Rare-Earth Information Center NEWS

SUPPORTED BY INSTITUTE FOR ATOMIC RESEARCH

IOWA STATE UNIVERSITY / AMES, IOWA

Volume III — September 1, 1968 — No. 3

Ames Laboratory––

Mössbauer, NMR Spectroscopy Group

Standing from left are R. Allan Reese, Dave Torgeson, Steve Smith, Don DeYoung, Roger Creel, Duane Will, Bill Smith and Tom Pinter. Seated from left are Barbara Lunde, Janet Smith and R. G. Barnes.

The research program of Crystal Physics Group V under Dr. Richard G. Barnes is concerned with measurements of nuclear hyperfine interactions in solids and with the utilization of such measurements in understanding the electronic and magnetic properties of solids.

Nuclear hyperfine interaction is concerned with the interactions of the nuclear magnetic dipole moment and of the nuclear electric quadrupole moment with the electromagnetic environment of the nucleus. The nucleus serves, in effect, as a microscopic probe for examining the interior of solids. Crystal Physics Group V is studying metals, alloys and intermetallic compounds, which often have interesting magnetic properties, by nuclear and electron spin magnetic resonance and the Mössbauer effect.

Mössbauer effect studies are being carried on by Dr. R. A. Reese, Postdoctoral Assoc., and Tom Pinter, Grad. Asst. Dr. Reese is studying the magnetic hyperfine interactions in the magnetically ordered state and the electric quadrupole interaction in the paramagnetic state of intermetallic compounds containing erbium and dysprosium. These measurements yield data on the crystalline electric fields acting on the metal ions in the lattice. Pinter is carrying on similar studies with thulium compounds, and is also making measurements of the effect of an applied magnetic field on the Mössbauer spectra. Helping out with the Mössbauer effect work are Stephen W. Smith, and Donald DeYoung, both new Grad. Assts.

Roger Creel, Grad. Asst., is investigating transition metal borides, by nuclear magnetic resonance (NMR) techniques using the B^{10} and B^{11} resonances as well as the metal nuclei resonances, e.g., Y^{89}. These

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Permanent Magnets Improved by RE's

In the June 1 issue of *Appl. Phys. Letters 12,* 361, E. A. Nesbitt and co-workers from Bell Telephone Laboratories at Murray Hill, New Jersey report on some new rare earth-containing permanent magnet materials. These materials are based on the hexagonal RCo_5 compounds, in which some of the Co atoms have been replaced by the Cu.

The Bell Telephone scientists found the coercive force is a maximum at $SmCo_3Cu_2$ in the $SmCo_{5-x}Cu_x$ system. In an as-cast alloy the coercive force was 10,500 Oe, increasing to 28,700 Oe upon annealing. This is the highest ever obtained on a sample at room temperature.

The calculated energy product of 9×10^6 G-Oe for $SmCo_3Cu_2$ is about twice that observed for $SmCo_5$ under the most favorable conditions. To date the authors claim to have obtained a value of 7×10^6 G-Oe for small solid pieces of $SmCo_3Cu_2$.

Rare Earths in Laser Development

The rare earths have been extensively used as basic materials for lasers since their appearance in 1950.

A look at the uses and applications of the several classes of lasers, and the present and future role of rare earths in laser development is provided in a review by B. I. Kogan and A. S. Kostygov in *Soviet J. of Non-Ferrous Metals 8,* (1), 109 (1967); 40 references are cited.

MEETING

ANNOUNCE SPEAKERS FOR RARE EARTH CONFERENCE

The Seventh Rare Earth Research Conference promises to have a heavy international flavor, according to J. F. Nachman, chairman.

In a partial list of seven invited speakers released in mid-July, six different countries were represented. Speakers who had accepted invitations included:

Frank Laves, Swiss Federal Institute of Technology, Zurich, Switzerland, "Radii and Volume Behavior of Rare Earths in Compounds."

Hans Nowotny, University of Vienna, Vienna, Austria, "Complex R. E. Metal Carbides and Nitrides."

George Brauer, University of Freidburg, Federal Republic of Germany, "Contributions to Solid State Chemistry of Rare-Earth Oxyfluorides."

