RARE-EARTH INFORMATION CENTER NEWS

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EDITOR'S TRIP REPORT

JUNE—GERMANY—WET
JULY—FRANCE—HOT

Although the two *three* letter words more or less summarizes the weather experienced by the editor in his brief two week visit to Karlsruhe, Munich, Paris, and Grenoble, the science was super and the hospitality was even greater.

The first stop was Karlsruhe, where I attended the IV Conference on Superconductivity in *d* and *f*-Band Metals. The highlights of the Conference were the new developments in organic superconductors, superconducting oxide phases (e.g. $BaPb_{1-x}Bi_xO_3$), the use of Raman scattering and tunneling to probe superconducting materials, superconductivity in epitaxial metal film sandwiches, and superconductivity in "heavy Fermions" (i.e. highly enhanced magnetic materials). The last topic was the only one which dealt with a rare earth material - $CeCu_2Si_2$ which exhibits, according to Dr. F. Steglich (Darmstadt), many unusual properties at low temperature before becoming superconducting at 0.5 K. Other work reported on rare earth materials included the Chevrel phases, ternary phases (e.g. RRh_4B_4), materials in which magnetism and superconductivity coexist, and a variety of other compounds. About 25% of the papers dealt with rare earth materials.

A four hour train ride to Munich and a 45 minute drive brought the editor to Garching, a science center which includes a nuclear research reactor, the low temperature laboratory of the Bavarian Academy of Science (Zentralinstitut für Tieftemperatureforschung - ZTTF) and the Technischen Universität München (TUM). Discussions were held with Drs. K. Neumaier (ZTTF) and H. Wipf (TUM) concerning joint research on hydrogen tunneling in lutetium metal. Other rare earth research is being done by Dr. E. Umlauf (ZTTF) on mixed-valent materials.

The next stop was Paris, where a half day was spent visiting the theoretical physicists Drs. M. T. Beál-Monod, B. Coqblin and R. Jullien of the Universitë de Paris-Sud. Our discussions included spin fluctuations in highly enhanced paramagnetic materials, magnetic behavior of rare earths and one dimensional solids.

The main reason for the editor's European trip was to discuss joint research on $LaNi_5$-base hydrogen storage materials with French scientists at Meudon (a Paris suburb) and Grenoble. For the past year and a half, the editor has been working with Dr. A. Percheron-Guegon of the C.N.R.S. (Centre National de la Recherche Scientifique) Laboratoirie de Chimie Metallurgique des Terres Rares and her student, C. Lartigue, who is doing her doctoral thesis research at the Institut Laue-Langevin in Grenoble. The alloys being studied are prepared either at Ames or at Meudon. The alloys are characterized and the hydrogenation behavior is determined at the respective laboratory where the samples were prepared. Neutron diffraction and magnetization studies are being carried out at Grenoble, while the low temperature heat capacity measurements are being made in Ames.

Other interesting research on a variety of rare earth materials is being carried out by Drs. J.-C. Achard, C. Godart, R. Ravot and P. Caro at the C.N.R.S. laboratories in Meudon. While in Grenoble the magnetic behavior of a variety of rare earth compounds are being investigated by Drs. R. Lemaire, B. Barbara and coworkers at Laboratoire Louis Néel,

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E.S.R. REVIEW

S. E. Barnes has reviewed at both a relatively elementary and more advanced level the interpretive theory of the electron spin resonance of magnetic ions in metals. Whenever possible the theoretical discussions are illustrated by experimental examples. The initial development is based on the Block-Hasegawa equations and the relationship of the advanced theory to this elementary theory is emphasized.

The review, published in *Advances in Physics* **30**, 801-938 (1981), has the following sections:
Introduction; Preliminary theoretical description of E.R.S.; Survey of experimental spectra; Block-Hasegawa equations; Solution of Block-Hasegawa equations; Multimagnetic impurity experiments; The skin depth problem; Analysis of exchange, hyperfine, and crystal field parameters; Redfield theory for magnetic ions in metals; Ionic and virtual bound state models; Implications of microscopic theory of magnetic impurities for E.S.R.; Kondo effect; and Outstanding problems and future developments. The review closes with a bibliography of 203 references.

In conclusion Barnes makes some recommendations as to how E.S.R. can be more widely and wisely utilized. Among these are: E.S.R. in metals could be more widely used as a complement to resistivity, susceptibility, and other measurements of dilute magnetic alloys; and E.S.R. can give valuable information about the valence state of several rare earth ions which have two possible valence states when substituted in a metal—one state is magnetic the other is not.

