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EDITOR'S TRIP REPORT

Elementary Excitations, Valence Fluctuations, Intermetallics

During the past summer, the editor made two trips to Europe to attend two conferences and a workshop, and to visit three European laboratories.

Elementary Excitations Workshop

In late May and early June a Workshop on Elementary Excitations and Fluctuations in Magnetic Systems was held in the picturesque countryside of northern Italy at the Cappuccini Conference Center in San Miniato, which lies half way between Pisa and Florence. Approximately 50 persons were in attendance and 39 papers (most of which were invited) were presented at the 4½ day meeting. An interesting aspect of this Workshop was that approximately ¾ of the papers were presented by theorists and the rest by experimentalists. The proceedings of the Workshop, *Magnetic Excitations and Fluctuations*, S. W. Lovesey, U. Balucani, F. Borsa and V. Tognetti, eds., has just been published by Springer-Verlag.

An elementary excitation is the quantum of energy of a vibration or a wave. These include photons, phonons, plasmons, magnons, paramagnons, polarons, and excitons.

Many of the papers dealt with lower dimensional materials: (1) linear (or chain) materials, e.g. Heisenberg (classical) and Ising magnetic chains, one dimensional solitons, and one dimensional antiferromagnets; and (2) planar materials, e.g. surface magnetism, two dimensional solitons, and classical two dimensional behavior. Several of the papers on three dimensional materials included some rare earth and actinide materials—CeBi, CeSb, PuP, PuAs, PuSb, CeSn₃, CeSi_{1.86}, RCo₂ (R = Sc, Y, Lu), UAl₂, Er and Ho in Ag solid solutions, HoRh₄B₄, CeAl₂, and EuO.

One of the best papers presented at the workshop was that by P. A. Lingard (Riso, Denmark), who gave a brief overview and tied together all aspects of the topics and showed how they are interrelated.

Valence Fluctuations Conference

The 4th International Conference on Valence Fluctuations (ICVF) was held in Cologne, West Germany in August at the Physikalische Institut, Universität zu Köln. The days were long and exhausting, but exciting and controversial. Each day began with five talks in the morning followed by lunch. After lunch four hours were set aside for the poster presentations (~ 50/day). This was followed by a snack at the conference site, and an evening session consisting of two or three more talks and

then a panel discussion. The only deviation from this schedule occurred on the evening of the conference dinner.

There were several controversies: the definition of valence, whether or not p-wave superconductivity has been found, and the various theories that are being used to explain the observed phenomena.

The valence controversy arose several years ago when D. Wohlleben (a conference co-chairman) proposed a valence scheme based on L_{III} spectra of compounds. The major problem arose when Wohlleben claimed that Ce and Eu have, respectively, maximum valences of 3.6 in CeO₂ and of 2.5 in Eu₂O₃. Most believe that Ce has a valence of 4 in CeO₂ and Eu of 3 in Eu₂O₃. A lot of interesting work has been generated by scientists trying to prove or disprove Wohlleben. Other high energy spectroscopic methods give similar results with the

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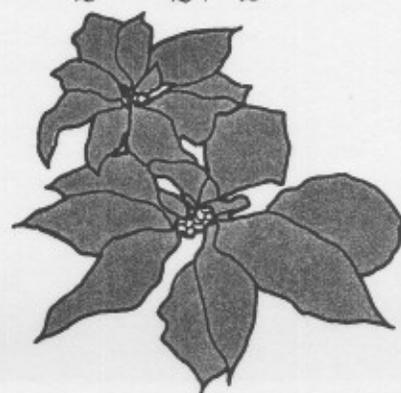
ORGANIC SYNTHESIS

In the past few years, there has been an explosive increase in the number of papers on the use of lanthanides in organic syntheses. Most chemists are familiar with lanthanides as NMR shift reagents and with the methodology found in cerium(IV) oxidations. Since these aspects of organolanthanide chemistry have already been reviewed, Nicholas R. Natale decided to focus his review [*Org. Prep. Proced. Int.* 15, 387-424 (1983)] on the exciting chemistry involving the lanthanide(II) and (III) oxidation states, as well as organolanthanide chemistry of particular interest to chemists involved with organic syntheses. This review covers the literature through early 1983 and explores the discovery of a new area of organic methodology.

