

RARE-EARTH INFORMATION CENTER NEWS

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IOWA STATE UNIVERSITY / AMES, IOWA

Volume VIII

March 1, 1973

No. 1



HEBREW UNIVERSITY Rare Earth Group. Pictured in the front row from left are A. Langer, I. J. Brandstadter, B. Barnett, E. Greenberg, N. Lieblich, L. Boehm, R. Reisfeld, M. BenAruch and D. Jacobson. In the

back row from left are D. Lubelchick, S. Kraus, A. Bornstein, H. Mack, J. Hormodaly, S. Nathanson and Y. Eckstein.

RE Optical Properties Studied—

Hebrew University Combines R & D

Rare earth studies at the Hebrew University in Jerusalem, under the direction of Dr. R. Reisfeld, are concerned mainly with the optical properties of the rare earths. The group, part of the Department of Inorganic and Analytical Chemistry at the University, carries out both basic research and developmental programs.

Ligand field theory, used for the interpretation of covalent bonding between rare earth ions and oxygen ions in glasses, can be extended as a general model of bonding in glass. Calculations are made of radiative and nonradiative electronic transition probabilities of rare earths in glasses and other media, and the influence of the host matrix on these transitions is studied. These studies are now being extended to systems of biological importance such as ATP (adenosine triphosphate).

The microstructures of glasses are investigated by defining the site symmetries from the number of lines in the emission or absorption spectra into which the free ion levels of the rare earths are split. Crystal field parameters are also deduced from the oscillator strengths of the $f-f$ transitions of the rare earths in glasses. The luminescences of the rare earth-doped glasses are studied by means of cathode ray excitation. The practical application of this investigation is the possible study of surface phenomena in glasses and the preparation of glass phosphors for color television and communication purposes.

(Continued on page 3)

Rare Earths In the News

AMORPHOUS BUBBLES

IBM scientists have reported the first observance of magnetic bubbles in amorphous films of gadolinium-cobalt and gadolinium-iron. These films are easier to make and less expensive than the crystalline materials previously developed for use in computer circuits, according to IBM.

RE's COMBAT NO_x

In preliminary tests, Bell Laboratories scientists have found that lanthanum lead manganite reduces most or all of the nitrogen oxides present in auto exhaust to nitrogen. Bell claims that the RE material is

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Rare Earths in the News
(Continued from page 1)

as effective at high temperatures as any other available catalyst and is even more effective at low temperatures. This is the same compound that last summer was reported to convert CO to CO₂, see *RIC News*, VII [3] 3 (1972).

DIAGNOSTIC LOCATOR

Ytterbium-169 has been found to be a highly effective cancer seeker when injected into the veins of cancer patients, according to Prof. K. Hisata of Kanazawa University in Japan. The isotope collects only in cancerous tissues where it can be detected by the characteristic gamma rays it emits, says Prof. Hisata. Moreover, the technique is effective in pursuing the spread of cancer.

RE X-RAY PHOSPHOR

Dr. V. A. Fassel and A. P. D'Silva at the AEC's Ames Laboratory have developed an yttrium-gadolinium phosphate phosphor containing a small amount of terbium which gives intense violet-blue fluorescence under x-ray irradiation. Terbium shifts the spectral emission into the blue region that matches the x-ray image response characteristic of blue-sensitive x-ray film used widely in industry and medicine. By substituting gadolinium-157 for natural gadolinium, the phosphor's neutron absorption characteristics are enhanced, permitting the phosphor to be used in an intensifier screen for neutron radiography.

Contributors at All Time High

With the addition of ten more contributors since the last issue of *RIC News* went to press, the total number of firms supporting the Center now stands at a record high of 38. We at RIC are extremely gratified that our efforts are so enthusiastically supported by the industry. Our contributors, too, can take justifiable pride in their efforts to provide the services their funding makes possible for the entire rare earth community.

Listed below are the ten additional contributors for Fiscal Year 1973; the number in parenthesis behind each contributor's name indicates the total number of years that firm has helped fund RIC.

- British Flint & Cerium Manufacturers, England (1)
- Companhia Industrial Fluminense, Brazil (1)
- Foote Mineral Co., U.S.A. (1)
- General Electric Co., Magnetic Materials Product Section, U.S.A. (1)
- General Electric Co., Research and Development Center, U.S.A. (1)
- GTE Laboratories, Inc., U.S.A. (1)
- Lim Fong Seng Sdn. Bhd., Malaysia (2)
- Nippon Yttrium Co., Ltd., Japan (3)
- Wako Bussan Co., Ltd., Japan (4)
- Westinghouse Electric Corp., U.S.A. (1)

Magnetism School

Up-dated papers on the magnetism of rare earth materials originally presented at the Third Simon Fraser University Summer School on Solid State Physics held at Alta Lake, B. C., Canada, Aug. 24 - Sept. 5, 1970, have been published in *CRC Crit. Rev. Solid State Sci.* 3, [1] and [2] 83-241 (1972).

B. R. Cooper, [1] pp. 83-129, reviews those aspects of rare earth magnetism in which the crystal lattice affects the nature of the magnetic behavior through large orbital contributions. Topics covered include magnetic ordering, crystal-field theory, lattice distortion effects and transitions between magnetic structures in the heavy rare earths. Cooper also treats the theoretical and experimental behavior of induced magnetic systems, such as dhcp Pr, fcc Pr and Pr-Th alloys, in which the relative strength of the crystal field and exchange interactions determine whether any magnetic ordering occurs.

The theory of magnetic semiconductors, their optical properties and *s-f* interactions are discussed by T. Kasuya, [2] pp. 131-165. His review includes an explanation of one-electron energy spectra and of the collective energy spectrum in magnetic semiconductors. The anomalous red shift in the magnetic exciton in EuF₂ and europium chalcogenides and the effect of the *s-f* interaction on the transport properties in magnetic semiconductors are also presented.

A. R. Mackintosh, [2] pp. 166-188, in a discussion of the electrons and spin waves in heavy rare earth metals reviews the results of energy band calculations with an emphasis on the manner in which the special characteristics of the atomic *s-p*, *d* and *f* electrons are reflected in the electronic and magnetic properties of the metals. Experimental evidence for the conduction band structure, Fermi surface and *4f* electrons is also presented.

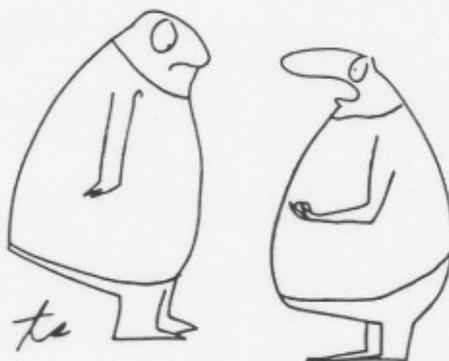
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"This sample came from a parking place. I guess that makes it one of the rare earths."

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Lanthanide Cyanides

The preparation of the first anhydrous lanthanide cyanides was reported by I. J. McColm and S. Thompson, *J. Inorg. Nucl. Chem.* 34, 3801-3807 (1972).

The compounds were obtained by a precipitation reaction between NH_4CN and a liquid ammonia solution of the lanthanide metals. The liquid ammonia-lanthanide solution was prepared by electrolysis. The cyanides were finely divided and difficult to handle or investigate. Previous attempts by other workers to prepare the cyanides in aqueous media resulted only in the precipitation of the metal hydroxides.

McColm and Thompson report analytical, infrared, x-ray and magnetic moment data for some of the cyanides and Mössbauer spectra for the europous and europic compounds.

Hebrew University

(Continued from page 1)

Investigations of energy transfer phenomena between rare earths and from mercury-like ions to rare earth ions in glasses are made. From the transfer rates, the role of glass matrix is deduced. The results obtained in glasses are extended to biological systems in which rare earths can serve as indicators of energy transfer. The role of glass phonons on energy transfer is studied and the suitability of glasses for new lasers is predicted.

Nondestructive analytical methods for determining rare earths are developed by making use of their fluorescent characteristics. Rare earth-doped glass standards for fluorescent measurements are developed.

Cooperation exists between this group and other institutions in Israel such as the Israel Ceramic Institute (Dr. Ish Shalom), Soreq Nuclear Research Center (Dr. Barnett), and Nuclear Research Center Negev (Mr. Brandstadter). There is also international cooperation with the U.S. National Bureau of Standards (Drs. Menis and Velapoldi) and with RCA (Dr. Larach).

Magnetism School

(Continued from page 2)

In the last paper in the series P. Wachter, [2] pp. 189-241, reviews the optical, electrical and magnetic properties of the europium chalcogenides and the rare earth pnictides. The absorption spectra of free RE ions, those diluted in a host matrix, and the spectra of RE compounds are explained. Wachter also discusses the influence of magnetic order on the optical spectra of solids and the luminescence of europium chalcogenides.

LOST LASER

A controversy has developed over the reported production of the first x-ray laser, *RIC News* VII [4] 4 (1972). In the original report a University of Utah team claimed they obtained coherent x-rays by focusing a Nd laser on a thin layer of gelatin containing a solution of CuSO_4 . Photographic film was used to detect the x-rays.

The spots observed on the film, according to T. A. Boster from the University of California's Lawrence Livermore Laboratory, were not caused by x-rays but were merely the result of an electrostatic effect observed when pieces of photographic film are rubbed together or subjected to impacts or shock waves. Boster's results were to be published in the February 1973 issue of *Applied Optics*.

Both sides of the controversy were presented in *C & E News* 51 [4] 27-28 (Jan. 22, 1973).

THERMAL CONDUCTIVITY

Recommended reference values for the thermal conductivity of all of the elements have been compiled by C. Y. Ho, R. W. Powell and P. E. Liley, *J. Phys. Chem. Ref. Data* 1, 279-421 (1972). The values are the result of critical evaluation, analysis and synthesis of all available data. Values were estimated for those elements for which data were not available. The results are presented in both graphical and

MEETING

PRELIMINARY PROGRAM

The Europhysics Study Conference committee has released the preliminary program for the conference which is to be held Aug. 29-Sept. 1, 1973, at Elsinore, Denmark (see *RIC News*, VII [4] 3 (1972)).

ELECTRONIC STRUCTURES: The Electronic Structures of the Rare Earth Metals and Actinides, A. J. Freeman; Photoemission Studies of Rare Earth Metals, Y. Baer; Renormalized Atom Theory of Rare Earth Metals, R. E. Watson.

VALENCE CHANGES: Theory of Valence Transitions, L. M. Falicov; The Electronic Properties of Ce, B. Coqblin; Metal-Insulator Transitions in Sm Monochalcogenides, D. B. McWhan.

MAGNETIC STRUCTURES AND MAGNETIZATION: Magnetic Structures and Conduction Electron Spin Densities, R. M. Moon; Magnetic Form Factors in Rare Earth Metals and Compounds, T. O. Brun; High Field Magnetization of Rare Earth Metals, L. W. Roeland.

MAGNONS AND PHONONS: Magnon Dispersion Relations and Exchange in Rare Earth Metals, R. M. Nicklow; Phonons, Magnon-Phonon Interactions and Magnetic Anisotropy from Inelastic Neutron Scattering, J. C. G. Houmann; Magnetoelastic Effects and Elastic Constants, J. Jensen.

SINGLET GROUND STATES AND HYPERFINE INTERACTIONS: Magnetic Properties of Pr, B. D. Rainford; Singlet Ground States in Rare Earth Compounds, R. J. Birgeneau; Rare Earth Hyperfine Interactions, B. Bleaney.

DILUTE ALLOYS AND DOMAINS: Electron Spin Resonance in Dilute Rare Earth Alloys, R. Orbach, Superconductivity and Electron Scattering in Dilute La Alloys, D. K. Finnemore; Magnetic Domains in Rare Earth Metals, T. Egami.

SUMMARY AND DISCUSSION: Theoretical, R. J. Elliott; Experimental, A. R. Mackintosh.

