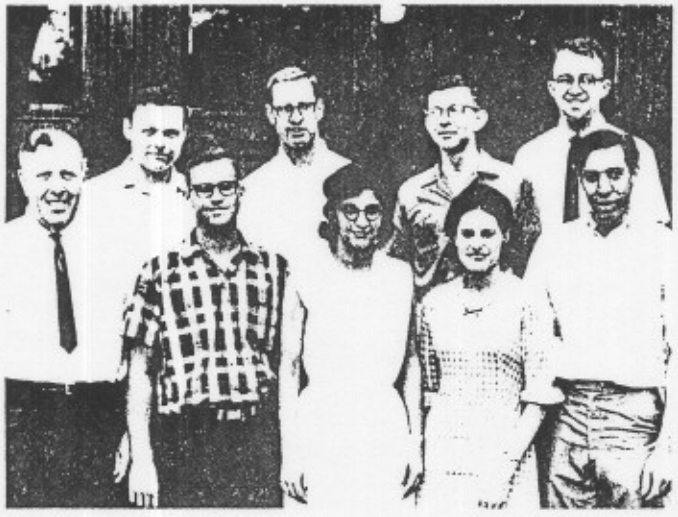
University of Illinois --

Rare-Earth Research Group

Primary emphasis is currently placed upon the coordination chemistry of the rare-earth metal ions. Broadly, complexes containing selected ligands are being studied in terms of their thermodynamic stabilities, bonding, structures, coordination numbers, and applications.



ILLINOIS GROUP — Pictured in the front row from left are Prof. Therald Moeller, John H. Forsberg, Louisa J. Sauro, Marcia L. Bengs and Edward R. Birnbaum. In the back row from left are Donald L. Campbell, Dr. Edmund Benson, Dr. William R. Stagg, and Robert B. Gayhart. Not present for the photo was Robert C. Grandey.

Pure nitrogen donors are being invesigated by E. R. Birnbaum, J. H. Forsberg, and R. C. Grandey, with emphasis upon:

1. nuclear magnetic resonance techniques to evaluate the degree of covalency in bonding;
2. infrared techniques to study metal-nitrogen interactions and determine the extent to which certain normally ionic groups function as ligands;
3. electronic spectral techniques to shed some light on energy relationships;
4. enthalpy titrations;
5. synthesis procedures that eliminate interference by potential oxygen donors; and
6. ultimately, single crystal analysis.

Somewhat parallel studies have enabled L. J. Sauro to establish both oxygen and nitrogen coordination sites in coordinating pyramidone molecules. Fluorescence studies are also in progress by these investigators.

Thermodynamic stability is being studied in terms of the effect of ligand structure and the nature of the rare earth-metal ion. Both formation constants and measured en-

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Far-Infrared Photoconductor

CdF_2 doped with rare-earth ions and baked in cadmium vapor is found to be a good photoconductor according to P. Eisenberger and P. S. Pershaw, *Appl. Phys. Letters 10*, 248 (1967).

They found that lightly doped samples have an absorption band in the far-infrared while more highly doped (0.1% Cd) samples extend well into the visible. Although the spectral response of the system is similar to thermal detectors, the response time of 10^{-6} sec is much faster.

A minimum measurement of D* (a measure of the signal produced by the incident radiation) obtained with 0.3% Y-doped samples was 4×10^9 cm (cps) $^{1/2}W^{-1}$. Higher values of D* are believed possible.

The authors believe that although the far-infrared photoconductivity is due to impurity banding effects, the pure host crystal has a conducting band of its own.

STEELS

A review of the effects of rare-earth additions to steel was written by Anderson and Spreadborough (*Rev. de Metal. 64*, 177-83 [Feb., 1967]). They discussed some of the effects the rare earths have on stainless steels, cast irons and construction steels; the influence of the individual metals on construction steels; and some of the physical properties of the rare-earth metals, oxides, and sulfides as related to steels.

They conclude that the rare earths in general improve the quality and the mechanical properties of steels. However, the exact effects depend quite closely upon the particular steel in question. For some steels the rare-earth additions actually inhibit the effect of other beneficial alloying elements and thus limit the usefulness of the rare-earth additive.

RARE EARTHS IN THE NEWS

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RARE-EARTH LUBRICANTS

Three rare-earth oxides, Y_2O_3, La_2O_3, and CeO_2 are being tested in a program aimed at developing superior lubricants for use in extruding high temperature refractory metals, such as molybdenum, tungsten, niobium and their alloys. The program is being conducted by Thompson Ramo Woolridge which plans lubricity, reactivity, and insulation tests as part of its evaluation scheme for the potential lubricants.

A NEW TELEVISION PHOSPHOR?

A yellow-emitting $Y_3AL_5O_{12} - Ce^{3+}$ phosphor has been reported in *J. Appl. Phys. Letters 11*, 53 (1967). This phosphor fluoresces under cathode-ray (electron) excitation at 550 nm with a decay time of 0.07-0.08 μsec. These properties make the phosphor suitable for flying-spot cathode-ray tubes for color television say the authors of the study, G. Blasse and A. Bril, both of Philips Research Laboratories, Eindhoven, The Netherlands.

AEC Honors F. H. Spedding

Frank H. Spedding, director of the Ames Laboratory of the U.S. Atomic Energy Commission, Ames, Ia., on Sept. 13 received the Atomic Energy Commission Citation for outstanding service in the United States' atomic energy program. The award, a citation and symbolic medallion, was presented to Spedding at the National Academy of Sciences in Washington, D.C.

Commissioner Gerald F. Tape (left), U.S. Atomic Energy Commission, presents the AEC Citation to F. H. Spedding, director of the AEC's Ames Laboratory.