Barnes also gives some areas where future developments are likely to occur. Some of these areas

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Seventh Rare Earth-Cobalt Permanent Magnet Workshop

The 7th International Workshop on Rare Earth-Cobalt Permanent Magnets and Their Applications will be held in Beijing, China on September 16-18, 1983. It is being sponsored by The Chinese Society of Rare Earth. The program will include oral presentations of invited and contributed papers, poster sessions, and an exhibition of rare earth related material. Invited papers and all accepted contributions will be printed in the proceedings (in English) and distributed to participants. The official language will be English and Chinese interpreters will be provided.

The working meetings will cover all aspects of the topic and tentative titles of the sessions are:

1. Theory and basic studies of rare earth-transition metal compounds and their hard-magnetic properties.
2. Characterization and properties.
3. Applications including uses in medicine.
4. Materials, processes, and production of magnets.

The choice of China for the seventh workshop is appropriate. Many laboratories in China have had success in advancing the scientific understanding, the production metallurgy, and engineering applications of rare earth permanent magnets. Several magnet types manufactured in China are commercially available in other countries. The identification and present development of the world's largest rare earth ore body near Baotou will affect the future raw material supply situation, especially for samarium.

For more information, a preregistration form should be mailed before December 1, 1982 and digests of papers (about 50 words) should be sent by January 15, 1983 to the general secretary of the seventh workshop, Ms. Fang Ying whose address is:

The Chinese Society of Rare Earth
2 Xin Jie Kou Wai Dajie
Beijing, People's Republic of China

A copy of the first circular containing the preregistration form can be obtained from the Rare-Earth Information Center or from the above address.

Mixed Up Valence

Some possible applications and some surprising properties of the intermediate valence compounds, especially those involving rare earth elements, were the subject of a one day meeting devoted to the physical properties of these materials. The meeting was held January 15, 1982 at the Long Range Research Laboratory of the General Electric Co., Ltd. Hirst Research Center in East Lane, Wembley, England.

Among the intermediate valence compounds discussed were those represented by SmS, SmB_6, and $EuCu_2Si_2$. SmS, normally a semiconductor, undergoes a first-order phase transition to a metallic state under modest pressure. An intrinsic metal-semiconductor contact can be generated by rubbing or scribing the surface. The low temperature electrical conductivity of SmB_6, and its sample dependence in particular, pose unanswered questions that impinge on the transport theories of disordered systems. Rare earth metals and their alloys, including those exemplified by $EuCu_2Si_2$, have optical, magnetic, and electronic transport properties that vary as the valence changes.

The metallic alloys are easy to prepare and analyze, and are proving a fertile testing ground for present theories of intermediate valence phenomena. The preparation of pure and stoichiometric sulfides, however, has proven difficult due to the volatility of sulfur with respect to the rare earth metals.

Other points raised in the open discussions were the inability of the pressure sensitive material to survive more than 10 transition cycles without damage and the fact that little work has been done with doping of the compounds but that nonstoichiometry is already providing a wealth of information. Catalytic properties have not been investigated but were the subject of speculation.

Despite our increased understanding of the intermediate valence compounds, better methods of preparation and a wider characterization of their properties must be undertaken before they replace existing materials or new devices are designed based on their unique combination of physical properties.

REers ON THE MOVE

President of France's Rhone-Poulenc Resigns

Jean Gandois has resigned from his job as head of Rhone-Poulenc, France's largest chemicals and fibers concern, which was nationalized last year. The company's top spot already has been filled by Loik Le Floch-Prigent, a government appointee, who arrived at Rhone-Poulenc headquarters two days after Gandois' departure. Floch-Prigent is 39 with a degree from the University of Missouri. He worked 10 years at the Paris-based government-run Delegation Generale a la Recherche Scientifique et Technique before moving to the Ministry of Industry a year ago.

Greinacher Moves

Dr. Ekkehart Greinacher has left the Board of Management of Th. Goldschmidt AG, Essen, West Germany and joined the Executive Board of Preussag AG, Hannover, West Germany. Dr. Ruf, Director of the Metallurgical Chemistry Division of Th. Goldschmidt, has taken over the responsibilities of Dr. Greinacher with respect to rare earth production and sales.

Amorphous Magnetism

Research on magnetically ordered *crystals* has greatly strengthened and extended our understanding of the nature of the condensed state in general and magnetic ordering in particular, resulting in the widespread technological use of magnetic materials. While there has been comparatively little study of magnetic ordering in *noncrystaline* media, interest has increased to the point where one can speak of the appearance of the new field of amorphous magnetism.