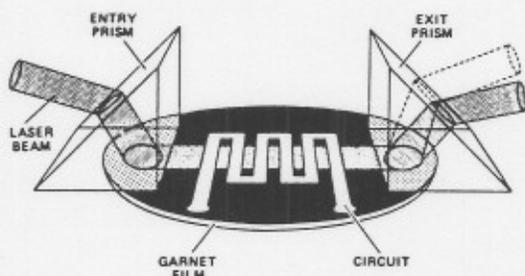
Applications for the conference, attendance is limited to 100 persons, should reach the committee before May 1, 1973; accepted applicants will be notified by about May 15. Registration fee for the conference has been set at \$110.

tabular form over the full temperature range of experimental data or for which reliable extrapolations or estimations could be made.

The compilation also includes summary graphs of the thermal conductivities of each group of elements in the periodic table and a summary of the general procedures used for the estimation of data.

GARNET SWITCH MODULATES LIGHT

A magnetically controlled switch which can modulate light has been developed by researchers at Bell Laboratories. The switch consists of a thin-film of single crystal yttrium-gallium-scandium-iron garnet in which the light is guided, and a tiny, serpentine-like electric circuit which imposes the required information on the light beam. The laser beam is guided into and out of the garnet by a prism at each end.



A magnetic field, created by passing an electric current through the circuit, causes the light beam in the garnet to change its polarization and the direction in which the light is refracted out of the garnet by the prism. Information can be coded on the light beam by switching the beam in or out of its original path in a controlled pattern of light pulses.

With the development of this light switch it may be possible to use laser beams to replace wire conductors, coaxial cables, and microwaves in future communications systems.

Soviet Collection

In the past few months RIC has received several Russian books dealing with rare earths. They are: a book dedicated to E. M. Savitskii on his 60th birthday, *Physico-chemistry of Rare Metals*, I. V. Tananaev, ed. (Nauka, Moscow, 1972); *Rare Earth Metals and Alloys* E. M. Savitskii and V. F. Terekhova, eds. (Nauka, Moscow, 1971); *Handbook of Rare Earth Metals and Their Refractory Compounds* by S. P. Gordienko, B. V. Fenochka and V. V. Fesenko (Naukova Dumka, Kiev, 1971); *Lanthanides in Minerals* by D. A. Mineev (Nedra, Moscow, 1969); *Hydrothermal Occurrence of Rare Earth Fluorocarbonates* by A. P. Khomyakov and E. I. Semenov (Nauka, Moscow, 1971); and *Electronic Structure and Physical Properties of the Solid State, parts I and II*, G. V. Samsonov, M. P. Arbutov, V. S. Neshpor, I. A. Podchernyaeva, V. S. Fomenko, eds. (Naukova Dumka, Kiev, 1972). We have been informed that the first three books are to be translated into English. *When the English versions are issued, reviews of the books and information concerning their availability will be published.*

Atomic Spectra Bibliography

A bibliography of atomic energy levels and spectra from July 1968 through June 1971 has been published by L. Hagen and W. C. Martin, *U.S. Nat. Bur. Stand. Spec. Publ. 363* (June 1972).

The bibliography contains 1100 references classified by subject for individual atoms and ions, including rare earths. The subjects indexed include energy levels, classified lines, wavelengths, Zeeman effect, Stark effect, hyperfine structures, isotope shifts and ionization potentials. The publication also contains an author index.

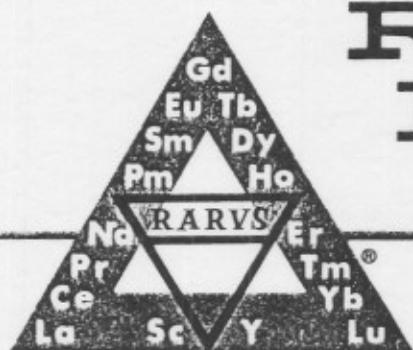
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The book, *Magnetic Properties of Rare Earth Metals*, edited by R. J. Elliott, summarizes the vast amount of information that has been published by many scientists from all corners of the earth in the past 10 years (some data, however, go back to the 1950's) on the magnetic behavior of these metals and their alloys. This was accomplished by contributions from nine experts dealing with seven aspects of rare earth magnetism, both experimental and theoretical.

A brief general introduction by the editor sets the tone for the rest of this volume. The remaining chapters deal with phenomenological theory of magnetic ordering by B. R. Cooper; magnetic structures by W. C. Koehler, bulk magnetic properties by J. J. Rhyne; spin waves by A. R. Mackintosh and H. Bjerrum-Møller; band structures, indirect exchange and magnetic ordering by A. J. Freeman; transport properties by S. Legvold; and hyperfine interactions by B. Bleaney.

Although the main emphasis of this book is on the metals themselves, some information is included on a selected number of alloys, especially the intra rare earth alloys. For anyone directly or indirectly involved with the magnetic behavior of rare earth metals and alloys, this outstanding book will prove to be a valuable addition to his bookshelf. This 425 page book is available for \$28.00 from Plenum Publishing Company.



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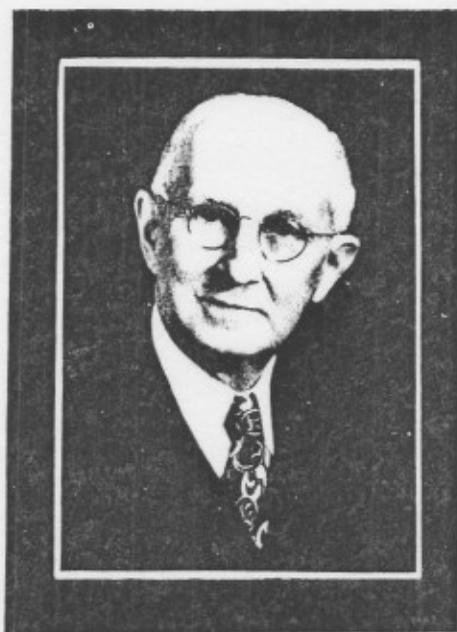
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MA Mixes With TO

In the past few years solid state physicists have been intensively investigating the magnon and phonon spectra of the heavy rare earths by neutron inelastic scattering. One of the interesting features is that the acoustical magnons (MA) mix with the transverse optical phonons (TO), and that an energy gap is associated with this mixing mode. Heretofore this mixing mode was not understood or explainable on the basis of existing theories, but in a recent paper S. H. Liu proposed a new interaction which could account for this, *Phys. Rev. Letters* 29, 793-795 (1972).

Liu proposed that this new magnetoelastic interaction involves an intermediate state in which an incoming phonon is absorbed by the conduction electrons producing an electron-hole pair, both of which have the same spin; but a magnon when absorbed produces an electron-hole pair with opposite spin. For these two modes to mix the spin-orbital coupling of the $4f$ electrons produces a spin-flip in one of the modes. Thus, a phonon can turn into a magnon or the magnon into a phonon.

Furthermore, he calculated the energy gaps that one might expect from this interaction to be 1.4 meV for Tb and 0.4 meV for Dy, which agree quite well with the experimental values of 1.7 and 0.5 meV, respectively. This model is also capable of explaining the insensitivity of the energy gap to temperature.



(Editor's note: This is one of a continuing series of articles commemorating the centennial of those scientists who made great contributions to the field of rare earths.)

B. Smith Hopkins has been described as a brilliant, patient and successful research worker and scientist. As part of his study of the separations and atomic weights of the rare elements, Hopkins in 1926 reported the discovery of the long-sought element 61, to which he gave the name "illinium." Hopkins and co-workers believed that they had found the spectral lines of this element in a fraction between neodymium and samarium from monazite sands. Their discovery touched off a controversy which was not resolved until the actual discovery of element 61, promethium, in 1947.

It is quite likely that Hopkins and L. L. Quill were the first to propose the use of non-aqueous solvents in the separation of the lanthanides. In his electrochemical studies Hopkins prepared divalent europium and ytterbium, rare earth amalgams and attempted to prepare the rare earth metals by electro-deposition from organic solvents. Hopkins also suggested the use of lanthanide metals as industrial catalysts.

Beyond his research on the rare elements, B. S. Hopkins was one of those rare persons who was a great teacher. Students who took his course in general chemistry at the University of Illinois received a truly liberal education, for the course involved the interweaving of chemistry with agriculture, engineering, medicine, economics, geography, foreign trade, philosophy and everyday living. Professor Hopkins devoted his life to teaching and would be remembered by many as the author of several general chemistry texts for colleges. Although Hopkins won honor and fame, he was essentially a humble man, friendly, enthusiastic and easy to approach with widely varying interests.

B.S. Hopkins was head of the Division of Inorganic Chemistry of the University of Illinois and was named professor emeritus in 1943. He was also a member of numerous honorary societies and Chairman of the Division of Chemical Education of the American Chemical Society.

Thulium-170 is used in industrial radiography and medical teletherapy.

RIC and the 40 Contributors

Records are made to be broken and the addition of two more contributors to the 38 record high reported last issue now means that RIC is receiving support from 40 concerned rare earth companies. Contributions this last quarter came from Sawyer-Adecor International, Inc., U.S.A., a three-time contributor to the Center, and from Allied Chemical Corp., U.S.A., which joins our ranks for the first time.

Liquid REM

Values for the spectral emissivities of liquid Y, Nd and Gd were determined by L. A. Stretz and R. G. Bautista, *Fifth Symposium on Temperature, Washington, D.C., June 21-24, 1971* (Instrument Society of America, Pittsburgh, PA, 1972), pp.489-499. Of interest to note is that the value for gadolinium at $0.645\mu\text{m}$, 0.342, is almost a factor of two greater than that of yttrium, 0.134, while the value for neodymium, 0.280, is about twice the yttrium value. The spectral emissivities of the metals above their melting points are essentially temperature independent.

The authors also measured the emittances of the solid surfaces of Y, Nd, Gd and Er. These values depended on the surface conditions of the samples but changed only slightly with temperature.

The spectral emissivities were determined by a method in which the surface brightness temperature is compared to the true sample temperature obtained from the brightness temperature of a blackbody cavity located within the sample crucible.

Faraday Effect

The Faraday effect in cerium phosphate glass at 4.2°K has proved to be useful for measuring the axial magnetic field distribution in superconducting lenses for high voltage electron microscopy. The method was reported by H. Dekker in

J. Phys. E. 5, 368-372 (1972).

The operation of an electron microscope objective is limited by the critical magnetic field when superconducting pole pieces are used. Dekker found that the magnetic field was proportional to the Faraday rotation (the rotation of a plane of linearly polarized light by a material in the direction of an applied magnetic field) of cerium phosphate at low temperatures, and could be easily measured using this effect. Errors in the measurement were small.

New Tm Polymorph

An x-ray diffraction study of Tm under pressure at room temperature revealed that Tm transformed from a hexagonal close packed structure to the Sm-type structure somewhere between 60 and 116 kbar, L. Liu, W. A. Bassett, M. S. Liu, *Science* 180, 298-299 (1973).

Unlike Gd, Tb, Dy and Ho which undergo the same transformation, Tm has an axial ratio which is independent of pressure; the transition in Tm is also reversible in contrast to the other rare earths.

POLYNITRIDES

Recently R. Kieffer, P. Ettmayer and Sw. Pajakoff claimed to have prepared rare earth nitrides with nitrogen concentrations greater than 50 at. %, *Monatsh. Chem.* 103, 1285-1298 (1972). As far as we know, this is the first report of rare earth nitrides having nitrogen concentrations greater than the mononitride composition.

The RN₂ compounds, where R = Ce, Pr and Nd, were prepared by heating the metals above 1150°C under 30 atm pressure of nitrogen gas. In general, below 1350°C a mixture of RN and RN₂ was obtained, but above this temperature single phase material was obtained. The crystal structure was reported to be hexagonal of the La₂O₃ type.