The American Chemical Society 23rd annual Midwest Award was presented to Spedding at ceremonies in St. Louis, Mo. on Nov. 18. He received the Iowa Medal of the ACS in 1948.

Spedding has been the director of the Ames Laboratory since its inception. The Laboratory grew from the Atomic Project he organized and directed at Iowa State University, beginning in 1942.

MEETINGS

DATES CHANGED FOR 7TH RARE EARTH CONFERENCE

Joe Nachman, chairman for the 7th Rare Earth Research Conference has announced that the conference will be held Oct. 28-30, 1968 instead of Oct. 13-16, as previously reported.

RARE-EARTH METAL COATINGS

General Electric announced in late June a new process for preparing special metal surfaces on base metals. This process, called *metalliding*, was developed by N. C. Cook.

Metalliding is accomplished by an electrolytic cell operating between 600° and 1200°C. The metal to be coated is the cathode and the coating metal is the anode. Molten fluoride salts not only serve as the electrolyte, but also clean the metal surfaces by dissolving oxide coatings on the cathode and anode. Because of the high temperatures involved, the anode metal diffuses into the surface of the cathode (base) metal.

A number of rare-earth metals, including scandium and yttrium, have been used as the anode metal to date. One example noted by Cook was a nickel base metal which was first metallided with scandium and then with gadolinium, giving a multiply coated nickel specimen.

In the case of rare-earth metals, according to Cook, the metalliding process is the only practical way to coat other metals with rare-earth metals. In the past electroplating and vapor deposition techniques of the rare-earth metals have met with limited success.

ELECTROMAGNETS

The high magnetic moments of the heavy lanthanide metals, especially Dy and Ho, have been known for many years. And just as with the weather, many people have talked about replacing Fe with Dy or Ho as pole pieces of electromagnets, but until just recently no one to our knowledge has done anything about it. P. Bonjour and A. Septier, *Compt. rend. 264B*, 747 (1967), have described such a magnet using superconducting excitation coils.

The Dy and Ho electromagnets were used as low bulk magnetic lenses for focusing high-energy

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Reports, Brochures, Booklets

PROGRESS ON RARE EARTHS

Another new collection of papers by rare-earth researchers from many countries brings together much up-to-date information. The book, *Progress in the Science and Technology of the Rare Earths, Vol. 2*, L. Eyring, ed., (Pergamon Press, Inc., New York, 1966) 366 pp., reviews progress in areas of rare-earth research and technology since 1960. The price of the book is $15.00.

Included are discussions on thermodynamic and magnetic properties of rare earths; structural and solid state chemistry; properties of rare-earth halides, chalcogenides and pnictides; methods of preparing rare earths; exchange couplings and rare-earth metal complexes; and uses and applications.

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Pa. Wollan was cited for "his early work in developing the equipment and techniques for study in neutron diffraction, and for his many investigations which resulted in the discovery of the magnetic structure of solids, especially the rare-earth metals."

Earlier Wollan was honored for his achievements in the field of neutron diffraction at the Fourth International Congress on Magnetism held in Boston, Mass., Sept. 11-15.

Radioactive Energy Sources

Radioisotopes are one possible answer to the problem of supplying power and heat to small manned research stations in Anarctica, according to R. M. Rodden, *Nuclear Applications* 3, 226 (1967). Two rare earths, ^{144}Ce and ^{147}Pm, are being considered along with five other isotopes. Relative costs and advantages were compared among these and the presently-used hydrocarbon fuels. For a 10 kw electrical power source, ^{144}Ce has a high initial cost plus a one year operation cost estimated at $272,000, whereas fossil-fuel costs are about $66,000. Although the ^{144}Ce source requires semi-annual replacement, after 5 years the costs are equal.

Studies show that radioisotopes are capable of providing power in the low kilowatt range, and waste heat from energy conversion processes would be adequate for six men in temperatures as low as −130°C (−200°F).

For inaccessible locations such as Anarctica, radioactive fuels would do away with the hazardous delivery of bulk fossil fuels and would be economically competitive.

[reaction couples: Nd_2O_3(A-type)-O_2, Sm_2O_3(B-type)-O_2, and (C-type)-O_2 as well as in the intermediate oxide phases.

4. *High Temperature X-ray Diffraction Studies*

Concomitant with the need for tensimetric studies of the regions of hysteresis and pseudo-phase formation in the higher oxides of the rare earths is the need for structural data. These regions must be studied at temperature eliminating the uncertainties of quenching by using high temperature x-ray diffraction.

It is very desirable to develop the techniques so that the subtle changes revealed by careful pressure - composition - temperature measurements can be observed and related by x-ray if possible. It will be necessary to develop the technique beyond its present state to accomplish this.

5. *Spectra of Metal Atoms in Oxides*

At present the exact positions of the oxygen atoms in oxide structures are in some doubt because of the relatively small scattering power of oxygen compared to the heavy metal atoms. A study of the optical spectra of atoms suffering transitions within the $4f^n$ ground

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thalpy changes are being evaluated via computer processing of experimental data.

Ligands under study are chosen for their abilty to impart high coordination numbers to the cations and for their ability to bond through a single type of donor atom. D. L. Campbell and R. B. Gayhart are carrying out these studies.

M. L. Bengs has begun the compilation of a punch-card file which, when completed, will include in an accessible fashion the available data on rare-earth metal complexes of all types.

During the past year, Drs. E. Benson and W. R. Stagg, both of whom carried out doctoral studies with rare-earth metal complexes, have provided advice and counsel. Drs. Benson and Stagg have pursued their own postdoctoral studies in the sulfur-nitrogen and phosphorus-nitrogen areas.

ELECTROMAGNETS

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electrons (1-5 MeV) with focal distances less than 10 mm. Fields as high as 43kG for a 2mm gap were obtained from Dy pole pieces. Construction of the magnet was also described.

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