Felix Trombe, Director, Central Research Laboratory, Bellevue, France, "Rare Earth Metals Distillation."

D.J.M. Bevan, University of Western Australia, Nedland, Australia, "New Yttrium and Rare-Earth Oxide-Fluoride Phases."

Karl J. Strnat, University of Dayton, Dayton, Ohio, USA, "Rare-Earth Cobalt Permanent Magnets."

Robert A. Penneman, Los Alamos Scientific Laboratory, Los Alamos, New Mexico, USA, "Composition of d and f Transition Metal Element Fluoride Complexes from Molar Refractivities."

Nachman also announced that there will be about 80 contributed papers presented at the conference, 13 of them from countries other than the USA. The breakdown of these 13 papers is six from France, two each from The Netherlands and India, and one each from Canada, Russia and Sweden.

For those of you who may not have received a formal announcement and would like more information about this year's conference, write: J. F. Nachman, Research Laboratories (R-1), Solar Division of International Harvester Co., 2200 Pacific Highway, San Diego, California 92112.

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measurements, when combined with resistivity and Hall effect, will improve our understanding of the electronic band structure of these materials.

A long-standing program of study, the NMR of the metals themselves, is being continued by Mrs. Barbara Lunde, Grad. Asst. She is measuring the temperature dependence of the magnetic shift parameters and quadrupole interaction in scandium and yttrium in strong magnetic fields (25 kG). Mrs. Lunde is also investigating the hyperfine interactions of scandium and of manganese in intermetallic compounds. Janet Smith is a new Grad. Asst. helping with these studies.

In another NMR experiment just started, William C. Smith, Grad. Asst., deals with the resonance of the thulium nucleus in paramagnetic compounds at high frequencies (200 megacycles), corresponding to magnetic fields at the nuclear site of the order of 10^6 G. These very high fields result from paramagnetic "anti-shielding" of the nucleus by the thulium electrons, and thesemeasurements will furnish new information on this unusual process.

Other members of the group who are working on non-rare-earth materials are: Duane Will, Grad. Asst., who has just completed a study of hydrogen diffusion in thorium hydrides using pulsed NMR methods (the so-called spin-echo experiment); David R. Torgeson, Assoc., who is responsible for significant advances in NMR instrumentation, in addition to making a continuing contribution to the study of NMR in the metals; and Richard Schoenberger, Grad. Asst., who is working on an experiment to measure the magnetic shift parameters of the NMR signal in paramagnetic nickel metal.

Radiation Indicating Glass

Soda lime glasses and/or borosilicate glasses with metal oxides added as coloring agents have been patented by F. L. Bishop, (U.S. Patent 3,359,125, April 1968). The metal oxides, consisting of manganese oxide, cobalt oxide, and cerium oxide are present in a range of 0.04 to 0.10, 0.002 to 0.005, and 0 to 0.2 wt %, respectively, depending on the total glass-forming oxide constituents.

This glass combination, which has a slight blue coloration, changes to a color which ranges from colorless to a light neutral gray on exposure to radiation.

NEW BOOKS

EUROPIUM

Europium, Volume VIII in the series Anorganische und allgemeine Chemie in Einzeldarstellungen, Springer-Verlag, Berlin, 1968, (164 pp., $9.75), is the first book which deals exclusively with the chemical and physical properties of one element of the lanthanide series. Written by S. P. Sinha, University of Leeds, the book discusses coordination chemistry, alloys and intermetallic compounds of europium and reviews their absorption and fluorescence.

Also included are separation techniques, spectroscopic properties and the possible uses of europium. This comprehensive book balances theoretical and experimental knowledge and should be of interest to our readers.

Special emphasis is focused on europium not only because of its dual valency, but also because of its recent industrial importance for use in color television, lasers, and nuclear energy.

Yttrium-90 is used in cancer therapy for the destruction of the pituitary gland.

SOCK IT TO'EM–

Lanthanides Gain Additional 4f Electron

The atomic volumes and atomic radii at O° K, and at pressures of 0.25, 1.0 and 4.0 Mbar (1Mbar=0.967 x 10^6 atm.) have been calculated by E. B. Royce from shock-wave data for many of the elements in the periodic table, *Phys. Rev. 164,* 929 (1967). By comparing the Z (atomic number) dependence of these experimental radii with the Z dependence of the radii calculated by using a Hartree-Fock method, he was able to deduce information concerning the electronic nature of many metals at these extremely high pressures.

