# 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 annhilation 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

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## *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, $Dy_3Al_5O_{12}$, $DyAlO_3$, $TbAlO_3$, $GdAlO_3$, and $ErCl_3 \cdot 6H_2O$ 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, $Dy_3Al_5O_{12}$, and $ErCl_3 \cdot 6H_2O$ 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 resistence 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

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

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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)
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Wako Bussan Co., Ltd., Japan (5)

RIC News
Vol. VIII, No. 3 September 1, 1973

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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Bernie Evans, Nancy Kippenhan and W.H. Smith
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)

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## 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.

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|---|---|
| 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 $Sm(Co, Cu)_5$ 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, ~920°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 $Sm_2Co_{17}$. 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 $Sm_2Co_{17}$. The presence of the $Sm_2Co_{17}$ 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.

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.

Rare Earth Spectroscopy Group

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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 $CaF_2:Er^{3+}$. 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."

## 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 4*f* 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.

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