Recent Advances in Rare Earth Chemistry: IREC 85

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The international rare earth conference, IREC 85, was held from 4 through 8 March 1985 in Switzerland. A blend of solid state and solution chemistries was a first for the conference and provided an excellent stage for discussions on the use of rare earths in glasses, ceramics, alloys, and catalysts.
Block 18 (Cont'd)

Permanent magnets,
Solution chemistry,
Hydrides,
Lanthanides,
Catalysts.
RECENT ADVANCES IN RARE EARTH CHEMISTRY: IREC 85

Introduction

For the first time, the international rare earth conference included solution and basic chemistry of the rare earths as well as their organometallic derivatives. However, the major portion of IREC 85 was devoted to the solid state physics of lanthanides and, in particular, valence instabilities, phase transitions, magnetism, and superconductivity. In addition, materials research and industrial applications were stressed in many presentations. The detailed proceedings of the conference will be published as a special issue of the Journal of Less Common Metals.

IREC 85 was held at the Eidgenössische Technische Hochschule (ETH) in Zurich, Switzerland, from 4 through 8 March 1985. Over 200 participants and guests from 25 nations gathered to present and discuss some 50 oral and 190 poster scientific papers. Participants were from as far away as Australia, China, and Japan. Unfortunately, nearly all of the USSR researchers who submitted abstracts for posters (approximately 50) did not attend.

Uses, Economics, and the Future for Rare Earth Elements

The rare earth elements, which are not "rare" by any means nor "earth" elements, comprise the lanthanide series of elements, atomic number 57 through 71, and yttrium, atomic number 39. The importance of these elements in today's technology was reviewed by B.T. Kilbourn (Molycorp, US) and P. Falconnet (Rhône-Poulenc, France). Their excellent presentations identified the shifting demand for the rare earths, from the misch metal for steel manufacture to the more recent emphasis in high-technology glasses, ceramics, permanent magnets, and catalysts (Table 1).

On the other hand, the monetary values of the products do not follow the weight demand, but are largest for the specialty items such as additives to color television monitors and magnetic recording tapes and devices. No large growth of rare earth consumption is expected in the near future, and only samarium (Sm) might be in short supply because of the high demand for permanent magnets.

As additives to synthetic ceramics, the rare earths impart mechanical and chemical properties, and electrical and magnetic properties; regulate specific emission of electromagnetic radiation; and promote interaction with electromagnetic radiation. After the potential economies were discussed and debated, the conference turned to the physics and chemistry of the rare earths in the solid state and in solution. The coordination chemistry of these elements having localized 4f and delocalized 5d electrons can affect significantly the properties of the material under investigation. The fundamental theories causing the physical and chemical changes were major issues of the conference.

Rare Earth Alloys

Laser-beam-addressable memory systems, recording heads, transformer cores, sensors, and transducers are the driving force behind the extensive investigation of amorphous alloys and the study of short-range interaction between atoms and ordering of atoms. K.H.J. Buschow (Phillips Research Laboratories, The Netherlands) discussed the general topic of amorphous alloys and their superiority as electroactive and optically active substances. As means to predict the properties of binary mixtures containing rare earth elements, K.A. Gschneidner (Iowa State University) and P. Villars (ETH, Zurich) discussed their attempts to systematically treat phase and stability diagrams of binary systems. Villars' treatment was most extensive, with over 3000 binary intermetallic compounds classified into distinct domains and only 2.5 percent violations if overlapping of polymorphic structures is accepted. Where crystal structures have not been determined, he predicted the structure type from experimentally determined phase diagrams.
Table 1

<table>
<thead>
<tr>
<th>Weight Percent of RE</th>
<th>1976</th>
<th>1984</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalysts</td>
<td>38</td>
<td>Phosphors</td>
</tr>
<tr>
<td>Metallurgy</td>
<td>33</td>
<td>Magnets</td>
</tr>
<tr>
<td>Glass/ceramics</td>
<td>27</td>
<td>Special glasses and ceramics</td>
</tr>
<tr>
<td>Other</td>
<td>2</td>
<td>Other</td>
</tr>
</tbody>
</table>

Another attempt to correlate trends and make predictions was presented by R. Ferro (Università di Genova, Italy) using a thermodynamic approach.

The valence fluctuations in the thulium-selenium (Tm-Se) system (NaCl structure) were investigated by studying the phase diagram, chemical and x-ray analysis, and solution and fluorine combustion calorimetry. E. Kaldis (ETH, Zurich) reported a large homogeneity range of Tm-Se, which includes a miscibility gap at Tm/Se=0.94. Whereas TmTe is a semiconductor, TmS is metallic, and TmSe has a homogeneously mixed valence due to a fluctuation of a 4f electron between the localized $4f^{13}5d^0(Tm^{2+})$ and the itinerant $4f^{12}5d^1(Tm^{3+})$ states. Fluorine combustion calorimetry was described in more detail in a poster by Kaldis' group.

