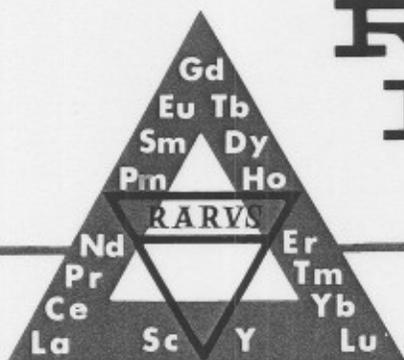


# RARE-EARTH INFORMATION CENTER NEWS



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

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March 1, 1984

No. 1

## GMELIN HANDBOOKS

Volumes D2 (1982) and D3 (1981) are the latest two volumes of *Gmelin Handbooks* from system number 39 to be reviewed in the *RIC News*. With these two we have now reviewed the 23 available volumes. The prices of volumes D2 (352 pages) and D3 (324 pages) are DM933 (~U.S.\$350) and DM793 (~U.S.\$300), respectively. They are both published in English. Information about the *Gmelin Handbooks* and addresses of their dealers may be obtained from Springer-Verlag, 4005-Marketing Gmelin, Heidelberger Platz 3, D-1000 Berlin, West Germany.

### O and N Donors

Volume D2 continues the discussion of complexes containing ligands with both oxygen and nitrogen donor sites begun in D1 [*RIC News*, XVIII, No. 4, 1 (1983)]. The donor terminology is primarily for classification and does not mean that the ligands are actually coordinated through both the oxygen and nitrogen sites. Many of the complexes are important in the analysis and separation of the rare earths.

Chapters 1 and 2 deal with complexes derived from aminoalcohols, aminophenols, and hydroxy compounds of pyridine or quinoline with most of chapter 2 devoted to 8-hydroxyquinoline and its derivatives. Formation constants for many of the complexes are presented.

Schiff base complexes derived from ligands obtained by reaction of aldehydes and ketones with ammonia, amines, or hydrazines are described in chapter 3. Bonding occurs with the nitrogen atom of the azomethine group as well as with other functional groups in the ligand, such as the hydroxy, carboxy, or amino groups.

Azo complexes, many being used in

## Rare Earthers

### Ronson General Manager

Wales "Bud" Otis has been appointed vice president and general manager of Ronson Metals Corporation, Newark, New Jersey. Bud will fill the position recently made vacant by the retirement of Is Hirschhorn.



Bud Otis has been with Ronson for 24 years. In recent years he has been vice president and director of marketing and during the past year, assistant general manager. RIC wishes to congratulate Bud for his promotion and wish him every success in his new position.

### Congratulations!

Dr. Leopoldo M. Falicov, University of California, Berkeley was among those elected to the National Academy of Sciences in 1983. He has been active in the study of the mixed or intermediate valences of rare earth compounds and alloys.

the quantitative analysis of rare earth ions in solution, are described in chapter 4. Complexes with oximes and nitroso compounds, also used for analytical purposes, are described in chapter 5. Limited data suggest that the oxime group is coordinated through the nitrogen atom and that the nitroso group bonds through the oxygen atom.

Chapter 6 deals with the preparation and properties of complexes with N-oxides. The solids have been studied by x-ray diffraction and fluorescence techniques. These complexes are coordinated through the neutral oxygen donor site and show high co-

(Continued on page 2)

## Medical Applications

Since most of our readers are not connected with the medical field, some papers that deal with rare earth medical applications might be of interest. This is not meant to be a review but only the presentation of some recent ideas on these applications.

M. D. Graham and P. R. Selvin have developed a new method for magnetic separation of cells. The use of erbium and dysprosium with whole blood as the sample has shown single-pass magnetic separation efficiencies much higher than those attainable with paramagnetic erythrocytic hemoglobin, e.g. 90 percent versus 37 percent at 0.3 Tesla. According to the authors, the method is not technically demanding and promises to provide a flexible and general technique for cell separations. The paper was published in *IEEE Transactions on Magnetics*, MAG-18, 1523-5 (1982).