For the heavy rare earths (R = Tb, Dy, Ho, Tm, Lu and Y) only two-phase mixtures were

Rare Earths In the News

Sc³H DETECTOR

A new Sc³H electron capture detector for use with a gas chromatograph improves its sensitivity for pesticides. The device, developed by Varian Instruments, can operate at 325°C because of the good hydrogen absorption properties of scandium. At these temperatures lipids present in vegetable samples do not build up on the foil with the attendant reduction in sensitivity and standing current. The detector has successfully analyzed pesticide residues in vegetable crops at the 0.1 ppm level. This, says Varian, exceeds the best performance characteristics of present ³H and ⁶³Ni detectors.

SINGLE-PHASE SINTERING

Hamilton Precision Metals reports development of a single-phase sintering process which yields high-performance samarium-cobalt permanent magnets of unexcelled uniformity. Magnets with a maximum energy product of 17 MGOe (136kJ/m³), using an aligning field of only 10 kOe (800 kA/m), have been produced. Densities obtained range from 95-99% of theoretical, Hamilton reports.

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obtained, RN + RN_{1+x}. The R_{1+x} compounds were reported to have the cubic C-form type structures of the R₂O₃ phases. In the case of Sm and Gd only the mononitride was obtained, even when the pressure was increased to 250 atm N₂.

WORKSHOP

The existing ideas on the theoretical aspects of the origin of high coercivity in SmCo_5 were discussed at a symposium-workshop session at the 18th Annual Conference on Magnetism and Magnetic Materials, Denver, Colorado, Nov. 28 - Dec. 1, 1972.

The panel, composed of K. Bachmann, G. Y. Chin, J. D. Livingston, R. A. McCurrie and K. J. Strnat, was organized and chaired by J. J. Becker. The symposium also included considerable discussion of the microstructure and metallurgy of the nominal SmCo_5 phase.

A brief review of this session is given by R. A. McCurrie in *Cobalt* 1973, 23-24, 28. Conference proceedings will be published by the American Institute of Physics.

Seek ^{244}Pu Tracks

In an attempt to provide support for the report of ^{244}Pu in Mountain Pass bastnasite, *RIC News* VI [4] 6 (1971), R. L. Fleischer and C. W. Naeser fission track-dated bastnasite and accessory minerals from adjacent rocks in the Mountain Pass, Calif., mine, *Nature* 240, 465 (1972).

If the mineral were sufficiently old, radiation damage tracks produced by the spontaneous fission of ^{244}Pu could be observed (^{244}Pu has a half-life of 82 million years). However, the authors found that the bastnasite and apatite have relatively young geologic ages, 50-80 million years, and that no excess of ^{244}Pu fission tracks over the ^{238}U background track density could be determined or would be expected. Fission tracks, therefore, according to the authors, cannot provide any support for the report of ^{244}Pu in Mountain Pass bastnasite.

Thulium, atomic number 69, was discovered in 1879 by P. T. Cleve and was named for Thule, the ancient name of Scandinavia.

CATALYSTS

Additional information has been published on the lanthanum lead manganite catalysts reported by Bell Laboratories scientists to reduce nitrogen oxides in auto exhaust, *RIC News* VIII [1] 1-2 (1973).

R. J. Voorhoeve, J. P. Remeika and D. W. Johnson, Jr., *Science* 180, 62-64 (1973), evaluated the $\text{La}_{1-x}\text{Pb}_x\text{MnO}_3$ compounds where $0.3 < x < 0.6$ and their perovskite-like homologs under laboratory conditions. The lanthanum lead manganites essentially completely reduced NO to N_2 and N_2O in mixtures of NO , CO , H_2O and H_2 . The N_2O produced is not expected to be a problem in exhaust treatment and is not covered under federal NO_x standards.

Presently known catalysts such as Cu-Ni and Pt-Ni reduce NO_x predominately to NH_3 which is then reoxidized to unacceptable NO_x in the second stage of the catalytic exhaust converters. In contrast, the rare earth manganites convert only 10% of the NO to NH_3 at 200-375°C and 25% at 450°C, thus the re-oxidation of NH_3 is not nearly as large a problem.

The authors found that crushed and etched single crystals of the manganites were particularly selective, and they suggested that these compounds should be further evaluated as promising catalysts for the reduction of NO_x in auto exhaust.

Catalytic Controversy

The same compounds were reported earlier as possible catalysts for the oxidation of CO to CO_2 in auto exhaust, *Science* 177, 353-354 (1972). However, J. C. Schlatter, R. L. Klimisch and K. C. Taylor, *Science* 179, 798-800 (1973), have taken issue with this earlier report. They claim that the test conditions were not relevant to automotive emission control applications because the feedstream did not contain H_2O or CO_2 which are important components of exhaust gas and have significant effects on the catalytic oxidation of CO . More

importantly, the CO concentration was 20-100 times higher than that in auto exhausts while the maximum space velocity was 20-200 times lower than the velocity of interest for exhaust catalysts. Schlatter and co-workers pointed out that the maximum conversion of CO reported was 20% while conversions above 90% would be required to meet the Clean Air Amendments of 1970. They therefore concluded that the extrapolation of laboratory results to automotive applications was not appropriate in the case of the rare earth oxides of manganese and cobalt.

Clearly more realistic tests must be made on these rare earth materials before their worth as auto exhaust catalysts are known.

Gd^{+3} EPR Survey

Although the ground state splittings of Gd^{+3} in crystalline electric potentials have been measured extensively using electron paramagnetic resonance (EPR) techniques, the existence and magnitude of these splittings have not yet been explained theoretically. H. A. Buckmaster and Y. H. Shing have surveyed the EPR spectra of Gd^{+3} in single crystals in the hope that the availability of such a review will encourage renewed theoretical effort to explain the ground state splittings, *Phys. Stat. Solidi (a)* 12, 325-361 (1972).

The authors discuss the spin Hamiltonian terms pertinent to the description of the EPR data of Gd^{+3} for both zero-magnetic field and linear magnetic field cases. The tables describing the EPR spectra of Gd^{+3} are grouped according to the site symmetry of the host lattice. Each table is introduced by a presentation of the appropriate spin Hamiltonian for each symmetry in both the operator equivalent and tensor operator formalism.

Data in the tables include the dilution of the Gd^{+3} ion with respect to the host ion, the measurement temperature and frequency, both fine and hyperfine structure constants and the g factor.

Carefree Rare Earth Research Conference

One of the largest rare earth conferences to date, the 10th, held at the Carefree Inn, Carefree, Arizona, boasted about 240 participants from the U.S. (about 75%) and 13 foreign countries (about 25%) with France, Germany, Japan, Canada and Israel each having 5 or more representatives. The conferees enjoyed the beauty of the Arizona desert and the late-blooming cactus in the area surrounding Carefree between conference sessions.

In the plenary address L. Glenn T. Seaborg presented a status report on the chemistry and oxidation states of the transuranium and lanthanide elements; he also speculated on the existence of the transactinide or super-actinide elements. Theoretical calculations of the ground states of these elements indicate that the chemistry and physics of these elements will be extremely complicated because of close proximity of the $6f$ and $5g$ levels. These calculations suggest that the $6f$ level begins to fill first, but before it is completely filled the $5g$ level starts to fill and is completely filled before the $6f$ level is filled. In addition to Prof. Seaborg's address, two special sessions were held on lanthanide-actinide chemistry.

Because of the large number of papers presented, three sessions were run simultaneously throughout the conference. The session on bio-inorganic chemistry initiated at the 9th Conference was continued. The note of pessimism concerning the usefulness of the lanthanide probes at the 9th Conference was not present at this conference. It was even speculated that within the year methods could be worked out whereby lanthanide ions could be used to determine the complete structure of proteins in solution. In a new session on NMR shift reagents, the controversies and problems associated with the use of these agents were discussed as well as the growing number of applications.

In the industrial technology sessions, the potential for pollution-free automotive transportation was pointed out. It was reported that the technical feasibility of continuously operating an internal combustion engine on hydrogen desorbed from a LaNi_5 source had been demonstrated. In addition to the usual number of papers on rare earth-cobalt permanent magnets, there was one paper concerning the use of gadolinium as a soft magnetic material at low temperatures. W. M. Swift pointed out that gadolinium has the smallest known BH hysteresis of any hexagonal metal, but it is still an order of magnitude larger than the best iron-silicon transformer core materials.

The complete program of the conference is printed below. Copies of the Proceedings of the Tenth Rare Earth Research Conference are available at a cost of \$30.00 for the two-volume set from:



Glenn T. Seaborg

Dr. Therald Moeller
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Tempe, AZ 85281 U.S.A.

We would like to thank Dr. Moeller and his co-workers for organizing a most enjoyable and stimulating conference.

The Eleventh Rare Earth Research Conference will be held in Autumn 1974 in Traverse City, Michigan under the organization of Dr. Harry A. Eick, Michigan State University. Details will be printed in the September 1973 RIC News.

Plenary Address: Status Report on the Transuranium and Lanthanide Elements, GLENN T. SEABORG.

LANTHANIDE-ACTINIDE CHEMISTRY I

The Actinide Metals, L. B. ASPREY

Absorption Spectra of f Transition Elements, J. C. CONWAY

Compounds of Divalent Lanthanides and Actinides, J. R. PETERSON

Organolanthanide and Organoactinide Chemistry: On the Role of the f -Electrons, R. D. FISCHER and H. -D. AMBERGER

LANTHANIDE-ACTINIDE CHEMISTRY II

Structural Studies on Organometallic Compounds of Lanthanides and Actinides, J. H. BURNS

Lanthanide and Actinide Cyanides, K. W. BAGNALL

Lanthanide and Actinide Mixed Oxide Systems, C. KELLER

Lanthanide and Actinide Phthalocyaninato Complexes, F. LUX

The Magnetic Properties of $4f$ - and $5f$ - Systems, B. KANELAKOPOULOS

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Production and Uses of Rare Earths in Japan, I. T. OIWA

Nature of Inclusions in Rare-Earth Containing Steels, W. G. WILSON

The Effect of Microstructure on Corrosion Behavior in Dilute Mischmetal-Mg Castings, S. G. FISHMAN and C. R. CROWE

Military Uses of Misch Metal, B. A. KULP

Precision Investment Casting of Mischmetal Alloys, G. D. CHANDLEY

INDUSTRIAL TECHNOLOGY II

Nuclear Powered Heart Pacemakers--A Biomedical Application of Rare Earths, A. L. RECCHIA and S. A. KOLENIK

Reclamation of Rare-Earth Red Phosphors, J. E. MATHERS and R. E. DODDS

The Use of Rare Earths in Glass Polishing, W. L. SILVERNAIL and N. J. GOETZINGER

The Use of LaNi_5 as a Hydrogen Source for Fueling a Non-Polluting, Internal Combustion Engine, C. E. LUNDIN

Recovery of Gadolinium and Yttrium Values from Scrap Garnet Powders, L. E. SCHULTZE, D. J. BAUER and R. E. LINDSTROM

Importance of Chemical and Physical Properties of Yttria and Gadolinia Used in Preparing Microwave Garnets, L. P. DOMINGUES, R. G. WEST and A. C. BLANKENSHIP

Microwave Garnets Prepared with Reclaimed Yttria and Gadolinia from Scrap Garnet, L. P. DOMINGUES, D. J. BAUER and R. E. LINDSTROM

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Magnetic and Structural Properties of Heavy-Rare-Earth Ferrite-Manganite Solid Solutions, V. E. WOOD, A. E. AUSTIN and R. SMITH

Magnetic Properties of $\text{LnFe}(\text{CN})_6 \cdot n\text{H}_2\text{O}$ and $\text{LnCo}(\text{CN})_6 \cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{La} \dots \text{Gd}$), F. HULLIGER, M. LANDOLT and H. VETSCH

Magnetic Properties of RCO_2Ge_2 Compounds ($\text{R} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}, \text{Lu}$ and Y). W. M. McCALL, K. S. V. L. NARASIMHAN and R. A. BUTERA

Some Aspects Concerning the Magnetism of Rare-Earth Intermetallic Compounds, E. BURZO

The Properties of Permanent Magnets Made from Reduction Diffusion Cobalt-Rare Earth Powders, D. L. MARTIN, R. P. LAFORCE, A. C. ROCKWOOD, C. M. McFARLAND and L. VALENTINE