A considerable number of poster reports dealt with phase studies of metal oxides and rare earth oxides, lanthanide metal-hydrogen, and double chlorides, such as NaCl/LaCl$_3$. Although several poster reports were related to the application of rare earths in structural alloys (especially reports from China), most alloying was directed to the magnetic behavior of the product. As stated earlier, the long-standing use of misch metal in the steel industry has been on a decline since the production of high-purity steels using new manufacturing processes.

Permanent Magnets: The Role of Rare Earth Elements

Permanent magnets of high uniform field strength, light weight, and broad temperature stabilities were reviewed by J. Ormerod (Mullard Magnetic Components, England). He outlined the recent developments of permanent magnets based on Nd$_2$Fe$_{14}$B. The process for the final magnetic material consists of powder metallurgy where metal as such is not essential, sintering for best coercivity, machining, and finally magnetizing. Most materials reported did not have suitable temperature ranges for use as automotive components such as starter motors and alternators. To overcome this disadvantage and open a large market for rare earths, a considerable effort is being directed toward understanding the physical metallurgy and processing that produce permanent magnets.

Rare earth borides and rare earth-platinum metal-boron systems were discussed by J. Etourneau (Centre National de la Recherche Scientifique [CNRS], Talence, France) and P. Rogl (Universität Wien, Austria), respectively. The physical properties of most interest were unusual magnetic and/or superconducting properties which vary with the structure of the materials. A major portion of the poster presentations dealing with permanent magnets dealt with magnetic properties of ternary systems and their relationship to composition, structure, and temperature. Table 2 gives the systems reported, the first author listed, and location.

Solution and Coordination Chemistries

A unique feature of the conference was the inclusion of solution chemistry in the discussions primarily concerned with solid state physics and chemistry. However, certain similarities soon became apparent, and many fruitful discussions arose between participants normally unaware of the research areas encompassing solution chemistry. Most of the interaction on related areas between solid and solution chemistries was directed to coordination chemistry, thermodynamics, and modeling.

Professor G.R. Choppin (Florida State University) began the solution chemistry session by discussing free energy, enthalpy, and entropy changes for the formation of 1:1 complexes. By
Table 2
Materials Reported at Poster Sessions

<table>
<thead>
<tr>
<th>Compounds Investigated</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Sm, Pr, Nd)-Co alloys</td>
<td>Velicescu, Lupfig</td>
</tr>
<tr>
<td>(Cd$<em>2$Y$</em>{1-x}$)$_2$Co compounds</td>
<td>Burzo, Romania</td>
</tr>
<tr>
<td>Y$<em>2$Fe$</em>{14-x}$TxB compounds (T=Co, Ni)</td>
<td>Wallace, Pittsburgh, PA</td>
</tr>
<tr>
<td>Nd-Fe-B magnets</td>
<td>Rodewald, West Germany</td>
</tr>
<tr>
<td>LnFe$_x$B compounds</td>
<td>van Noort, Eindhoven</td>
</tr>
<tr>
<td>Nd-Fe and Nd-B-Fe</td>
<td>Li-Chi Tai, China</td>
</tr>
<tr>
<td>Eu, Sr and Mg with Th$<em>2$Ni$</em>{17}$</td>
<td>Lueken, Aachen</td>
</tr>
<tr>
<td>PrFeO$_3$ crystals</td>
<td>Sosnowska, Poland</td>
</tr>
<tr>
<td>Nd$_2$O$_3$·(1-x)[2B$_2$O$_3$·PbO] glasses</td>
<td>Ardelean, Romania</td>
</tr>
<tr>
<td>EuLn$_2$S$_4$ compounds</td>
<td>Lemoine, Paris</td>
</tr>
<tr>
<td>PrGe, NdGe, and ErGe crystals</td>
<td>Buschow, The Netherlands</td>
</tr>
<tr>
<td>Ln$_{1-x}$M$_x$Al$_2$ solid solutions</td>
<td>Iandelli, Italy</td>
</tr>
<tr>
<td>Y$<em>{0.5}$R$</em>{0.5}$Cu single crystals</td>
<td>Chelkowski, Poland</td>
</tr>
<tr>
<td>RRh$_2$Si$_2$ &amp; RRu$_2$Si$_2$ compounds</td>
<td>Chevalier, France</td>
</tr>
</tbody>
</table>

using potentiometric and calorimetric titrations he studied aliphatic dicarboxylic acid ligands and conjugated pi systems such as ortho and para phthalic acids. J.F. Desreux (University of Liege, Belgium) described host/guest interactions of rare earth ions with a variety of polycyclic macrocycles. The nuclear magnetic resonance investigation included as ligands crown ethers and cryptates. The latter ligands were prepared by J.M. Lehn’s group at the University Louis Pasteur, France (see Science, 227 [1985], 849).