In the lanthanide(II) oxidation state, the driving force for most reactions is electron transfer and the formation of the lanthanide(III) species. The reactions involve reductions or reductive couplings. Samarium might be the best rare earth for reactions of this type since its reduction potential is reported to be among the highest for species soluble in organic media: E_o aq Sm²⁺/Sm³⁺ = 1.55 V.

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*Greetings of the Season
and best wishes for the New Year*



Editor's Trip

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exception of the $M_{4,5}$ spectra (G. Kaindl, Freie Universität, Berlin), which are in good agreement with the "low energy" type measurements that have been used since ~1950 to define valence—lattice constants, volume changes, and magnetic susceptibilities. The major problem with the high energy spectroscopies is that when a phonon displaces an electron it disturbs the entire electronic structure and the resultant observed spectra is that of some excited state and not the undisturbed ground state.

Another problem in the valence fluctuations field is the use of the terms "intermediate valence" and "mixed valence." Many scientists incorrectly use these terms interchangeably according to P. Wachter (Eidgenössische Technische Hochschule, Zürich). A mixed valence system is one where there are two distinct valence species in a compound, each occupying a specific lattice site, i.e. Fe^{2+} and Fe^{3+} in Fe_3O_4 . An intermediate valence system is one in which each ion has a non-integral valence.

The second major controversy centered on heavy ion Fermion superconductors. F. Steglich (Technische Hochschule, Darmstadt) claimed that all of the experimental evidence for $CeCu_2Si_2$ based materials indicates that it is a singlet or s-type superconductor. Measurements on the uranium based heavy Fermion superconductors, carried out at Los Alamos National Laboratory (Z. Fisk, J. L. Smith, G. Stewart) and Eidgenössische Technische Hochschule, Zürich, (H. R. Ott) show unusual behaviors that are inconsistent with s-like superconductivity, and could be due to p-wave superconductivity. C. Varma (AT & T Bell Laboratory), on the other hand, believes that UPt_3 and UBe_{13} , and even $CeCu_2Si_2$ are p-like superconductors.

The Conference Proceedings will be published as a special volume of the *Journal of Magnetism and Magnetic Materials*.

Intermetallic Conference

The Conference on Electronic Structure and Properties of Rare Earth and Actinide Intermetallics was held in the town of St. Pölten, about an hour's train ride from Vienna. The Conference ran for 3½

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days. There were generally five papers in the morning, and after lunch, two hours were set aside for posters and this was followed by four more oral presentations. There were 33 talks and ~150 posters. About 200 persons attended this Conference, and about ½ of these had also attended the Valence Fluctuation Conference in Cologne. Of the invited speakers, 4 talked at both Conferences—P. Wachter (Eidgenössische Technische Hochschule, Zürich), James L. Smith and Z. Fisk (both of Los Alamos National Laboratory), and K. A. Gschneidner, Jr. (Ames Laboratory, Iowa State University). A number of poster presentations of nearly identical subject matter were presented at both Conferences. As a whole, however, there was not a great deal of duplication of material. There was a higher percentage of Eastern European scientists at St. Pölten than at Cologne and not nearly as much controversy.

The major differences in content of the two meetings can be summarized as follows: The Rare Earth/Actinide Conference had a much larger fraction of papers on magnetism and actinides, but much less on high energy spectroscopies and valence fluctuation materials.

University of Genoa, Genoa, Italy

The editor had visited the Institute of Physical Chemistry 18 years ago and since that time the staff has approximately doubled. The Institute is still headed by Professor Aldo Iandelli, but he will be retiring in a few years when he turns 70 years old. The main emphasis of their research is concerned with crystallography and phase diagram research on the alkaline earth, rare earth and thorium metals alloyed with the late transition metals and the early non-transition metals. Over the past 10 years, their research efforts have been expanded to include thermodynamic measurements and studies on mixed valence materials.