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Magnetic Interactions and Spin-Wave Dispersion in Rare Earth Metals, R. M. NICKLOW

Magnetic Properties of $\text{Gd}_{1-x}\text{Th}_x\text{Fe}_2$ and $\text{Gd}_{1-x}\text{Ce}_x\text{Fe}_2$, E. T. MISKINIS, K. S. V. L. NARASIMHAN, W. E. WALLACE and R. S. CRAIG

Dipolar Contributions to Magnetic Hyperfine Fields in $\text{Er}_x\text{Y}_{1-x}\text{Fe}_2$ and $\text{Tb}_x\text{Y}_{1-x}\text{Fe}_2$ Compounds, M. P. DARIEL, U. ATZMONY and D. LEBENBAUM

Magnetostrictive Properties of $\text{Ho}_x\text{Tb}_{1-x}\text{Fe}_2$ Intermetallic Compounds, N. C. KOON, A. I. SCHINDLER and F. L. CARTER

Magnetization and Magnetostriction in Y_2Co_{17} and $\text{Dy}_2\text{Co}_{17}$, T. D'SILVA, H. IGARASHI and A. E. MILLER

An Analysis of the Rare Earth Contribution to the Magnetic Anisotropy in RCO_5 and R_2Co_{17} Compounds, J. E. GREEDAN and V. U. S. RAO

Saturation Magnetization of Rare Earth-Transition Metal Phases of the Type $\text{R}_2(\text{Co}, \text{Fe})_{17}$, H. MILDREUM, J. TRONT, M. HARTINGS and K. STRNAT

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Spin Densities in Rare-Earth Metals and Compounds, R. M. MOON

Physical Properties of CeCrSe_3 -Type Compounds, O. GOROCHOV and H. MCKINZIE

Importance of the Crystal Field on the Magnetic Moment Orientation in the Equiatomic Rare Earth-Nickel RNi Compounds ($\text{R} = \text{Tb}$ to Tm), D. GIGNOUX, D. PACCARD, J. ROSSAT-MIGNOD and F. TCHÉOU

Spin Reorientation in SmFe_2 , U. ATZMONY, M. P. DARIEL, E. R. BAUMINGER, D. LEBENBAUM, I. NOWIK and S. OFER

Magnetic Properties of ^{147}Pm and ^{147}Pm - ^{147}Sm Alloys, W. C. KOEHLER and R. M. MOON

Magnetic Properties of Ln_3In Intermetallic Compounds, R. D. HUTCHENS, W. E. WALLACE and N. NERESON

Magnetic Susceptibilities of Heavy Rare-Earth Metals Near the Néel Points, L. A. BOYARSKY and M. A. STARIKOV

Influence of Pr^{3+} on the Magnetic Properties of YIG Crystal, R. KRISHNAN

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Mapping of Inhibitor Molecules in $\text{Gd}(\text{III})/\text{Lysozyme}/\text{Inhibitor}$ Complexes Using Nuclear Magnetic Resonance, R. A. DWEK, S. J. FERGUSON, G. K. RADDLE, R. J. P. WILLIAMS and A. V. XAVIER

Lanthanide Ions as Calcium Ion Substitutes in Trypsin and Trypsinogen, D. W. DARNALL, E. R. BIRNBAUM, A. D. SHERRY and J. E. GOMEZ

Studies of the Calcium Binding Site of Trypsin Using Rare Earth Ions, M. EPSTEIN, A. LEVITZKI and J. RUEBEN

Water Proton Relaxation Rate Studies of the Interaction of Gadolinium with Rabbit Muscle Pyruvate Kinase, K. M. VALENTINE and G. L. COTTAM

$\text{Nd}(\text{III})$ as a Probe for Metal-Protein-Small Molecule Interactions in Glutamine Synthetase of *E. coli*, F. C. WEDLER and V. D'AURORA

Use of Lanthanum to Delineate Mechanisms of Calcium-Dependent Actions in Different Isolated Muscle Systems, G. B. WEISS

BIO-INORGANIC CHEMISTRY II

A Study of Carboxylic and Amino Acid Complexes of $\text{Nd}(\text{III})$ in Solution by Difference Absorption Spectroscopy and NMR Spectroscopy, E. R. BIRNBAUM, A. D. SHERRY and D. W. DARNALL

Proton Magnetic Resonance Studies of Rare-Earth Ion Binding Interactions with Staphylococcal Nuclease, E. NIEBOER, D. EAST, J. S. COHEN, B. FURIE and A. N. SCHECHTER

Proton Relaxation Rate and Fluorometric Studies of Manganese and Rare Earth Binding to Concanavalin A, A. D. SHERRY and G. L. COTTAM

Physical Studies of Lanthanide-Macromolecule Interactions, J. A. GLASEL

The Use of Lanthanide Ions for the Determination of the 3D Structure of Proteins in Solution, I. D. CAMPBELL, C. M. DOBSON, R. J. P. WILLIAMS and A. V. XAVIER

Rare Earth Binding to Thermolysin, B. W. MATTHEWS and L. H. WEAVER

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Phase Equilibria in the Ytterbium-Carbon-Hydrogen System, J. M. HASCHKE

Hydrothermal Synthesis of $\text{La}(\text{HO})_3$ Single Crystals from Incongruent Stability Conditions, S. MROCZKOWSKI and J. W. NIELSEN

Catalysis of CO to CO_2 by Rare Earth Oxides; Activation of Tb_4O_7 , B. C. GERSTEIN, D. MACAULAY and K. CHANG

Oxidation States in the System $\text{PrO}_x\text{-CeO}_2$ at Various Oxygen Pressures, G. BRAUER and B. WILLAREDT

Oxygen Transport in $\text{Pr}_7\text{O}_{12} \pm \delta$ Single Crystals, K. H. LAU and L. EYRING

The Preparation and Some Structural and Magnetic Properties of Perovskite Oxides Containing Tetravalent Rare Earth Ions, A. J. JACOBSON, B. C. TOFIELD and B. E. F. FENDER

A Semiconductor-Metal Transition in Samarium Selenide, R. G. BRECKENRIDGE, A. J. DARNELL and N. C. MILLER

On a New Method to Study the Polar Properties of Matrix and Impurity Cations in Dielectric Solids by Spark Source Mass Spectrography—With Particular Reference to Eu- and Gd-Chalcogenides and -Prictides, J. T. MUHEIM

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A Neutron-Diffraction Study of LaNi_5D_7 , A. L. BOWMAN, J. L. ANDERSON and N. G. NERESON

The Crystal Structures of Two Modifications of the New $\text{Eu}(\text{II})\text{-Eu}(\text{III})$ Compound $\text{Li}_2\text{Eu}_5\text{O}_8$ and the Crystal Data of the Isostructural Compounds $\text{Li}_2\text{SrEu}_4\text{O}_8$ and $\text{Li}_2\text{BaEu}_4\text{O}_8$, H. BÄRNIGHAUSEN, R. SCHUSTER and K. VOGT

Ternary Compounds Formed by Sulfides of Two Rare Earths, J. FLAHAUT, P. LAURELLE, T. VOVAN, N. RODIER and D. CARRÉ

The Synthesis and Crystal Structure of Triytterbium Chloro-Orthosilicate: $\text{Yb}_3(\text{SiO}_4)_2\text{Cl}$, C. AYASSEE and H. A. EICK

Polymorphism in Rare-Earth Molybdates and Tungstates of the Types $\text{R}_2(\text{MO}_4)_3$ and R_2MO_6 , A. W. SLEIGHT and L. H. BRIXNER

Structural Studies in the System KF-YF_3 , J. W. PIERCE and H. Y-P. HONG

Rare Earth Chalcogenides Glasses, J. FLAHAUT, M. GUITTARD, A. -M. LOZACH and P. BESANCON

An Electron Optical Study of the Crystal Chemistry of the Terbium-Oxygen System, P. KUNZMANN and L. EYRING

The Solubility of RH_2 in R Between Ambient and 850°C ($\text{R} = \text{Gd}, \text{Er}, \text{Tm}, \text{and Lu}$), B. J. BEAUDRY and F. H. SPEDDING

Reduction sous Vide du Sesquioxyde d'Ytterbium par le Graphite à Haute Temperature, O. de POUS, L. ALBERT, M. FROMAGET and J. -C. ACHARD

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New Method for the Monoclinic B Form Preparation of Yttrium Rare Earth Sesquioxides, J. -P. COUTURES and R. RENARD

Crystal Chemistry and Magnetic Properties of Eu²⁺ Ternary Oxides, G. J. McCARTHY, R. JOHNSTON and J. F. HOULIHAN

Thermogravimetric Studies of La₂O₃-Cr₂O₃-O₂ System: Lanthanum Oxichromate, R. BERJOAN and J. -P. COUTURES

Electron Transport Properties of Rare Earth Perovskites and Related Systems, C. N. R. RAO

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Calculation of the Electronic Structure of Some Cubic Intermetallic Compounds of Yttrium and Dysprosium, M. BELAKHOVSKY, J. PIERRE and D. K. RAY

Energy Band Calculations for Cubic Laves Compounds LaAl₂, LuAl₂ and YAl₂, A. C. SWITENDICK

Atomic Contractions and Resonant Bonds in Some Rare Earth-Transition Metal Alloy Phases, A. RAMAN

Effect of Grain Size on the Electronic Distribution in Very Thin Films of Ytterbium, C. BONNELLE, F. VERGAND and R. C. KARNATAK

Heat Capacity Studies on DyFe_{3-x}Ni_x Compounds, K. S. V. L. NARASIMHAN, R. J. CATO and R. A. BUTERA

Heat Capacity Behavior of DyNi₅, HoNi₅ and ErNi₅ Between 4° and 300°K, S. G. SANKAR, D. A. KELLER, R. S. CRAIG, W. E. WALLACE and V. U. S. RAO

Magnetic Properties of R_{2-x}R₁_xCo₁₇ Compounds (R = Gd, Dy, Ho, or Er, R₁ = Th or Ce), K. S. V. L. NARASIMHAN and W. E. WALLACE

Structural and Magnetic Properties of Some R_{1-x}Th_xFe₃ (R = Sc, Y, Pr, Ce, Dy, Lu) Intermetallic Compounds, C. J. KUNESH, K. S. V. L. NARASIMHAN and R. A. BUTERA

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Cobalt-Rare Earth Powders by the Reduction-Diffusion Process, C. M. McFARLAND

Purification of Rare Earth Metals by Electrotransport, O. N. CARLSON, F. A. SCHMIDT and D. T. PETERSON

Revised Phase Diagrams for the Binary Systems Cerium-Cobalt, Praseodymium-Cobalt, and Neodymium-Cobalt, A. E. RAY, A. T. BIEMANN, R. S. HARMER and J. E. DAVISON

Effect of Alloying on the Superconducting Temperature of La₃In, K. A. GSCHNEIDNER, JR., O. D. McMASTERS and J. E. OSTENSON

Elastic Behavior of Polycrystalline Rare Earth-Iron Laves Compounds, M. ROSEN, H. KLIMKER, U. ATZMONY and M. P. DARIEL

Rolling and Annealing Textures of Gadolinium, W. M. SWIFT and W. T. REYNOLDS

Mechanical and Electrical Properties of Diluted Gd-Fe Alloys Near the Curie Point, O. A. NABUTOVSKAYA

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Mössbauer and Crystallographic Study of DyFe_{3-x}Ni_x Compounds, S. C. TSAI, K. S. V. L. NARASIMHAN, C. J. KUNESH and R. A. BUTERA

Crystallographic and Mössbauer Study of (Sc, Y, Ln) (Fe,Al)₂ Intermetallic Compounds, A. E. DWIGHT, C. W. KIMBALL, R. S. PRESTON, S. P. TANEJA and L. WEBER

Mössbauer Investigation of Dilute Er Impurities in Au and Pd, G. K. SHENOY, J. STÖHR and G. M. KALVIUS