An ultrasonic absorption technique, which is based upon spectroscopic observations, was described by H.B. Silber (University of Texas at San Antonio). The technique was reported to determine the coordination number, reflect structural changes in the series of rare earth ions with specific ligands, and distinguish between inner- and outer-sphere association of ligands. The last point raised a considerable amount of discussion. The reliability of any technique now available to determine the type of solution association with a high degree of certainty is questionable. In contrast with problems confronting the solution chemist, P.E. Caro (Meudon, France) described rare-earth inorganic and organic materials of low symmetry that exhibit vibronic transitions resulting in very sharp fluorescence spectra in the range of 14600 cm$^{-1}$. For organic material the method is blind to the nature of the bonding, but Caro’s procedure could be important when combined with other analytical tools–especially for biological systems.

Solid state and solution dipole moments were compared with magnetic moments by B. Kanellakopulos (Kernforschungszentrum, Karlsruhe). The cyclopentadienyl compounds discussed have an orthorhombic structure, and the lighter rare earth elements show a different structure than the heavier ones. Many properties were correlated with the magnetic moments and even extended to the actinide elements. Only cerium appears
to have an anomalous moment that cannot be explained.

In his usual witty manner, Professor C.F. Jørgensen (Université de Genève) gave an excellent review of the influence of 4f electrons on the chemistry and spectroscopy of the rare earth metals and compounds. The examples were from his book on the excited states in rare earth compounds. Lanthanide complexes with macrocyclic ligands were extensively reviewed by J.C.G. Bünzli (Université de Lausanne). Changes in crystal-field splitting were determined by using Eu(III) ion as a structural spectroscopic probe, a technique employed since 1979. The polyfunctional ligands (L) included crown ethers and cryptands and formed compounds according to the equation $a(LnX_3\cdot nS) + bL \rightarrow [(LnX_3)_a(L)_b] \cdot anS$, where S is a solvent molecule and X an anion such as nitrate. At 77K, the emission spectra in the range of 750 to 550 nm resulted from excitation at 395 nm. Inelastic neutron scattering, another method for probing the structure of rare earth compounds (for example Cs$_3$Ln$_2$X$_9$), was presented by A. Furrer (ETHZ, Würenlingen).

Lanthanide ions (Eu$^{3+}$ or Tb$^{3+}$) as probes in calcium binding were laser-excited and the luminescence used by W.D. Horrocks (Pennsylvania State University) to characterize the Ca$^{2+}$ binding sites of native proteins. He reported on the following: excited state lifetimes in H$_2$O and D$_2$O to determine coordinated water; excitation spectroscopy of the $^7F_0 \rightarrow ^5D_0$ transition of Eu$^{3+}$ to characterize individual binding sites and determine total net charge on the coordinating groups; intermetal ion energy transfer measurements; direct or indirect protein-sensitized excitation of bound Tb$^{3+}$ to determine the sequence of metal ion binding; relative binding constants in the presence of competing metal ions; and the kinetics of metal ion exchange and removal by luminescence-monitored stopped-flow.

Table 3 shows a selection of topics from the poster sessions that were related to solution and coordination chemistry of the rare earths. I have listed only the topics that I consider interesting.

**Rare Earth Elements in Excited States**

The session on excited states in rare earth compounds was introduced by an excellent presentation by G. Blasse (State University Utrecht, The Netherlands). He discussed the probabilities of the excited state of a rare earth solid to "end its life" by returning to the ground state radiatively or nonradiatively, or by the trapping and "killing" of excitons by other atoms in the lattice. Gd$^{3+}$ and Eu$^{3+}$ compounds were studied using time-resolved spectroscopy, and the probabilities of all the processes were determined for materials such as EuAl$_3$B$_4$O$_{12}$ (migration in