A review of thermoluminescence dosimetry (TLD) generally recognized as one of the most versatile techniques for the quantitative measurement of x, gamma, or beta radiations, appeared in *Radiation Protection Dosimetry*, 1, No 3, 153-67 (1981). A. S. Pradhan reviewed the developments in TLD, the importance of the method, and the characteristics of some commercially available systems and their associated problems. The usefulness of  $\text{CaSO}_4:\text{Dy}$  detectors for dose measurement of x and gamma rays in medicine is also discussed.

S. E. Seltzer, *et al.*, of the Harvard Medical School have shown that rare earth oxides can be used as particulate contrast agents which are especially well suited for use with computed tomography (CT). Their goal was to find extremely radiopa-

(Continued on page 4)

## Gmelin Handbooks

(Continued from page 1)

ordination numbers and sometimes high site symmetries.

Complexes with amides and hydrazides of carboxylic acids, urea, and related neutral ligands and complexes with anionic donors, such as the conjugate bases of hydroxamic acids, are reviewed together in chapter 7. Chapter 8 deals with complexes with oxo compounds of N-heterocycles, including cyclic amides and imides, cyclic ureas, and pyrazalones. Included is an extensive treatment of antipyrine derivatives. The majority of complexes in these two chapters coordinate through the oxygen sites.

The remaining N- and O-donors, including the important class of polyoxazamacrocyclic ligands, are covered in the last chapter. Coordination through both the oxygen and nitrogen donor sites is demonstrated for the "(2.2.2)" cryptate complexes by single crystal x-ray analysis.

A formula index at the end of this volume as well as **D1** and **D3** lists all ligands and their empirical molecular formulas.

### Oxygen Donors

Volume **D3** of the *Gmelin Handbooks* is concerned with complexes with oxygen donor sites through which coordination or bonding takes place.

Chapter 1 deals with the simplest complexes, i.e. those derived from water. Cross references are made to hydrates of rare earth salts described in volumes of the **B** and **C** series. Coordination numbers of trivalent rare earth ions toward water molecules in aqueous solution are discussed in terms of interpretations of physical data.

The next three chapters deal with complexes derived from alcohols and alcoholates, aromatic hydroxy compounds, and aldehydes and mono-ketones, respectively. Tetravalent cerium complexes, when known, are described after the trivalent rare earth complexes.

Complexes with 1,3-diketones and other polyketones are described in chapter 5. Laser action in rare earth diketonates, discovered in 1963, led to the investigation of their fluorescence spectra and resulted in the isolation and characterization of the first eight-coordinate rare earth complexes. The luminescence of these

(Continued in next column)

## AB<sub>2</sub> COMPOUNDS

The behavior of AB<sub>2</sub>-type compounds at high pressures and temperatures has been reviewed by Leo Merrill. This review is the third in a series, the earlier ones by J. F. Cannon (1974) and L. Merrill (1977) dealt with the elements and AB-type compounds, respectively. The most recent review follows a similar format and emphasizes thermodynamic parameters of the solid state equilibrium phase boundaries and melting curves. Crystallographic data are tabulated for most of the high pressure phases discussed. This paper includes information on 168 AB<sub>2</sub>-type compounds and some 332 separate phases, and includes a bibliography with 290 entries. Fifty-five of these compounds involve a rare earth as the A atom. The compounds include rare earth antimonides, carbides, sulfides, selenides and tellurides, and intermetallic compounds with cobalt, iron, ruthenium, and osmium. The review was published in *J. Phys. Chem. Ref. Data*, **11**, 1005-64 (1982). It can be purchased as Reprint No. 208 for U.S.\$8.00 from the American Chemical Society, 1155 16th Street N.W., Washington, D.C. 20036, U.S.A.

(Continued from previous column)

compounds is reviewed as an introduction to the chapter. Since 1969, several hundred publications have been published on the ability of certain tris(diketonato) chelates to act as NMR shift reagents. Since these applications are the subject of several reviews, the sections on shift reagent adducts deal mainly with their preparation, characterization and physicochemical properties. The use of volatile, thermally stable tris(dipivaloylmethanato) and tris(heptafluorodimethyloctanedionato) chelates for gas chromatographic separation of the rare earths is discussed. The chapter closes with a section on such things as squaric, croconic and rhodizonic acids.