Magnetic amorphous materials and their properties are the subject of review by G. A. Petrakovskii in *Usp. Fiz. Nauk,* **134,** 305-31 (1981): Engl. Trans. *Sov. Phys. Usp.* **24,** 511-25 (1981).

The most important question in research on amorphous magnetic materials is that of their magnetic structure and the role played by the amorphous structure in the establishment of magnetic order. There is

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Wieder Seltene Erden

The fourth revised and expanded edition of *Ullmanns Encyklopadie der technischen Chemie* has in Volume **21,** (Verlag Chemie GmbH, Weinheim, 1982) a new section on the rare earths (pp. 235-271). It was written by Jacques Helgorsky, Alain Léveque, Thomas Petzel and Klaus Reinhardt.

The section is in German with an additional English Table of Contents. The review covers the history, mineralogy, and physical and chemical properties of the rare earth elements; the abundance, occurrence, and processing of their ores; the separation and preparation of individual rare earth metals and compounds; and the uses, economics, and toxicology of the rare earths. The section ends with a bibliography of 188 entries.

E.S.R. Review

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are: Type I superconductors might be measured if systems with suitable zero field splittings can be found, e.g. superconductors containing Er^{167}; the origin of the residual width; multi-impurity experiments such as forced double bottlenecks which should enable determinations of the intrinsic impurity g-factors of rare earth ions which normally do not exhibit bottlenecks; and spin-glasses and weak intermediate valence systems.

This is a review that is a must for those just getting into the E.S.R. field and a refresher course for those experienced with the technique.

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JSAC Medal

Dr. Velmer Fassel, deputy director of the Ames Laboratory of the U.S. Department of Energy and professor of chemistry, Iowa State University, has been inducted as an honorary member of the Japan Society for Analytical Chemistry and presented with its highest award, the JSAC Medal.

Fassel was honored primarily for his role in the development of the inductively coupled plasma-atomic emission spectroscopy (ICP-AES) technique, which has the capability of determining many elemental components of a sample in one minute. Fassel's research group at the Ames Laboratory has pioneered the conception and development of this technique over the past 19 years. On a percentage basis, ICP-AES is now the most rapidly growing analytical tool available. Almost all of the commercial models now in worldwide use are based on the work performed at the Ames Laboratory.

Fassel, who holds the rank of distinguished professor in the College of Sciences and Humanities at Iowa State University, also presented the opening scientific lecture at the joint International Conference on Atomic Spectroscopy and the 22nd Colloquim Spectroscopicum Internationale in Tokyo.

Amorphous Magnetism

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no longer any doubt that magnetic order does exist in an amorphous material. This point has been demonstrated by many experimental and theoretical studies. However, the effort to construct a general classification of amorphous magnetic materials on the basis of their magnetic structure is still in a beginning stage.

The review is divided into seven sections with the following headings: 1. Introduction; 2. Atomic structure of an amorphous magnetic material; 3. Magnetic structures of amorphous magnetic materials; 4. Magnetic excitations in amorphous ferromagnets; 5. Critical phenomena in amorphous magnetic materials; 6. Some physical properties of amorphous magnetic materials; and 7. Conclusion. The report includes a bibliography with 154 citations.

One important class of amorphous materials covered are alloys of rare earths and 3*d* metals. These alloys have been used to produce amorphous magnetic films with magnetic bubbles and high coercivity.

Rare Earth-Organic Chemistry

In two separate investigations, lanthanide organic complexes have been synthesized and characterized. This may be only the top of the iceberg as far as future discoveries are concerned as this is a new and very promising field.

Dr. A. Sen and graduate student R. R. Thomas have synthesized a series of cationic europium(III) complexes that can serve as catalysts for certain organic reactions. They reported to the American Chemical Society meeting in Las Vegas that these compounds are among the first cationic lanthanide metal complexes to be studied. They reported that the complex $[Eu(CH_3Cn)_x](BF_4)_3$, an orange solid, appears to catalyze a wide range of olefin reactions including polymerization and linear and cyclic oligomerizations. They said that some of its reactions, such as cyclodimerization of styrene derivatives and certain ring opening polymerizations, have no precedent among either lanthanide or transition metal catalysts.