Bonding Effects in the Rare Earth Laves Phases, F. L. CARTER and G. C. CARTER

Etude Calorimétrique de Quelques Metaux de Terres Rares et Leurs Composés LnSn₃, A. PERCHERON-GUEGAN, J. -C. ACHARD, A. BACHA, C. CHATILLON and J. -C. MATHIEU

Physical Study of Some Metallic Ytterbium Compounds, A. PERCHERON-GUEGAN, J. -C. ACHARD and O. GOROCHOV

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Lanthanide Complexes of Some Macrocyclic Polyethers, P. R. HECKLEY and R. B. KING

Some Isocyanate Complexes of the Lanthanides, R. L. DIECK and T. MOELLER

Rare Earth Complexes with Diphenyl Sulfoxide, O. A. SERRA and L. C. THOMPSON

Structures of Some Rare-Earth β-Diketonate Complexes and Their Adducts with Organic Nucleophiles, J. A. CUNNINGHAM and R. E. SIEVERS

Lanthanide Complexes with Phthalate Ligand, W. R. STAGG and B. L. ANDREWS

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Structural Studies of the Double Isopropoxides of Lanthanons with Aluminum, R. C. MEHROTRA and A. MEHROTRA

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The Thermal Decomposition of Berkelium Compounds, R. G. HAIRE

A Study of the La₂O₃-H₄EDTA-Metal Hydroxide System, S. CANTRELL, J. L. MACKAY and W. L. POWELL

Modes of Decomposition of Rare Earth Metal Benzoates, Enthalpies of Transition, and Activation Energies of Decomposition, M. D. TAYLOR and R. PANAYAPPAN

Spectral Studies of Actinide Ions in Molten Fluoride Salts, J. P. YOUNG

The Shape of Thermodynamic Functions Associated with the Complexation of Lanthanides by Organophosphorus Ligands. Practical Significance of the Double-Double (Tetrad) Effect, I. FIDELIS and S. SIEKIERSKI

Spectral Investigations of Some Lanthanide β-Diketonates in Ultraviolet Region, P. C. MEHTA, S. S. L. SURANA and S. P. TANDON

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Mass Spectrometric Analysis of Rare Earth Elements Contained in Very Small Quantities of Lunar Samples: Implications for Cosmo-chemistry, L. -D. NGUYEN, M. de SAINT SIMON, G. PUIL and Y. YOKOYAMA

Spectrofluorimetric Determination of Rare Earths in Uranium after Separation and Concentration of Total Lanthanides Onto an Alumina Column, R. I. CAZOTTI and A. ABRÃO

Fractional Precipitation of Rare Earth Iodates Using Complexation Hydrolysis of Dimethyl Sulfate, F. H. FIRSCHING, M. T. BERGER, P. G. TAYLOR and D. W. THURSTON

Rapid Lanthanide and Actinide Separations with Pressurized Ion Exchange Chromatography, D. O. CAMPBELL

Removal of Phosphates from Wastewaters with Electrochemically Generated Gadolinium Ions, E. I. ONSTOTT

Standard Potentials of Rare-Earth Couples in Liquid Ammonia, R. N. KRISHNAN and J. C. WARF

Direct Spectrofluorimetric Determination of Cerium and Other Rare Earth Elements in Thorium Solution, R. I. CAZOTTI and A. ABRÃO

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Shift Reagents in Polyfunctional Systems, J. K. M. SANDERS

The Lanthanide Cations as NMR Probes: A Novel Approach to Organic Shift Reagent Studies and Amino Acid Sequence Determination of Simple Peptides, E. NIEBOER, W. P. FLORA, M. PODOLSKI and H. FALTER

Magnetic Anisotropy and Dipolar Shifts in Shift Reagent Systems, W. DeW. HORROCKS, JR., J. P. SIPE, III and D. SUDNICK

Determination of the Structure of Organic Molecules by Lanthanide-Induced Chemical Shifts in Theory and Practice, M. R. WILLCOTT and R. E. DAVIS

Computer Program for Automatic Interpretation of NMR Spectra on the Basis of Dipolar Lanthanide Shifts, J. BARCISZEWSKI, A. J. RAFALSKI and M. KARONSKI

Lanthanide Shift Reagent-Substrate Equilibria: Some Implications for Structural Considerations, B. L. SHAPIRO, M. D. JOHNSTON, JR., T. W. PROULX, H. L. PEARCE, A. D. GODWIN, M. J. SHAPIRO and C. A. REILLY

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Keynote Address— V.A. FASSEL, X-Ray Excited Optical Fluorescence Spectra and Their Analytical and Technological Applications

Cathode-Ray-Excited Emission (CREE) Spectroscopic Analysis of Trace Rare Earths, S. LARACH

Conversion of $Y_2O_3:Eu$ into $Y_2O_2S:Eu$ at the Same Color and Brightness, H. FOREST and L. OZAWA

Quantum Efficiency of Liquid Laser Solutions, $Nd^{+3}:POCl_3/ZrCl_4$, E. J. SCHIMITSCHEK and J. A. TRIAS

Laser Optical Double Resonance and Efficient Infrared Quantum Counter Upconversion in $LaCl_3:Pr^{+3}$ and $LaF_3:Pr^{+3}$, J. C. WRIGHT, D. J. ZALUCHA, H. V. LAUER, D. E. COX and F. K. FONG

Computer Analysis of Fluorescence Quantum Yields of Rare Earth Chelates. A Comparative Study of ML_n^{q+} Complexes in Solution, C. GÖRLLER-WALRAND, E. GRAUWMANS and S. De JAEGERE

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Radiative and Nonradiative Decay of Rare Earth Ions in $YAlO_3$, M. J. WEBER

Multi-Quantum Scattering Processes in Radiation-less Relaxation of Electronically Excited Ions in Crystals, F. K. FONG and W. A. WASSAM

Energy Transfer Between Er^{3+} and Yb^{3+} Ions Diluted into Cadmium Fluoride Crystals, M. BANCIE-GRILLOT and E. GRILLOT

Thermal and Concentration Dependence of Ce-Tb Transfer in $La_{1-x}Ce_xTb_yPO_4$ Compounds, J. C. BOURCET, J. JANIN, J. P. DENIS and J. A. LORIERIS

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The Tb^{+3} Ion as a Probe for Hot Electron Distributions in $ZnS:Tb^{+3}$ Thin Films, D. C. KRUPKA

Application of the Superposition Model of Some Oxygenated Lattices Doped with Eu^{3+} , F. GAUME, C. LINARES and M. BLANCHARD

Superposition Model of Lanthanide Crystal Fields, D. J. NEWMAN

Ligand Field Parameters in Glasses, R. REISFELD, L. BOEHM, N. LIEBLICH and B. BARNETT

Optical Properties of Sm^{3+} in Borate and Phosphate Glasses, R. REISFELD, L. BOEHM and E. GREENBERG

Sensitization of the Fluorescence of Eu^{3+} Doped ZnS by Gadolinium or Lanthanum Ions, E. GRILLOT and M. BANCIE-GRILLOT

Luminescence, Structural Properties and Energy Transfer Mechanisms in Some Rare Earth Ultra-Phosphates, B. BLANZAT, J. P. DENIS and J. LORIERIS

Low Temperature Optical Absorption and Photoconductivity in $YbTe$, R. SURYANARAYANAN

Clarification on RE Cyanides

Since the last issue of the *RIC News* was published, we received two interesting letters from Dr. K. Rossmannith from the University of Vienna. In the first letter he pointed out that he had prepared rare earth cyanides, *Monatsh. Chem.* 97, 1698-1712 (1966), six years before McCollm and Thompson, *J. Inorg. Nucl. Chem.* 34, 3801-3807 (1972). In the March 1973 issue of the *RIC News* VIII, 3, we stated that the latter authors were the first to prepare anhydrous lanthanide cyanides.

According to the information given by Rossmannith in his published article, he had prepared rare earth cyanide complexes with tetrahydrofuran, $R(CN)_3 \cdot 2THF$, and according to his second letter "the THF can be easily removed in vacuo" to give $R(CN)_3$.

According to the published information we are aware of,

SHIFT REAGENT REVIEW

The growing importance of rare earth shift reagents in NMR spectroscopy in organic and biological chemistry is reviewed by J. M. Sanders and D. H. Williams, *Nature* 240, 385-390 (1972).

The shift reagents simplify NMR spectra by separating resonances that would otherwise overlap. In the most commonly used shift reagent, *tris*-(2, 2, 6, 6-tetramethylheptane-3, 5-dionato) europium (III), $Eu(DPM)_3$, the europium complex associates with the substrate being studied at its polar functional group. Eu provides a local magnetic field which falls off as the inverse cube of distance from the Eu atom and thus spreads out the spectrum.

The authors discuss the mechanism of shifts, the nature of the interactions and also provide an illustrative rather than an exhaustive list of the applications of these reagents in mixture analysis, structural assignments and geometrical relations. The authors point out the implications of shift reagents in biochemistry. The lanthanide ions could substitute for Ca^{+2} and Mg^{+2} while maintaining biological activity thus allowing the possibility of investigating the shapes and sizes of active sites in biological molecules.

Form Magnet Company

Hitachi Metals America and the General Electric Company have formed a new company, Hitachi Magnetics Corporation (HMC), to manufacture and market permanent magnets. HMC's manufacturing facility will be GE's former Magnetic Materials Product Section at Edmore, Mich.

McCollm and Thompson were the first to record the preparation of pure anhydrous simple lanthanide cyanides, but Rossmannith was the first to prepare anhydrous rare earth cyanide-THF complexes.

RIC Adds Document Depository Service

RIC is pleased to announce yet another service for the rare earth community, a Center-supported document depository. In it authors can place documents concerning the rare earths which, because of their nature or length, may not otherwise be suitable for publication in the literature.

All documents deposited with RIC will receive an identification number, *i.e.*, RIC-DD-000, and can be retrieved by the scientific community on a cost recovery basis. There will be no charge to the depositor.

Documents placed on deposit with RIC will be announced regularly in the *RIC News*. However, because of the limited distribution of our publication, authors may wish to obtain an RIC-DD number for their material in advance and reference it in their journal publications to insure wider announcement of its availability. For those choosing this option, RIC will determine the price of the document so that can be included in the reference.

RIC-DD documents will be priced to include the cost of first-class surface mail to any requester. Documents will be sent airmail to requesters upon payment of the appropriate airmail schedule for each document in addition to its stated price. The airmail rate schedule is shown below:

Airmail Rate Schedule—U.S. \$

Rate	A	B	C
U.S., Canada, Mexico	\$.40	\$1.00	\$1.30
Central and South America	\$.90	\$2.80	\$3.40
Elsewhere	\$1.00	\$4.50	\$5.50

Institutions and businesses may obtain documents by sending payment in advance or by an authorized purchase order. Individual orders must be accompanied by payment.

Three documents have already been placed in the RIC Document Depository. They are:

RIC-DD-1 Hartree-Fock Expectation Values and Parameters for the Atoms Rubidium to Nobelium, by S. Fraga and K. M. S. Saxena (1972) 121 pp. (U.S. \$12.10) [Airmail Rate C]

RIC-DD-2 Electronic Structure of Atoms, Hartree-Fock values of energies, interaction constants, and atomic properties for the ground states of the neutral atoms and first four positive ions from Rubidium to Nobelium, by S. Fraga and K. M. S. Saxena (1972), 94 pp. (U.S. \$9.40) [Airmail Rate B]

RIC-DD-3 Electronic Structure of Atoms, Hartree-Fock values of energies, interaction constants, and atomic properties for the ground states of dN_5O configurations and the first excited states of pN , dN_5O , dN_5^2 , fN_5O , and fN_5^2 configurations of the neutral atoms and first four positive ions from Rubidium to Nobelium, by S. Fraga and J. Karwowski (1973) 82 pp. (U.S. \$8.20) [Airmail Rate B]

Structure and Bonding

Volume 13 of *Structure and Bonding* (Springer-Verlag, New York, 1973) contains three review articles pertaining to the rare earths.