The solution chemistry of complexes with quinones and triphenylmethane dyes is the main emphasis of chapter 6. This includes the use of triphenylmethane dyes as reagents for the quantitative determination of rare earth ions.

Chapter 7 covers complexes with ethers and O-heterocycles, including

(Continued on page 4)

## Silicon Nitride

Alpha and beta silicon nitride (Si<sub>3</sub>N<sub>4</sub>) is an interesting material described by K. H. Jack, [*Metals Technology*, **9**, 297-301 (July 1982)] as having high strength and hardness, good wear resistance, thermal stability to temperature greater than 2,000 K, oxidation resistance, and excellent shock resistance. The only trouble is that its production is expensive and limited to simple shapes that can be ground only with diamond powders. In an attempt to make a more usable material with some of the same properties, oxide additions to Si<sub>3</sub>N<sub>4</sub> have been studied. Two research groups, one in England and one in Japan, discovered that Al<sub>2</sub>O<sub>3</sub> had nearly the same crystal structure and that Al<sup>3+</sup> could replace Si<sup>4+</sup> as long as valence compensation is made by replacing N<sup>3-</sup> with O<sup>2-</sup>. This was named Sialon from the 4 main ingredients Si-Al-O-N. Since its discovery about 10 years ago, researchers have been adding other compounds to it to modify its properties.

Mixed aluminum oxide and silicon nitride powders, corresponding to sialon compositions, produce larger volumes of lower viscosity liquids with additives such as magnesia and yttria. This allows the β' form to be sintered to theoretical density without the application of pressure. After densification with yttria, the mixture if cooled rapidly forms β' sialon with a grain boundary of Y-Si-Al-O-N glass. Heat treatment at about 1670 K, or controlled cooling of the original mixture, causes the matrix and the grain boundary glass to react to give a slightly changed β' composition and intergranular crystalline yttrium-aluminum garnet (YAG). Because the grain boundary phase is an oxide, the product shows excellent oxidation resistance and contains negligible amounts of glass, so, according to the author, it has good high temperature creep properties. It is said to be the strongest ceramic found so far. By changing powder composition and heat treatment the final mechanical and physical properties may be modified to suit particular applications. Cutting tools formed from a glassy version are much better than those made from hardmetal or alumina. The rate of tool wear actually decreases with an

(Continued on page 4)

## RE's in the News Magnetic Alloy

A metallic glass alloy of high magnetic energy storage capacity that can be used as lightweight permanent magnets has been developed by scientists at General Motors' Technical Center in Warren, Michigan. The amorphous Nd-B-Fe alloy has a magnetic energy storage capacity of 30 million gauss-oersteds compared to conventional ferrite magnets 4 million gauss-oersteds. John Croat, who along with Jan Herbst, Robert Lee and Frederick Pinkerton developed the new magnetic material, described the alloy and its properties at the Pittsburgh Conference on Magnetism and Magnetic Materials. The magnets first use will be in cranking motors for auto starting systems at GM's Remy Division.

### Production Startup

Ronson Metals Corporation, Newark, New Jersey, has announced the start of production of neodymium for the developing neodymium-iron magnet market. Neodymium-iron magnets can be used in motors, meters, computers, audio and video equipment and other devices where reduction in size and weight is advantageous. The magnet's large energy-product makes such weight and size reductions possible. Ronson Metals' production of neodymium is an outgrowth of its long experience in making other rare earth metal products.

(Continued in next column)

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K. A. Gschneidner, Jr. . . . Editor  
Jennings Capellen . . . Staff Writer

(Continued from previous column)

## It's Blue

A nationwide advertising campaign has been launched by General Electric to promote their new Neo-Vision<sup>®</sup> system television picture tube. The new blue picture tube employs a rare earth element (neodymium) as an integral part of the glass. It selectively filters out unwanted light that can fade images on ordinary picture tubes, according to General Electric.