Some time was also spent visiting Professor Riccardo Ferro's Institute of General Chemistry. Professor Ferro and his colleagues are carrying out research on phase diagrams and thermodynamic properties of the intermediate phases formed in rare earth/nontransition metal systems. The work at the two Institutes complement one another.

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Laboratory of Chemical Metallurgy of Rare Earths, National Center of Scientific Research, Meudon (Paris), France

The visit with Dr. Annick Percheron-Guegan at the Rare Earth Laboratory centered on our joint research efforts on hydrogen in rare earth intermetallic compounds. Most of the work is concerned with the $LaNi_5$ based alloys with non-rare earth metals substituted for Ni, and it involves pressure-volume, neutron diffraction, magnetization, catalysis, EXAFS, and low temperature (1-20 K) heat capacity measurements. Some of the studies are carried out on the intermetallic compound before and after it has been hydrided.

Technical University of Darmstadt, West Germany

The visit to the Technical University was made between the Cologne and St. Pölten Conferences. Our discussions centered on heavy Fermion superconductivity in $CeCu_2Si_2$ based materials and spin fluctuations while visiting Professor Frank Steglich's solid state physics group. Also visiting at the same time was Dr. T. Satoh from the Physics Department, Tokoku University, Sendai, Japan. This was a real plus because this gave us a chance to discuss complementary research being carried out in Sendai and Ames on the $CeSi_3$ system ($x \leq 2$).

Russian Book

The RIC recently received a copy of *Crystal Chemistry of Intermetallic Compounds of the Rare Earth Metals*. The book is authored by E. I. Gladyshevskii and O. I. Bodak. It was published in 1982 by Izdatel'stvo PRI L'vovskom, Gosundavstrennom Universitete, Izdatel'stro Ob'endineniya "Vischcha Shkola," L'vov.

The book is divided into three parts. The first part lists over 2,100 binary compounds of the rare earths with 27 other elements. Also listed are many ternary and quaternary systems. It lists the structure type, lattice parameters, and references for each compound. The second part describes the structure types with two dimensional projections of many of them. The third part has a short discussion on the relationships between different systems. The book concludes with a bibliography of 1,702 citations on the subject of rare earth intermetallic compounds.

of the *f*-transition (Lanthanide and Actinide) and Related Elements (2nd I.C.L.A.) will be held September 1-5, 1986 in Lisbon, Portugal, in the Gulbenkian Foundation Centre. A provisional list of topics includes: coordination and organometallic chemistry, theory and spectroscopy, reactivity and catalysis, solid state chemistry, analytical chemistry, and industrial applications. A Conference Proceedings, consisting of invited and contributed papers, will be available before the conference. For additional information, contact the Scientific Conference Secretary, Dr. A. Pires de Matos, Dep. de Quimica, Instituto de Energia, LNETI, Estrada Nacional 10, 2686 Sacavem Codex, Portugal.

ICCF 5

The RIC has received a notice that the deadline for submittal of abstracts to the 5th International Conference on Crystalline Field and Anomalous Mixing Effects in *f*-Electron Systems (ICCF-5) is December 20, 1984. The dates of the conference are changed also by one day to April 15-18, 1985. For further information see *RIC News* XIX [2] 2 (1984) or write to Professor O. Sakai, Conference Secretary, Department of Physics, Faculty of Science, Tohoku University, Sendai 980, Japan.

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ling of acid chlorides to yield α -diketones and aromatic aldehydes or ketones to yield pinacols.

Lanthanide(III) additions are used to halt a reaction at a desired step or as a regioselective reagent. For example, it has been found that cyclopentenone when reduced with NaBH_4 alone forms cyclopentanol, but when RCl_3 ($\text{R} = \text{Ce}, \text{Sm}$ or Yb), is added the reduction ends at the allylic alcohol step with yields of ~95 percent. This process is known as the Luche reduction and recently has been used in the synthesis of many complicated organic compounds including prostaglandins, epi-pentenomyins, casbene and bertyadinol.