In the meantime back at the ranch, that is the University of Chicago and University of Alabama, chemists were for the first time, synthesizing and crystallographically characterizing molecular lanthanide and yttrium hydride complexes. Dr. W. J. Evans and his graduate students, A. L. Wayda and J. H. Meadows, synthesized the new compounds, and Dr. J. L. Atwood and graduate student W. E. Hunter carried out the x-ray structure determinations. The rare earth elements were the last group of *d*- or *f*- metals for which molecular organometallic hydrides had not been synthesized and crystallographically characterized. Evans and his co-workers efforts were published in *J. Am. Chem. Soc.*, **104,** 2008 (1982). Included in the compounds synthesized are two remarkable trimetallic hydrides with hydrogens at the center of the triangle.

$$ 1983 $$

Fiscal year 1983 is off to a slow start as far as number of contributors go but you sure can't beat the quality. We thank our long time benefactors who have come through for us again in the first quarter. The contributors are listed below with the number of years of support shown in parentheses.

Companhia Industrial Fluminense, Brazil (10)
Davison Specialty Chemical Co., Subsidiary of W. R. Grace & Co U.S.A. (15)
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Shin-Etsu Chemical Co., Ltd., Japan (13)
Treibacher Chemische Werke AG, Austria (11)

Rare Earth Chemistry

C. K. Jorgensen and R. Reisfeld have compiled a very comprehensive review "Chemistry and Spectroscopy of Rare Earths" which appears in *Topics in Current Chemistry,* 100, 127-167, 1982. It is published by Springer-Verlag of Berlin, Heidelberg. They start with a discussion of the position of the rare earth elements in the periodic tables, both the chemical and spectroscopic version. This is followed by sections on aqua ions and oxides; sulfides and low-electronegativity ligands; organolanthanide chemistry; electron configurations, spin-pairing energy, and nephelauxetic effects; inductive quantum chemistry; and lasers, cathodoluminescent television, and candoluminescence. They end the review with 265 references.

In the various sections they have detailed discussions of coordination numbers, bonding, valences, energy levels, crystal spacings, and crystal types of the different rare earth compounds. Also included are discussions on absorption band intensities, luminescence, and J-level configuration.

RE's In The News

Laser Spectroscopy

Researchers at Los Alamos National Laboratory, New Mexico, are applying laser spectroscopy techniques to solve a specific practical problem in the analysis of rare earths. The problem: Separating the low levels of lutetium-174 (produced when a nuclear weapon is tested) from a roughly equal amount of ytterbium-174 that occurs naturally in soil samples. Lutetium, with normal isotopes of 175 and 176, often is added to a nuclear weapon as a detector element during weapons testing. In the course of a thermonuclear reaction one-millionth of the Lu-175 is converted to Lu-174. An accurate measure of how much Lu-174 is formed helps to evaluate the performance of the nuclear weapon but the soil sample containing the desired Lu-174 also contains Yb-174.

In the new technique, the soil sample undergoes preliminary chemical purification which produces a mixture of rare earth elements in an acidic, aqueous solution. This solution is placed on the metal filament of a mass spectrometer and when the water is removed the rare earth elements are left on the filament. The filament is heated to vaporize these elements and a laser beam in the blue visible region that selectively will ionize only the lutetium is passed through the vapor. The lutetium ions produced are swept through the mass spectrometer in a conventional manner and measured by the instrument's detector. The effect is to increase the selectivity of lutetium over ytterbium by 50,000 without the corresponding decrease in sensitivity that ordinarily would accompany such a selectivity gain.

Zirconia Conferences

Advances in Ceramics Vol. 3. Science and Technology of Zirconia [The American Ceramic Society, Columbus, Ohio, 1981] reports the proceedings of the First International Conference on the Science and Technology of Zirconia held on June 16-18, 1980 in Cleveland, Ohio at Case Western Reserve University. The Conference was organized and the proceedings edited by A. H. Heuer and L. W. Hobbs of the host school. The proceedings are priced at $40 for members of the society and $50 for nonmembers.

The book contains 30 papers including invited review lectures by 18 noted experts covering the scientific bases and industrial implications of defect and phase equilibria, fracture and transformation toughening, and transport properties in zirconia-based systems. Seventeen of the papers are of interest to rare earthers with many dealing with the ZrO_2-Y_2O_3 system.

A second international conference on the science and technology of zirconia has been scheduled for June 21-23, 1983 in Stuttgart, West Germany. For more information contact:

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Editor's Report
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and various neutron scattering experiments are being made on several rare earth materials by the permanent and visiting staff of the Institut Laue-Langevin, including Drs. F. Tasset and K. A. McEwen.

It was a wonderful and successful trip—

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