### New Ownership

ERGENICS, Inc. has reorganized as a private corporation, independent of its former parent company, INCO, Ltd. The change in ownership was the result of an employee buy-out of the ERGENICS technology, patents and equipment from INCO. The new company, located in Wyckoff, New Jersey, is active in the area of commercial application of metal hydride technology, including LaNi<sub>5</sub> based materials. The officers of ERGENICS are E. L. Huston (President and General Manager), G. D. Sandrock (V.P. and Technical Director), M. J. Rosso, Jr. (Marketing and Manufacturing Director) and P. M. Golben (Engineering Director).

## Russian Acquisitions

The RIC has recently acquired the Russian book *Splavy Redkikh Metallov s Osobymi Fizicheskimi Svoistvami. Redkozemelnye i Blagorodnye Metally* [Alloys of Rare Metals with Special Physical Properties, Rare Earth and Noble Metals]. The 224 page book is edited by E. M. Savitskii, V. F. Terekhova, and I. A. Markova and published in 1983 by Izdatelstvo Nauka, Moscow. The book deals with binary and ternary alloys of the rare earths with special emphasis on the physical and thermodynamic properties of the alloys and intermetallic compounds.

The RIC has also received number 18 of *Redkozemelnye Poluprovodniki. Ukazatel Otechestvennoi i Inostranoi Literatury* [Rare Earth Semiconductors. Index of Russian and Foreign Literature] edited by V. P. Zhuze. The bibliography was published in 1983 by Fiziko-Tekhnicheskii Institut im A. F. Ioffe, Akademii Nauk SSSR, Leningrad. The eighteenth bibliography has 588 citations

(Continued on page 4)

## 7th REPM Workshop

The *Proceedings of the Seventh International Workshop on Rare Earth-Cobalt Permanent Magnets and Their Applications* sponsored and organized by the Chinese Society of Rare Earths are available to the public. The workshop was held in Beijing, People's Republic of China on September 16-18, 1983. The proceedings contain 558 pages and were edited by Pan Xiaoshuo, Ho Wenwang, and Yu Chengzhou. They were published in 1983 by China Academic Publishers from camera-ready copies and distributed at the meeting.

Among the session subject headings are electro-mechanical applications, medical applications, magneto-mechanical devices and electronic applications, structure and magnetic properties, anisotropy and coercivity, measurement methods and standards, and new materials and processes. General Chairman Karl Strnat noted the strong representation of magneto-biological and medical research papers. He stated that there is clearly more interest in Asia than in the occident in this area of application. The proceedings should help scientists active in magnet research to better understand the possibilities and problems associated with rare earth permanent magnets.

The proceedings may be ordered from two sources. Copies are available from Export Department, China National Publications, Import and Export Corporation, 137 Chaonei Dajie, P.O. Box 88, Beijing, People's Republic of China. The payment should accompany actual order and is U.S. \$39.00 (surface mail), \$45.00 (airmail to countries in Asia), and \$50.00 (airmail to countries outside Asia). Readers in the western hemisphere may order their copies for U.S. \$40.00 (plus postage) from Dr. K. Strnat, University of Dayton, Electrical Engineering/Magnetics, KL-365, Dayton, Ohio 45469, U.S.A. Dr. Strnat should also be contacted regarding the Eighth Workshop and Fourth International Symposium on Magnetic Anisotropy and Coercivity in RE-Transition Metal Alloys. The combined workshop and symposium are to be held May 6-9, 1985 in Dayton, Ohio following the 1985 Inter-mag Conference, which is being held April 28 to May 2, 1985 in St. Paul, Minnesota, U.S.A.

### Medical Applications

(Continued from page 1)

que compounds with highly selective biodistribution to the normal liver. Suspensions of cerium, gadolinium and dysprosium oxide particles were compared to standard iodide compounds. One hour after an intravenous dose of 0.4 grams, at least 90 percent of the oxide was present in the liver, spleen and bone marrow of the nine rabbits used in the experiment. Histological examination of the liver confirmed particle localization in the reticuloendothelial systems. The oxides produced greater and longer opacification of normal livers and larger liver-to-tumor differences in rabbits with hepatic tumors than the standard, iodinated agents. Lesions as small as 5 mm were visible with CT. Future studies will be concerned with possible toxicological effects and long term retention of the oxides. For more information see *J. Computer Assisted Tomography*, 5, No. 3, 370-4 (1981).