For the lanthanide metals Royce noted an unusually high compressibility and that their radii are essentially the same, regardless of whether they are trivalent or divalent at atmospheric pressure. He concluded that the 5d electron of the normally trivalent lanthanide is promoted to the 4f level and thus they become divalent. The large compressibility is due in part to this promotion and to the compressible nature of the outer 6s electrons of these metals.

This state of affairs is interesting, especially in view of the fact that most of the gaseous free lanthanide atoms have an extra 4f electron and an outer configuration of two electrons in the 6s level (the exceptions are La, Ce, Gd, Tb, and Lu). From this we see that when there are no interactions between atoms (gaseous and free) or when the interaction is very strong (at high pressures) most of the lanthanides have an outer electronic configuration with only two electrons. This is in contrast to the standard state (O° K and 1 atm.) which has three outer electrons in the valence level (the exceptions are Eu and Yb), and which lies somewhere between these two extremes.

Is the normal trivalent state of the lanthanides anomalous from this perspective? Yes, we think so.

Patent Granted For RE Suboxides

A patent for rare earth suboxides of lanthanum, praseodymium, promethium, yttrium, gadolinium, dysprosium, holmium, erbium and lutetium has been granted to A. E. Miller of the University of Notre Dame. The suboxides have the

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Rare Earths in Drug Control

Two major problems in drug control are the manfacture of counterfeit drugs and the smuggling or illicit distribution of drugs, especially with the introduction of hallucinogens, amphetamines and tranquilizers. It is now possible to use neutron activation analysis to identify the source of drug products by analysis of trace elements added during manufacture or the natural tracers already present, according to L. M. Reynolds, *J. Pharm. Sci. 56*(4), 437 (1967).

Some of the identifying markers used are ^{139}La, ^{151}Eu, ^{152}Sm, ^{164}Dy, ^{174}Yb, and ^{175}Lu. Criteria for selection of additives depend on several factors: natural isotopic abundance, high neutron activation cross section and short half-life, interferences with other isotopes present, simplicity of the γ-ray spectrum, nontoxicity, cost and availability.

Amphetamine products from different manufacturers were used in Reynold's study. Seven additive tracers were prepared in physiologically safe concentrations from 10^{-6} to 2% depending on the natural contaminants present. The samples were then placed in a reactor with a flux of 2 x 10^{10} thermal neutrons/cm^2/sec. Counting was begun after ^{24}Na background no longer interfered with the measurments. Analysis showed that the amphetamines from different manufacturers were clearly and readily distinguishable from each other on the basis of contaminants present and their relative concentrations.

Mössbauer Effect

The recent book, *The Mössbauer Effect and Its Application in Chemistry,* No. 68 of the Advances in Chemistry Series published by the American Chemical Society, contained a review by A. F. Clifford on the applications of Mössbauer spectroscopy to lanthanide chemical problems. Clifford, who is from the Virginia Polytechnic Institute in Blackburg, noted that not many Mössbauer studies are of a chemical nature, but even so one can infer information which is of interest to the chemist.

Several examples are discussed to show how chemical information can be obtained from the isomer shift of the Mössbauer spectra of a series of compounds containing a given lanthanide. For europium compounds which contain divalent europium, negative isomer shifts are always observed, and for those which contain trivalent europium, positive shifts are obtained. Furthermore, the magnitude of the shift indicates the degree of the ionic nature of the solid.

Clifford made an attempt to determine the valence of Dy in intermetallic compounds from the Dy isomer shift.

Some problems which might be studied by Mössbauer techniques, Clifford suggested, are: non-stoichiometric systems, and the electronic states of catalysts and rare-earth dopants in phosphors.

RIC News
Vol. III. No. 3 September 1, 1968

published in
March, June, September and December
by
Rare-Earth Information Center
Institute for Atomic Research
Iowa State University

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Second-Class postage
paid at Ames, Iowa.