Another use of lanthanide(III) compounds is the formation of acetals using ErCl_3 or YbCl_3 . An example is the synthesis of a bicyclo[5.1.0] enone, a versatile intermediate, by selective acetalization. Other uses are the nitration of phenols using $\text{La}(\text{NO}_3)_3$ as a catalyst, oxidation of benzoin to benzil by $\text{Yb}(\text{NO}_3)_3$, bromination of benzylic hydrocarbons using $\text{La}(\text{OAc})_3$ as a catalyst, and dehalogenation of α -halocarbonyl compounds by CeI_3 .

The final use described in the review is the use of lanthanide(III) as catalysts in the synthesis of heterocyclic compounds. One example is the formation of 4-substituted-2,6-dimethyl pyrimidines from monodentate cyclic secondary amines and acetonitrile. Another exciting discovery is that trace amounts of europium shift reagents act as catalysts for mediating hetero Diels-Alder reactions. For example, a trace amount of tris-(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium ($\text{Eu}(\text{fod})_3$) acts as a catalyst in the stereospecific synthesis of carbon branched pyranosides. Endoselectivity is maintained, and three chiral centers are established through this suprafacial endo-cycloaddition process.

The last section of the review treats the miscellaneous uses of organolanthanides with special emphasis on those transformations of special interest to the synthetic organic chemist. Among the reactions discussed are the

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(the rare earths), bringing the number of published volumes to 27.

Volume C7 covers the sulfides, oxide sulfides, and alkali thiometalates of the rare earths. Published in 1983 by Springer-Verlag, Berlin-Heidelberg, and containing 607 pages, the book costs DM1926 (~U.S.\$648). The *Gmelin Handbooks* may be ordered from Springer-Verlag, 4005-Marketing Gmelin, Heidelberger Platz 3, D-1000 Berlin 33, West Germany.

The first part of volume C7 (132 pages) is devoted to general and comparative discussions of the rare earth sulfides, their preparation, and various properties (e.g. chemical, physical, mechanical, electrical, optical, thermal, magnetic, thermodynamic, and crystallographic). The bulk of the book (425 pages) is devoted to the discussion of the individual R_2S_3 and $(\text{R},\text{R}')_2\text{S}_3$ compounds. Most of this portion of the book is devoted to the systems involving samarium (210 pages) or europium (88 pages).

The long section on samarium is due to the large number of papers published on SmS in the intermediate valence state. This state may be effected by application of pressure, alloying, or polishing SmS surfaces. The experimental and theoretical work (primarily the electrical properties and the electronic structure of SmS and its solid solutions) is reviewed here, along with theoretical models for the mixed valence state.

The section on ferromagnetic EuS mainly deals with the magnetic properties and the electronic structure. EuS and the other europium chalcogenides are considered model substances for Heisenberg magnets.

Crystallographic and magnetic properties are the main topics of the small section on rare earth oxide sulfides. These materials are utilized as phosphors, lasers, and magnets. A comprehensive discussion of rare earth luminophors and lasers is planned for a later volume of the *Gmelin Handbooks*.

The small section on the alkali thiometalates of the RMS_2 composition deals with their preparation and crystallographic properties.

\$\$ SPONSORS \$\$

The second quarter of fiscal year 1985 has been a pleasant one. We are still facing a financial crisis and an effort is being made to find new benefactors. The response has been heart warming. We had 9 new companies join our family of sponsors and another rejoin the family after an absence. Added to the 10 regular, highly-valued sponsors that renewed their support, this brings the number of companies that pledged support this quarter to 20. We are ahead of last year's pace and wish to thank everyone for their contribution to the RIC. If your company is involved with the production or application of rare earths there is still plenty of room on our list of sponsors so inquire as to how you can join our growing family.

The 20 companies that gave this quarter are listed below with the number of years that company has been a sponsor of the Center given in parentheses.