In the first article, pp. 53-98, R. Reisfeld makes use of ligand field theory in interpreting bonding, energy transfer and absorption and emission spectra of rare earths in glasses. The four main sections of the paper discuss the absorption and fluorescence spectra of rare earths in glasses arising from $f-f$ transitions, the absorption spectra of Ce^{+3} and Tb^{+3} arising from $f-d$ transitions, the charge transfer bands of Eu^{+3} and the energy transfer between rare earth ions in a glass matrix. Where possible, the author compares spectral data from borate, silicate, phosphate, germanate and tungstate glasses with aqueous solution and crystal data.

J. Felsche in the second paper,

Two RIC Reports Reprinted

Both IS-RIC-4, *Rare-Earth Metals in Steels*, and IS-RIC-5, *Thermochemistry of the Rare Earth Carbides, Nitrides and Sulfides for Steelmaking*, are in their second printing. Copies are free for the asking.

pp. 99-197, presents a detailed structural description of all rare earth silicate compounds known, except those more complex than ternary or those containing hydroxide groups or molecular water. The polymorphism of the silicates, variation of the R-O bond lengths and the coordination polyhedra are discussed as a function of lanthanide periodicity, and discontinuities are pointed out. The configuration and geometrical distortion of the SiO_4 tetrahedra are also of interest to the author in relation to RE periodicity. The article contains numerous diagrams and tables.

The last paper, "The Inner Mechanism of Rare Earths Elucidated by Photo-Electron Spectra," pp. 199-253, by C. K. Jørgensen, begins with quite an interesting historical introduction to the discovery of the rare earths and atomic spectra. The spectra of solutions and crystals are then discussed in terms of internal transitions in partly filled $4f$ shells, $4f-5d$ transitions and energy transfer. Refined spin-pairing energy theory is applied to spectra and also discussed in relation to standard oxidation potentials and the tetrad effect. The last section summarizes the photo-electron spectrometry of the rare earth compounds and the ionization energies derived therefrom.

Rare-Earth Information Center
Institute for Atomic Research
Iowa State University
Ames, Iowa 50010



RARE-EARTH INFORMATION CENTER NEWS

SUPPORTED BY INSTITUTE FOR ATOMIC RESEARCH
IOWA STATE UNIVERSITY / AMES, IOWA

Volume VIII

September 1, 1973

No. 3



PURDUE UNIVERSITY Rare Earth Group—Standing from left are Howard V. Lauer, John S. Polles, Denis J. Zalucha and Daniel E. Cox. Seated from left are Roland E. Menzel, Cynthia S. Crystal, James C.

Bellows, Francis K. Fong, Steven L. Naberhuis, Michael N. Sundberg and William A. Wassam.

Purdue University—

Rare Earth Spectroscopy Group

The rare earth spectroscopy group at Purdue University, under the direction of F. K. Fong, is concerned with two main areas of solid state research: (1) energy upconversion and non-radiative processes, and (2) statistical distribution of defect interactions in rare earth-doped single crystals. The research group is currently composed of two postdoctoral fellows, seven chemistry graduate students, and one senior undergraduate research assistant. Also associated with this group are Prof. M. M. Miller of the School of Electrical Engineering, Purdue, and visiting NATO scholar, Dr. J.-C. Bourcet of the Laboratory of Spectroscopy and Luminescence, University of Lyons.

In close collaboration, Miller and Fong have applied the basic theory of the nonadiabatic approximation to the radiationless relaxation of excited rare earth ions in crystals. Bourcet is working on certain aspects of energy transfer processes in rare earth phosphors. The basic theoretical aspects of radiationless relaxation and energy transfer processes are germane to the upconversion of infrared photons in rare earth-doped crystals.

In upconversion studies, two phenomena are emphasized: (1) the infrared quantum counter (IRQC) upconversion making use of a continuously tunable cw dye laser, and (2) energy upconversion via exciton annihilation processes. Most of the investigations have been carried out in lanthanide halides, and the spectroscopic studies are accompanied by an intense effort to grow optically pure single crystalline materials. As a result large single

(Continued on Page 6)

RIC Support For FY 1974

Three months into Fiscal Year 1974, RIC has already received contributions from more than half of the 40 rare earth companies that gave financial support to the Center last year. Many supporters have managed to increase their previous contributions, including some foreign firms who are taking advantage of the devalued U.S. dollar.

We are grateful to all our contributors because the Center is solely dependent upon private, commercial concerns for its monies. Iowa State University, through its Institute for Atomic Research, continues to supply logistical support for our activities.

Listed below are the 23 contributors to the Center to date. The

(Continued on Page 2)

Specific Heat

In "Analysis of Specific Heat Data in the Critical Region of Magnetic Solids," *J. Phys. Chem. Ref. Data* 2, 11-24 (1973), F. J. Cook uses an inverse power law to describe temperature dependence of magnetic specific heat. Advanced methods of data analysis were used to provide the best fit of parameters to the data collected. Cook found that the temperature dependence of the magnetic specific heat is not symmetric around the transition point (most materials have negative exponents below the transition point) and that the exponents do not correlate to material characteristics.

Experiments on magnetic specific heat in the critical region are tabulated chronologically. References for Gd, Dy, Tb, Sm, EuO, EuS, Dy₃Al₅O₁₂, DyAlO₃, TbAlO₃, GdAlO₃, and ErCl₃·6H₂O are included along with their critical temperatures.

EuO and Gd are discussed in the text, while the critical parameters for Gd, Tb, Sm, EuO, EuS, Dy₃Al₅O₁₂, and ErCl₃·6H₂O are given only in tabular form.

New Metal Phase

Face centered cubic (fcc) structures have been observed in thin films of Gd, Tb, Dy, Ho, Er and Tm by A. E. Curzon and H. G. Chlebek, *J. Phys. F*, 3, 1-5 (1973). In bulk form these metals usually have a hexagonal close-packed (hcp) structure.

For erbium the authors found that films 140Å thick had only the fcc structure, while 195Å films had both the fcc and the hcp structures. Thick films had only the hcp structure.

Rare earth metal vapors were condensed on thin carbon films supported on electron microscope grids and coated with a film of vacuum deposited carbon to reduce oxidation. The films studied had metallic reflectivity, the low electrical resistance of metal films, and transformed into oxides when heated in an intense electron beam.

Rare Earth Physics

If you are a postgraduate or a research physicist or someone just looking for a review on the subject of rare earth physics, then *Physics of Rare Earth Solids* by K. N. R. Taylor and M. I. Darby is for you. In this book the fundamental physical properties of rare earths in the solid state are described. Also, the theory used to interpret and correlate these properties is discussed.

The subjects dealt with include: ionic properties, structural behavior of the rare earth metals and alloys, band structures, magnetic properties, transport properties, and some properties of several of the rare earth compounds. The compounds covered include the oxides, chalcogenides, pnictides, and intermetallic compounds formed with the transition metals. Each of these general headings is broken down to cover a wide range of topics, and each chapter is well referenced.

Published by Chapman & Hall Ltd., London, in 1972, the book contains 308 pages and sells for £7 in the United Kingdom. It is also available from Halsted Press, a division of John Wiley, New York, N. Y. 10016, for \$22.00.

RIC Staff Changes

Bernie Evans, a recent graduate of Iowa State University, joined the RIC staff in June as a replacement for Nancy Kippenhan. Evans has a B.S. degree in chemistry and will be responsible for answering information inquiries, writing many of the *RIC News* articles, and maintaining our information files.

Mrs. Kippenhan, who has been with RIC for the last four years, will be leaving about mid-September for the Philadelphia area because her husband has finished
(Continued on Page 6)



Bernie Evans

RIC Support for FY 1974

(Continued from Page 1)

number in parentheses behind the names of contributors indicates the total number of years they have supported us.

Atomergic Chemetals Co., U.S.A. (2)

Cometals, Inc., U.S.A. (2)

Companhia Brasileira de Tecnologia Nuclear (formerly APROMON), Brazil (2)

Denison Mines Limited, Canada (2)

General Electric Co., Lamp Materials Research Laboratory (formerly Phosphor Research Laboratory), U.S.A. (4)

Th. Goldschmidt AG, Germany (5)

W. R. Grace & Co., U.S.A. (6)

Indian Rare Earths Ltd., India (5)

Kolon Trading Co., Inc., U.S.A. (1)

Leico Industries, Inc., U.S.A. (5)

Lunex Company, U.S.A. (4)

A/S Megon & Co., Norway (5)

Mitsubishi Chemical Industries Ltd., Japan (1)

Molybdenum Corporation of America, U.S.A. (6)

Nippon Yttrium Co., Ltd., Japan (4)

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Staff Writers

11th Rare Earth Research Conference

The 11th Rare Earth Research Conference has been scheduled for October 7-10, 1974, at the Park Place Hotel, Traverse City, Michigan 49684. The general plan of the Conference will follow that of earlier conferences.

The program will include sessions on Bioinorganic Chemistry, Solid State Chemistry, General Chemistry, Solution Chemistry, Coordination Chemistry, Metallurgy, Industrial Applications, Spectroscopy, Physics, Magnetic Properties, and Crystal and Molecular Structure. Special sessions on Geochemistry and Electron Spectroscopy for Chemical Analysis (ESCA) may be arranged. We hope that this conference can maintain the international flavor of the preceding ones.

Planning will be assisted greatly if each person who is interested in attending will complete and return before October 15, 1973, the preliminary information form included below.

(Detach)

11TH RARE EARTH RESEARCH CONFERENCE

Traverse City, Michigan, U.S.A.

October 7-10, 1974

Please complete the following and send before October 15, 1973, to:

Dr. Harry A. Eick
Department of Chemistry
Michigan State University
East Lansing, MI 48824 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)]

Book 1, \$7.60, Book 2-6, \$5.45 each.

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. \$13.60.

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., \$10.60 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.

NATO Advanced Study Institute on Analysis and Application of Rare Earth Materials, Kjeller, Norway, August 23-29, 1972.

Analysis and Application of Rare Earth Materials, O. B. Michelsen, ed., Universitetsforlaget, Oslo, Norway (1973). To be available shortly from Universitetsforlaget, P. O. Box 307, Blindern, Oslo 3, Norway, \$28.00.

Proceedings of the 10th Rare Earth Research Conference, Carefree, Arizona, April 30-May 3, 1973, available from Dr. Moeller, Department of Chemistry, Arizona State University, Tempe, AZ 85281, U.S.A., \$30.00.

Besides "doing time" as a pigment, gadolinium, because of its high neutron cross section, reduces the slow neutron flow in these rooms.

An article by B. E. Leonard, C. D. Penny, and V. L. McManaman, *Health Phys.* 23, 239-240 (1972), describes how the paint was tested. The results showed that ^{41}Ar production was reduced by a factor of 30 and residual activity in the room by a factor of 10. The paint was also tested for hardness and durability. It resisted peeling for a three year period in thermal neutron fluence of up to 10^{15} neutrons/cm 2 .

Prospector's Handbook

Prospectors need gamble no more when looking for rare earths almost anywhere this side of the moon. All they have to do is pick up a copy of the *Bibliography of the Geology and Mineralogy of the Rare Earths and Scandium to 1971*, Geological Survey Bulletin No. 1366 (1973) by J. W. Adams and E. R. Iberall. It is available from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402, for \$2.10 domestic postpaid and \$1.75 when purchased from the GPO Bookstore.

This bibliography contains 2092 entries concerning the geologic occurrence, geochemistry, and mineralogy of the rare earths including scandium. Some references dealing with beneficiation, physical properties, uses, and analytical chemistry are also listed; however, these topics are not covered extensively.

RIC-DD Acquisitions

RIC-DD-4 Matrix Elements for Many-Electron Atoms. Electrostatic Interaction Energies for One-Open-Shell Configurations, by J. Karwowski and S. Fraga (1973) 81 pp. (U.S. \$8.10) ([Airmail Rate B] see *RIC News VIII* [2] 8 (1973)).

employed. It will involve forwarding all of the European issues to Th. Goldschmidt AG. and all of the Japanese issues to Metal Traders Far East, Inc. They will then dispatch copies to subscribers in Europe and Japan. This method will be tested for a year and if no difficulties arise it should become a permanent procedure.