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Telephone: Area Code 515 294-2272
K.A. Gschneidner, Jr. . . . . .Editor
Charla Bertrand and W.H. Smith
Staff Writers

Rare Earths In the News

Nd-DOPED LASER

Westinghouse Electric has announced the development of a new laser material, Nd-doped calcium fluorophosphate, which promises to be an efficient generator of pure infrared laser light. Nd emission from the new material is said to be unusual compared to Nd emission from the more common yttrium-aluminum-garnet host crystal. Westinghouse claims the new material has the lowest energy threshold of any room-temperature laser crystal.

Nd-GLASS REFLECTOR LAMP

A reflector incandescent lamp made of pure Nd glass containing La_2O_3 has been developed by Airam of Helsinki, Finland. The Nd-glass acts as a yellow filter, thus accentuating red, pure green, blue and violet. The new lamp is claimed to have an 1800 hour average life under normal burning conditions.

EUROPIUM FOR CONTROL RODS

Molybdenum Corporation of America has contracted to supply approximately 500 lbs. of Eu_2O_3 to Union Carbide Corporation's Nuclear Division at Oak Ridge, Tenn., over the next three years. The Eu_2O_3 is used in control rods for the Oak Ridge National Laboratory's High Flux Isotope Reactor to assure even burning of the nuclear fuel.

Yttrium Oxide Capacitors

Electrical properties of thin-film yttrium oxide capacitors formed by different electrochemical techniques were compared by R. M. Goldstein, *Electrochem. Tech. 6,* 186(1968). In one method, yttrium metal is anodized in an electrolytic cell which allows for cutoff of a constant current density of 1.8 ma/cm^2. In the second method, reactive sputtering of the oxide is done under an argon atomosphere in a pressure-controlled sputtering chamber.

Comparisons of the anodized and sputtered capacitors indicated oxide growth rates of 50 Å/sec and 3 Å/sec, respectively; breakdown field strengths of 4.4×10^6 v/cm and 3.5×10^6 v/cm, respectively; and dielectric constants of 17 and 15, respectively.

Since the sputtering technique is a "dry" process, it produces a dissipation factor (0.004) twice as low as that formed by anodization. Anodized yttrium oxide capacitors, therefore, have great potential for future use in microelectronic applications.

Yttrium Ion Pump

Yttrium is a getter for producing an ultrahigh vacuum in an electrostatic, triode, getter-ion pump. Details were presented by D. R. Dennison at the 4th Triennial Internat. Vac. Congress, Manchester, England, Apr. 17-20, 1968. A ceramic core sublimator with an yttrium helical core was constructed and mounted to a pump system. Hydrogen admitted to the system at an yttrium sublimation rate of 6.5×10^{-7} g/sec yielded a pumping speed of 62.5 l/sec. This pumping speed corresponds with the formation of YH_3. If either nitrogen or oxygen gases were admitted to the system, the formation of a nitride or an oxide coating resulted. Neither the yttrium nor the coating would diffuse through each other, causing sublimation to cease.

From the data available, the use of the yttrium sublimator is limited to two situations; where only pure hydrogen with low concentrations of other getterable gases are used, and at very low pressures where hydrogen is the main residual gas and the poisoning rate of other gases would be slow.

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formula Re_2O_x where $2.900 < x < 3.00$.

Miller developed the compounds while employed at the Ames Laboratory of the U.S. Atomic Energy Commission, to which the patent has been assigned. (U.S. Patent 3,380,805, dated April 30, 1968.)

The compounds exhibit enhanced color intensity, electrical resistivity and magnetic properties as compared to the normal stoichiometric sesquioxides. Because of these enhanced characteristics, the Miller-developed suboxides have potential for use in microwave devices and magnetic cores, and could be utilized as semiconductors, thermoelectric generators and as elements in lasers.

More recently, H.K. Müller-Buschbaum, writing in J. *Inorg. Nucl. Chem. 30,* 895 (1968), reported he had prepared the hexagonal form of nonstoichiometric La_2O_{3-x} by heating La_2O_3 (α-form, hexagonal) *in vacuo* at high temperature. The author gave no further details of his work.

Promethium-147 is used in thermoelectric generators, industrial gages and industrial x-ray fluorescence.

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