- Aran Isles Chemicals, Incorporated, U.S.A. (1)
- Cabot Corporation, U.S.A. (2)
- CERAC, Incorporated, U.S.A. (9)
- Eastman Kodak Company, U.S.A. (8)
- Globe Metallurgical, Incorporated, U.S.A. (1)
- Th. Goldschmidt AG, West Germany (16)
- Haber, Incorporated, U.S.A. (1)
- Iron Ore Company of Canada, Canada (1)
- Mitsubishi Metals Company, Limited, Japan (1)
- Molycorp, Incorporated, U.S.A. (17)
- NUCLEMON-Nuclebrás de Monazita e Associados, Limited, Brazil (11)
- The Ore and Chemical Corporation, U.S.A. (1)
- Rhone-Poulenc, Incorporated, U.S.A. (5)
- Rhone-Poulenc Specialites Chimiques, France (15)
- Santoku Metal Industry Company, Limited, Japan (15)
- Sherritt Gordon Mines Limited, Canada (1)
- Shin-Etsu Chemical Company, Limited, Japan (15)
- Sumitomo Light Metal Industries, Limited, Japan (1)
- U.S.R. Optonix, Incorporated, U.S.A. (15)
- Vacuumschmelze GmbH, West Germany (1)

CONFERENCE CALENDAR

Intl. Rare Earth Conf.: Materials and Chemistry (IREC 85)
Zürich, Switzerland
March 4-8, 1985
RIC News XVIII [3] 3 (1983) and *XIX* [3] 2 (1984)

*5th Intl. Conf. on Crystalline Field and Anomalous Mixing Effects in *f*-Electron Systems (ICCF 5)
Sendai, Japan
April 15-18, 1985
This issue and *RIC News XIX* [2] 2 (1984)

8th Intl. Workshop of Rare-Earth Magnets and Their Applications and 4th Intl. Symp. on Magnetic Anisotropy and Coercivity in Rare Earth-Transition Metal Alloys
Dayton, Ohio, U.S.A.
May 6-9, 1985
RIC News XIX [1] 3 and [3] 2 (1984)

Materials and Mechanisms of Superconductivity
Ames, Iowa U.S.A.
May 29-31, 1985
RIC News XIX [3] 2 (1984)

Magnetic Materials for Applications (M.M.A. 85)
Grenoble, France
June 3-5, 1985
RIC News XIX [3] 2 (1984)

Int. Conf. on Rare Earth Developments and Applications and Intl. Fair for Rare Earths and Their Application Products
Beijing, People's Republic of China
September 10-14, 1985
RIC News XIX [2] 2 (1984)

17th Rare Earth Research Conference
Hamilton, Ontario, Canada
June 8-12, 1986
RIC News XIX [2] 3 (1984)

*2nd Intl. Conf. on the Basic and Applied Chemistry of the *f*-Transition (Lanthanide and Actinide) and Related Elements (2nd I.C.L.A.)
Lisbon, Portugal
September 1-5, 1986
This issue

*New listing or change

Rare Earthers Reorganization

The Rhone Poulenc Group of France has announced a commitment to expand its United States activities. According to Loik LeFloch-Prigent, president of the French group, Rhone-Poulenc Inc. of Monmouth Junction, New Jersey will be responsible for the expansion.

Jean-Paul Marx, Rhone-Poulenc Inc.'s chief operating officer, said the company has been reorganized into the following divisions: chemical market, agricultural market, pharmaceutical market, and systems division.

Dr. Frank P. Darmory has been appointed corporate vice president and will head the chemical market area. This area will encompass the efforts of the specialty plastics, organic chemicals, and special products divisions, which includes the production and marketing of rare earth products. Dr. Darmory had been vice president/general manager of the specialty plastics division.

Synthesis

(Continued from page 3)

Ziegler-Natta polymerization, β -alkyl-transfers, and C-H bond activations. Of all the carbon-hydrogen bonds, the most difficult to activate are those of methane with a bond energy of 104 kilocalories per mole. The first unequivocal illustration of the activation of a methane C-H bond was reported using an organolutetium complex.

This review is written in such a manner that even a chemist not up-to-date on his organic chemistry can understand what is being said in most instances. Much of the exploratory ground work has been done and the door opened to a new and promising methodology for organic syntheses.

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