RIC thanks Th. Goldschmidt AG., and Molycorp and their Japanese representative, Metal Traders Far East, Inc., for providing this service.

Sm-Co-Cu Magnets

Variation of the magnetic properties of $\text{Sm}(\text{Co}, \text{Cu})_5$ alloys with temperature was the subject of a study by K. Kamino, Y. Kimura, T. Suzuki and Y. Itayama reported in *Trans. Jap. Inst. Metals* 14, 135-139 (1973). Optimum magnetic values were found in samarium-poor alloys having copper compositions from 0 to 75 at. %.

Differential thermal analysis (DTA) indicated that for copper compositions ranging from 16 to 66 at. %, a phase transformation occurred at approximately the same temperature, $\sim 920^\circ\text{C}$. Intrinsic coercive force was greatly enhanced when the samples were aged four hours at 400°C . It was also found that for maximum intrinsic coercive force a lower aging temperature could be used with increasing copper content.

Magnetic analysis revealed one or two Curie temperatures in the samples depending on the heat treating conditions. All samples exhibited the SmCo_5 Curie point, but for those with two transitions, the second was due to $\text{Sm}_2\text{Co}_{17}$. In cooling the samples down to -193°C no Curie point was observed for SmCu_5 . These observations underline the value of rapid cooling from the melt since slow cooling allows the growth of the $\text{Sm}_2\text{Co}_{17}$.

semiconductors and insulators, *J. Phys. Chem. Ref. Data* 2, 163-193 (1973). This report contains 1504 entries compiled from 723 sources.

Besides the energy band gap, the temperature at which the measurement was made, method of determination, form of the sample, and the transition involved are given. Information concerning temperature dependence of band gaps and special effects, such as luminescence, is included when available. An attempt has been made to cover the literature through 1971.

This compilation is of interest to rare earthers since compounds formed by the rare earths with Al, As, B, Cl, F, N, O, P, S, Sb, Se, and Te are included.

M Cubed

The proceedings of the 18th Annual Conference on Magnetism and Magnetic Materials held in Denver, Nov. 28-Dec. 1, 1972, are now available as *AIP Conference Proceedings No. 10, Magnetism and Magnetic Materials-1972*, C. D. Graham, Jr. and J. J. Rhyne, eds. (American Institute of Physics, New York, 1973). These proceedings are available as a cloth-bound, two-volume set for \$24.00.

More than 300 papers and abstracts are presented. Fully a third of the entries deal with rare earth metals, alloys, compounds, and complexes. Some of the properties discussed include magnetic ordering and resonance, magnetoelastic interactions, lattice effects, optical effects, and bubble domain physics.

The presence of the $\text{Sm}_2\text{Co}_{17}$ has a detrimental effect on the intrinsic coercive force.

A hypothetical Sm-Co-Cu ternary phase diagram is presented and it is proposed that decomposition in alloys containing 24-40 at. % copper occurs spinodally.

Rare Earth Spectroscopy Group

(Continued from Page 1)

crystals of rare earth chlorides and bromides can now be reproducibly grown in this laboratory.

The optical spectroscopic properties of the lanthanide ions are exploited in the study of impurity defect interactions. By means of Zeeman anisotropy, polarization, and lifetime measurements, the symmetry distributions of rare earth sites in compensated lattices at varying rare earth concentrations are determined. A compensated lattice is one in which the dopant impurity ion is compensated by an intrinsic ion defect. Typical examples are KCl:Sm^{2+} and $\text{CaF}_2:\text{Er}^{3+}$. The spectroscopically-determined symmetry distributions are then correlated to statistical mechanical calculations. The goal is the understanding of ion-defect pair formation and clustering of large defect centers in crystals.

These two areas of investigation have instigated related problems in molecular chemical physics. For example, the study of radiationless relaxation processes has led to a quantum statistical theory of activated rate processes such as atomic diffusion in solids and *cis-trans* isomerization in alkenes. Also, the understanding of energy up-conversion processes in rare earth materials has led to a new theory of the utilization of sunlight in photosynthetic processes.

Rare Earth Radioactive Arms

Monazite from the Van Rhynsdorp district of the Union of South Africa was probably the first radioactive ore used as a weapon. The high specific gravity of the heavy monazite fragments made this material ideal for slingshot stones which were used by bushmen in the area.

RIC Staff Changes

(Continued from Page 2)

his doctoral work at Iowa State. We will miss her enthusiasm, sparkling personality and scientific talents. We wish her the best in her new endeavors.

Rare Earths In the News

SOLAR LASER

A solar-activated neodymium laser system to test the possibility of direct optical communication via satellite using lasers is under development at the Air Force Avionics Laboratory, Wright-Patterson AFB, Ohio. The lasing material is a neodymium-doped yttrium aluminum garnet that can be activated by auxiliary lamps in the absence of sunlight.

AIRCRAFT TACHOMETERS

General Electric reports the development of aircraft engine tachometers employing cobalt-rare earth magnets that eliminate the need for rotor shaft bearings and permit a 30% reduction in weight of the instruments. GE claims improved reliability and service life for the RE-Co tachometers.

UNDERWATER RE DEPOSITS

A University of Wisconsin-University of Alaska team has located mineral deposits of rare earths, gold, tin, chromium and tungsten off of Alaska's shores. Expedition leader J. R. Moore of Wisconsin claims that the deposits could be mined profitably within five years and calls the regions off the Seward Peninsula "the most favorable sites for underwater mining in North America."

Rare-Earth Information Center
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MOLYCORP MOVES

Molycorp has established new headquarters in suburban New York. The new address is: Molybdenum Corporation of America, 6 Corporate Park Drive, White Plains, New York 10604. Their new telephone number is (914) 694-1700.

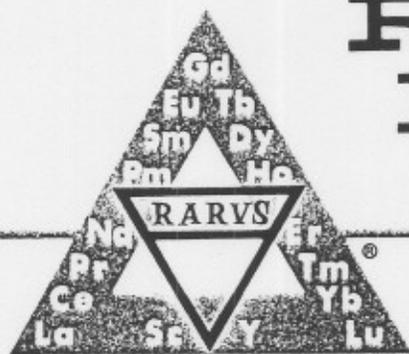
Energy Levels

R. C. Ropp and B. Carroll have undertaken a comparison of calculated vs experimental energy levels in the rare earths as a basis for studying $4f$ multiplets, *J. Phys. Chem.* 77, 339-346 (1973). They contend that of the three factors involved in interpreting free-ion spectra—crystal field effect, nephelauxetic effect, and symmetry effect—the apparent baricenter shift is determined chiefly by symmetry.

Observations of reflectance spectrum indicate that crystal field has only a minor effect and that the differences in baricenters is dependent upon the number of Stark lines observed. Only a fraction of the possible Stark lines appear because of the crystal symmetry limitations.

The degree of broadening of an energy level is related to crystal field perturbation. However, from the experimental half-widths it can be observed that two related terms of a multiplet are affected differently by the crystal field.

Finally, the authors point out that the density of states makes a correlation between calculated and experimental values difficult. They conclude that the calculated energy levels are more desirable as a reference state than the experimental (baricentered) free ion.



RARE-EARTH INFORMATION CENTER NEWS

SUPPORTED BY INSTITUTE FOR ATOMIC RESEARCH

IOWA STATE UNIVERSITY / AMES, IOWA

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No. 4

Euophysys RE Meeting Summary

The Euophysys Study Conference on the Physics of the Rare Earth Metals was held at the LO-Højskole, Elsinore, Denmark, Aug. 29-Sept. 1, 1973. The aim of the conference was to review the present experimental and theoretical understanding of the physics of the rare earth metals. This was accomplished through invited half-hour review papers followed by extensive discussions and by the presentation of five-minute contributed papers.

A. R. Mackintosh and J. G. Houmann, conference organizers, provided *RIC News* with the following summary of the conference.

"As a result of these lectures, the short communications and the extensive discussions which took place, our present understanding of the rare earth metals was reviewed and placed in perspective, while promising lines for future research were outlined.

"Our experimental understanding of the magnetic properties of the heavy rare earths has reached a very sophisticated level, so that subtle effects of, for example, anisotropic exchange interactions may be studied in great detail.

"On the other hand, the theoretical understanding of the magnetic interactions is less satisfactory and further theoretical and experimental studies of the origins of the crystalline electric fields are now required. These crystal fields are of particular importance in the light rare earths, which have been relatively little studied experimentally, although a fairly thorough understanding of praseodymium is beginning to emerge. The valence changes which occur in cerium and a number of rare earth compounds, due to the partial promotion of a 4f electron to the conduction band, give rise to a fascinating variety of physical phenomena which are not

yet understood in detail.

"During recent years a large amount of systematic work has been performed on well-characterized rare earth compounds, in which the environment of the rare earth ion has a decisive effect on the magnetic properties. A striking example of such behaviour is provided by ions whose crystal field ground-state is a non-magnetic singlet. Both the experimental and theoretical understanding of such systems contain obscurities which require further examination.

"In general, it was felt that the complex magnetic interactions to which rare earth ions may be subjected, and the resulting rich variety of magnetic properties, are most likely to be further elucidated in the future by measurements on single crystals of compounds and on dilute alloys, using the extensive selection of experimental techniques, such as magnetization and transport measurements, electron spin- and nuclear-resonance, photoemission and especially neutron diffraction, which were discussed at the conference."

(Continued on Page 4)

Explosive

An explosive transition in Gd-doped SmS has been discovered by Bell Laboratory scientists A. Jayaraman, E. Bucker, P. D. Dernier and L. D. Longinotti [*Phys. Rev. Letters* 31, 700-703 (1973)].

When a SmS sample, in which 15 to 22% of the Sm atoms have been substituted for by Gd atoms, is cooled to below 120°K (-150°C) the golden-yellow metallic crystals explosively disintegrate to a black powder. Upon warming the black powder regains its golden-yellow color.

The explosive nature of this material is due to a sudden expansion of the lattice from a lattice parameter of 5.68 to 5.82 Å (a volume change of 7.5%). There is no change in the crystal structure; both phases have the NaCl-type structure. The authors believe this expansion is due to the transfer of about half a valence electron per Sm atom to a localized 4f level which causes the lattice to expand because of this fractional loss of a bonding electron.

Season's Greetings
best wishes for the New Year
from RIC

Alcohol Intake

A study on the accumulation of yttrium and lanthanides in human and rat tissues by M. -L. Sihvonen has been published in *Ann. Acad. Sci. Fennicae, Ser. A, II. Chem.* [168] 1-62 (1972). Mrs. Sihvonen has analyzed by mass spectrometric methods the rare earth contents of several organs of humans who died suddenly. The organs studied were the spleen, kidney, liver, pancreas, hypothalamus, thyroid gland and heart.

In some samples rare earth distribution did not resemble that found in plants or rare earth minerals. One noticeable difference was the high samarium and europium contents of the spleen of alcoholics as compared to non-alcoholics.

On the basis of this observation, Sihvonen began experiments on two strains of rats by including rare earths in their diets and offering a free choice between alcohol and water. One strain preferred alcohol to water and the second abstained from alcohol. She found that the rare earth accumulation in the livers, kidneys, pancreases and spleens of both strains of rats to be about the same. But the alcohol consumption for both strains increased within a few days after beginning the rare earth-containing diet.

RIC-DD Acquisitions

New additions to RIC's Document Depository include two theses. Although we receive a number of theses each year they are usually not included in our Document Depository, since most of the information contained in a thesis also appears in a scientific journal. However, if a person sending us a thesis states that *most of the information in the thesis will not be published elsewhere, we will include it in our Document Depository holdings.*

RIC-DD-5 *A Model Useful in Interpreting the Behavior of Binary Oxide Systems: With Application to Rare Earth Catalysts*, by J. L. Moriarty, Jr., (1971) 12 pp + 1 glossy print (U.S. \$1.60) [Airmail Rate A].*

RIC-DD-6 *A Structural Study of Thin Films of the Lanthanide Metals, Hydrides, and Sesquioxides*, (in French) thesis by M. Gagnier (1973) 173 pp + 11 glossy prints (U.S. \$21.70) [Airmail Rate C].*

RIC-DD-7 *An Electron Microscope Study of the Twinned Sesquioxides of the Monoclinic Rare Earths*, (in French) thesis by C. Losier (1973) 56 pp + 25 glossy prints (U.S. \$15.60) [Airmail Rate B].*

*See *RIC News* VIII, [2], 8 (1973).

