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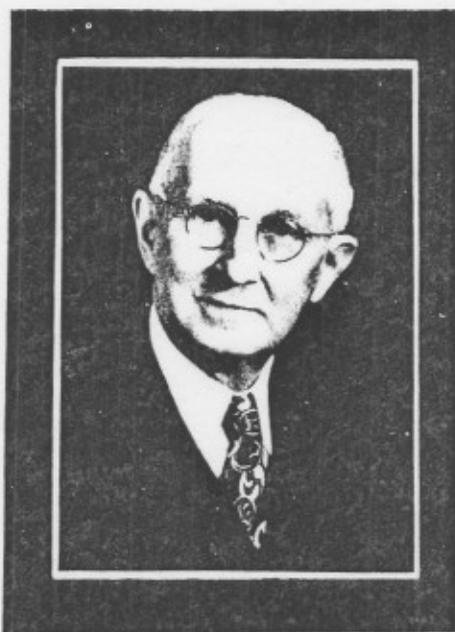
No. 2

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

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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.

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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.

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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.

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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_sO configurations and the first excited states of pN , dN_sO , dN_s^2 , fN_sO , and fN_s^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,

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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.