Materials used as scintillation detectors for positron CT must have high atomic numbers and short decay constants. K. Takagi and T. Fukazawa [*Appl. Phys. Lett.*, 42, 43-5 (1983)] discuss the characteristics of a cerium-activated  $Gd_2SiO_5$  single crystal scintillator and compare it with  $Bi_4Ge_3O_{12}$ , one of the normally used scintillators. The light output was 1.3 times larger and the decay constant was 5 times smaller than those of  $Bi_4Ge_3O_{12}$ .

Rare earth phosphors have been used as phosphors for x-ray screens for some time (since 1970). One of the newest applications of gadolinium oxysulfide intensifying screens is discussed by A. E. Bradeur, *et al.* of the St. Louis University School of Medicine. By judicious use of the right film to go with the intensifying screen and a professional judgment of the level of detail required, exposure to x-rays can be cut by up to 6 times. The results of 5,806 radiograph examinations were evaluated and reported in *American Journal of Radiology*, 136, 755-8 (1981).

### Gmelin Handbooks

(Continued from page 2)

crown ethers, derivatives of coumarin, hydroxyflavones, and hemein. While emphasis is on preparation, data on crystal and molecular structures and solution chemistry are included when available.

## \*CONTRIBUTORS\*

The third quarter of our fiscal year is usually slow and this year is no exception. Only 5 companies renewed their support which brings the number for the year to 27, which compares to 30 during the same period last year. The 5 companies who contributed to our financial health this quarter are listed below with the number of years the company has supported the Center given in parentheses.

Eastman Kodak Company, U.S.A. (7)  
Mitsubishi Chemical Industries,  
Ltd., Japan (10)

Nissho-Iwai American Corporation,  
U.S.A. (3)

Research Chemicals, U.S.A. (16)

U.S.R. Optonix, Inc., U.S.A. (14)

### HOT MAGNETS

*The Physics of Actinide Compounds*, written by P. Erdős and J. M. Robinson, is a plenary review of the theoretical basis of and experimental research on the physical properties of actinide compounds. Emphasis is placed by the authors on low temperature magnetic properties, highlighted by the first-order phase transitions occurring in a number of actinide compounds. Over 120 diagrams and 20 tables make this review a useful reference work. Scientists working with the rare earths or with the actinides can profit by a comparison of their electronic and magnetic properties. Several such comparisons are made in the book, especially on the subject of valence fluctuations. The 226 page book was published in 1983 and is available for U.S.\$39.50 from Plenum Publishing Corporation, 233 Spring Street, New York, N.Y. 10013 U.S.A.

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## Michell J. Sienko

Michell (Mike) Sienko passed away December 4, 1983 after a brief illness. He was 60 years old and had been a professor at Cornell University, Ithaca, New York, U.S.A., for more than 30 years. He was co-founder and editor of the *Journal of Solid State Chemistry* and had published more than 100 articles on his research. Mike's early research in the rare earth field was on magnetic interactions in the rare earth hexaborides. More recent work involved ternary rare earth-transition metal borides, especially  $RM_2B_4$  and the Chevrel phases—rare earth molybdenum chalcogenides. He was interested in magnetic and electrical transport properties, nonstoichiometry, superconductivity, and layered compounds. Among his awards were the Clark Distinguished Teaching Award in Arts and Science from Cornell University in 1981 and the 1983 American Chemical Society's Award for Excellence in Chemical Education.

### Silicon Nitride

(Continued from page 2)

increase in cutting speed. Rolls-Royce is said to have reduced from 22 to 5 weeks the lead time for machining their RB211 aeroengine turbine discs. Other applications under consideration include metal tube and wire drawing dies, ball and journal bearings, welding shields and nozzles, and many others.

### Russian Acquisitions

(Continued from page 3)

in their original language. Foreign references have a Russian translation while Russian references have an English translation. The bibliography has both an English and Russian Table of Contents and Author Index.