Shifty Characters

R. E. Sievers has recently rounded up several shifty characters from the Lanthanide gang who have "complexed" the scientific community for some time now and the police aren't even interested! For anyone who is interested, however, descriptions can be found in *Nuclear Magnetic Resonance Shift Reagents* edited by R. E. Sievers (Academic Press, Inc., New York, 1973) 428 pp. \$9.50.

Samples of the voluminous research currently being undertaken in the field of lanthanide shift reagents are included. Sixteen articles which cover the spectrum from theory to application, are based on the papers presented at the Symposium on the Chemistry of NMR Shift Reagents held at the 165th National American Chemical Society Meeting in Dallas, April 9-11, 1973.

A 50-page bibliography is divided into topics for easier access. Among them are fundamental aspects, chemical and physical properties, structural determinations, and general applications of lanthanide shift reagents.

Chemical Thermodynamics

In continuing a comprehensive revision of NBS Circular 500, the National Bureau of Standards has announced the publication of NBS-270-7, *Selected Values of Chemical Thermodynamic Properties, Tables for the Lanthanide (Rare Earth) Elements (Elements 62 through 76 in the Standard Order of Arrangement)*. (Editor's note: This arrangement of elements is unique to the NBS Circular 500 and NBS-270-X series.)

This report gives in tabular form the standard heats and Gibb's energies of formation, entropies, enthalpies, and heat capacities at 298.15°K and the heats of formation at 0°K for the rare earth elements, their ions, and a wide variety of rare earth compounds. Also included is a list of corrections for NBS Technical Notes 270-3, 270-4, 270-5, and 270-6. Unfortunately, no references are given to

RIC to Initiate Service Charge

Effective January 1, 1974, the Rare-Earth Information Center will collect a service charge for answering most information inquiries. A minimum charge of \$25 has been set to cover the expenses involved in answering most typical inquiries. If a particular inquiry requires more work the charges will be increased accordingly. If the charges are expected to be more than \$50 the requester will be notified and we will proceed with the request only upon his approval.

There are some exceptions to imposing the service charge: (1) No charges will be assessed to those companies which contribute to the support of RIC—at least up to the amount of their contribution. (2) Charges will be waived for those who certify they do not have resources available to pay for the service, e.g., students. (3) No charges will be made for (a) routine requests, such as information about a rare earth conference, (b) requests for information about the availability of commercial rare earth products or (c) requests for additional information on articles or material presented in the *RIC News*.

The rationale behind this change is that the users of the Information Center benefit from the information obtained, and thus they or their institutions should be willing to pay for these services.

We believe that one of our important functions is to make information available to *anyone who needs it*. It is for this reason that we have attempted to keep the service charges as low as possible and to waive charges when imposing them would constitute a hardship.

the original source of information which, in many cases, is quite valuable.

NBS-270-7 is available from the Superintendent of Documents, Government Printing Office, Washington, D.C. 20402, for \$1.25 Domestic Postpaid or \$1.00 if purchased at the GPO bookstore.

MEETING

OPTICAL PROCESSES OF PHOSPHORS

The Spring 1974 meeting of the Electro Chemical Society to be held in San Francisco, Calif., May 12-17, will include a symposium on the optical processes in rare earth phosphors, according to Melvin Tecotzky, symposium chairman.

Materials of interest are rare earth-activated materials in powder, single crystal, liquid, thin-film, or glass form. Tecotzky listed the following topics of interest: 1. relation of structure and spectra, 2. charge transfer, 3. energy transfer—up conversion, 4. radiative and non-radiative transitions, and 5. thermal and concentration quenching.

Papers of approximately 25-minute duration (including discussion) are being solicited. Direct inquiries to Tecotzky at United States Radium Corp., P.O. Box 409, Hackettstown, N.J. 07840, U.S.A.

Rare Earths In the News

BUBBLE MEMORIES

A bismuth thulium garnet film developed by RCA's physical electronics laboratory could make computer "bubble" memories a reality. The film forms magnetic "bubbles"—tiny cylinders of reversed magnetism—having greater light sensitivity than earlier films. This makes possible optical readout at about one hundred times the rate of nonoptical methods.

COMING ATTRACTIONS

Another new rare earth-cobalt permanent magnet, this one by Hitachi Metals Ltd., has proceeded to the commercial development stage. A samarium-cobalt material, the magnet has a maximum energy product of 23 MG·Oe (184 kJ/M³) thus making it the most powerful on the present market, say its makers.

(Continued on Page 4)

Langmuir Award

Prof. Harry G. Drickamer, department of chemical engineering, University of Illinois at Urbana-Champaign, has won the 1974 Langmuir Award in Chemical Physics for his use of very high pressure to study the electronic structure of solids, including new states of matter not attainable at lower pressures.

Drickamer's high pressure work on the rare earths includes x-ray, compressibility and electrical resistivity measurements on the metals and alloys and optical properties of the ions in CaF₂ and other saline hosts.

The Langmuir Award, sponsored by the General Electric Foundation, is given in alternate years by the American Chemical Society (ACS) and the American Physical Society. The ACS named this year's award winner and will present it to Drickamer in Los Angeles next April.



H. G. Drickamer

INTERMETALLICS

Persons interested in bulk magnetic properties and low temperature specific heats of rare earth intermetallic compounds will be naturally attracted to a book by W. E. Wallace entitled *Rare Earth Intermetallics*. In 266 pages Wallace reviews the magnetic and low temperature specific heat research of the last ten years covering the elements of the groups VIIIA - IVB. Approximately one-eighth of the book is devoted to theory while the remainder, richly illustrated with tables and figures, treats susceptibility, magnetic moments, Weiss constants, ordering temperatures, specific heats and third law entropies.

Rare Earth Intermetallics is available from Academic Press, Inc., New York (1973) for \$22.50.

Letters

To the Editor:

In the last issue of *RIC News* you reported on "a new metal phase" observed in thin films of Gd, Tb, Dy, Ho, Er and Tm, whose structures in bulk form are usually hexagonal close-packed. I think that the authors, A. E. Curzon and A. G. Chlebek, mislead when they attribute this new observed structure to a metal phase, because the lattice parameters they give for this face-centered cubic structure are practically the same as those of the corresponding dihydrides. The dihydrides have been extensively studied in the two last decades not only by our team, but also by other research workers in the United States and Eastern Europe. In a recent thesis (May, 1973), M. Gasgnier of the Faculté des Sciences d'Orsay concluded, as I do, that the observed structure is not that of a metal phase. [*This thesis is available as RIC-DD-6, see p. 2.*] I add that dihydride surfaces may show metallic reflectivity, and that these compounds possess a lower resistivity than the corresponding metals.

Sincerely yours,

R. Viillard

Directeur de Recherche au C. N. R. S.
Laboratoire de Chimie Physique
Université de Paris, France

(Dr. Paul Caro, Laboratoire de Terres Rares, Bellevue, France, who recently visited the Information Center also verbally expressed a similar view concerning the "new metal phase" reported by Curzon and Chlebek.—Ed.)

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Additional Support

Contributions from four more firms have come in since September when support from 23 companies was reported. Financial support was received from Brown, Boveri & Co., Ltd., Switzerland, and from GTE Sylvania, Inc., Chemical and Metallurgical Division, U.S.A., both contributing for the second time, from five-time contributor American Metallurgical Products Co., U.S.A., and from Research Chemicals, U.S.A., which is a six-year contributor to RIC.

Europhysics RE Meeting Summary (Continued from Page 1)

PROGRAMME†

Electronic Structures

The Electronic Structures of the Rare Earth Metals and Actinides, A. J. Freeman

Photoemission Studies of Rare Earth Metals, Y. Baer

Renormalized Atom Theory of Rare Earth Metals, R. E. Watson

Magnetic Structures and Magnetization

Magnetic Structures and Conduction Electron Spin Densities, R. M. Moon

Magnetic Form Factors in Rare Earth Metals and Compounds, T. O. Brun

High Field Magnetization of Rare Earth Metals, L. W. Roeland

Valence Changes

Theory of Valence Transitions, L. M. Falicov
The Electronic Properties of Ce, B. Coqblin
Demagnetization of Rare Earth Ions during Valence Changes, D. Wohlleben

Magnons and Phonons

Magnon Dispersion Relations and Exchange in Rare Earth Metals, R. M. Nicklow

Magnetoelastic Effects and Elastic Constants, J. Jensen

Phonons, Magnon-Phonon Interactions and Magnetic Anisotropy, J. C. G. Houmann

Singlet Ground States and Hyperfine Interactions

Magnetic Properties of Pr, B. D. Rainford

Singlet Ground States in Rare Earth Compounds, R. J. Birgeneau

Rare Earth Hyperfine Interactions, R. L. Cohen

Dilute Alloys and Domains

Electron Spin Resonance in Dilute Rare Earth Alloys, R. Orbach

Superconductivity and Electron Scattering in Dilute La Alloys, D. K. Finnemore

Magnetic Domains in Rare Earth Metals, T. Egami

Summary and Discussion

Theoretical, R. J. Elliott

Experimental, A. R. Mackintosh

†There will not be a published proceedings.

Replacement of calcium by lanthanide ions forms isomorphous heavy atom derivatives suitable for x-ray analysis of calcium binding proteins.

ANALYSIS AND APPLICATIONS

In an attempt to form a closer alliance between those working in analytical and technological areas of the rare earths, the NATO Advanced Study Institute sponsored a conference entitled "Analysis and Application of Rare Earth Materials" at Kjeller, Norway, in August 1972. Twelve papers dealing with chromatography, various spectroscopic methods, and neutron activation were presented. The uses of rare earth materials were discussed in eleven papers which covered optical, magnetic, ceramic, nuclear, catalytic and metallurgical applications.

The proceedings of this conference are now available in a book entitled *Analysis and Applications of Rare Earth Materials*, O. B. Michelsen, ed. (Universitetsforlaget, Blindern, Oslo, 1973) 375 pp., \$28.00.

RE in the News

(Continued from Page 3)

CATALYST MAKES TOP 100

A rare earth phosphate catalyst for the production of synthetic cresol and xylenols has made *Industrial Research's* list of the top 100 new products introduced during 1973. The catalysts, either lanthanum or cerium phosphate, made by Gulf Research & Development Co., eliminate the corrosion and pollution problems associated with the presently used caustic hydrolysis process and cut production costs in half.

Rare-Earth Information Center
Institute for Atomic Research
Iowa State University
Ames, Iowa 50010

Thermochemistry Report Issued

In continuing a study and analysis of the thermochemical data of rare earth compounds involved in the manufacture of steel, the Rare-Earth Information Center has just published *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* (IS-RIC-6). It contains a complete compilation of heats and free energies of formation of the rare earth oxides in the temperature range 25 to 2500°C. A two-color figure compares the free energies of formation of these compounds with common non-rare earth oxides. Revised and estimated formation values for the rare earth oxysulfides are presented, as well as a summary of the available thermochemical data for rare earth compounds containing B, Sn, Pb, Sb and As. For rare earth compounds containing P, Bi, Cu and Ag, the free energy of formation values were estimated.

This report is a follow-up to *Thermochemistry of the Rare Earth Carbides, Nitrides, and Sulfides for Steelmaking*, (IS-RIC-5), published August 1971. The preparation and publication of both IS-RIC-5 and IS-RIC-6 were sponsored by Molybdenum Corporation of America. Copies of either or both of these reports may be obtained free from RIC or from Molycorp, 6 Corporate Park Drive, White Plains, NY 10604, U.S.A.