| Table 3 |

**Rare Earth Complexes Reported**

- Aqueous complexes with cyclic polyethers crown ethers, Alstad, University of Oslo.
- Lanthanide cryptates. Schwing, CNRS, Strasbourg, France.
- Ethylene bis(oxyethylendinitrilo)tetraacetic acid complexes. Brücher, Kossuth University, Hungary.
- Rare earth chlorocomplexes. Vierling, CNRS, Strasbourg, France.
- Chelates with axially symmetric macrocyclic triaza ligand. Sherry, University of Texas at Dallas.
- Shift reagents with adducts containing nitrogen donor atoms. Thompson, University of Minnesota.
- Phthalocyanine and β-diketone mixed ligands. Sugimoto, Osaka City University, Japan.
- Dimethylsulfoxide complexes. Zinner, University de São Paulo, Brazil.
the crystal is three-dimensional), NaEuTiO₄ (two-dimensional migration), and EuMgB₅O₁₀ (one-dimensional migration). A consequence of this fundamental study is the transition to new luminescent materials which may bring about a revolution in fluorescent lamp lighting. For example, GdMgB₅O₁₀ can replace the two components, Tb³⁺ and Eu³⁺, used in lamps for green and red light.

R. Reisfeld (Hebrew University, Israel) presented one of the most intriguing and significant applications for rare earths. Based on the excited J-levels of lanthanides in transparent media, the transition probabilities from the ground states can be predicted and the theory used to derive radiative lifetimes and the branching ratio to any lower J-level. Matrix elements with suitable parameters were used to calculate most transitions, but calculations for praseodymium did not work. A systematic dependence was observed for rare earth ions in fluoride glasses with a good correlation between experimental and calculated data. The major problem is that nonradiative processes relax to vibronic states or to combinations of electronic states of adjacent systems. Energy transfer can be beneficial if the receptor luminescence is at a desired wavelength. The conditions for high quantum yields are similar for glass plates trapping solar energy and for tunable lasers.

Reisfeld described the luminescent solar concentrator, which uses their principles (Figure 1). Nonradiative decay can be diminished in fluoride, sulfide, and telluride glass with low phonon energies; in glass ceramics containing microcrystallites (below 200 Å) dispersed in a vitreous matrix; and in porous or gel-glasses incorporating isolated luminophores. The research group, which is being supported by the US Air Force, has a model house that is demonstrating the solar collector and photovoltaic cell for producing electricity direct from the sun. (I visited Reisfeld in May 1985, and will publish a more detailed report of her research in European Science Notes.)

Other papers on the topic of rare earth excited states included an excellent review by L. Brixner (du Pont, US) of developments related to rare earth phosphors for x-ray intensifying screens--radiography. First used in 1896, CaWO₄ remains the most-used phosphor, even after screening several hundred thousand compounds over the years. Several rare-earth-containing compounds have shown promise, but none have become commercially important. The materials include: Gd₂O₂S with Tb³⁺ (blue/green phosphor used by Kodak); LaOBr with Tm³⁺ (800 speed used by General Electric in the blue/ultraviolet region), and several rare earth tantalates, M'YTaO₄, where Y is a rare earth element.

Rare Earths in Glasses and Ceramics

P. Maestro (Rhone-Poulenc Recherches, France) gave a tutorial on color synthesis in products containing the

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Figure 1. Luminescent solar concentrator.
The use of rare earths in catalytic processes was introduced by reviewing organometallic complexes. H.D. Amberger (Universität Hamburg, West Germany) described optical properties of tris(cyclopentadienyl)lanthanides with D$_{3h}$ symmetry in solution using magnetic circular dichroism (MCD). R.D. Fischer (Universität Hamburg, West Germany) used the solid-angle-sum rule to predict structural variations in organolanthanides. H. Schumann (Technische Universität Berlin) concluded the organolanthanides discussion by reviewing the work presented at the North Atlantic Treaty Organization Advanced Study Institute 84/71 meeting on the synthesis, structure, and reactivity of homoaleptic organolanthanides. The type of materials reported are [Li(tmed)$_3$][LnMe$_6$], where tmed is tetramethylenediamine. The materials were reported to be useful in organic syntheses for the methylation of 1,8-unsaturated aldehydes and ketones, where 1,2-methylation is favored over 1,4-addition. Some success as catalysts for polymerization was reported. G.N. Sauvion (Rhône-Poulenc Specialities, France) reported that rare-earth-containing catalysts are now used in automobile pollution control systems and in fluid cracking in the petroleum industry. He predicted future uses as polymerization catalysts and for selectivity in CO$+$H$_2$ reactions.

Rare Earth Hydrides

L. Schlapbach (ETH, Zurich) presented convincing evidence that hydrides of rare earth metals and rare earth intermetallic compounds exhibit fascinating properties of current interest in solid state science. He demonstrated the well-known hydrogen storage capabilities by operating a single cylinder engine without pollution in the lecture room. Other uses of hydrides included a heat pump, fire detector, and biomedical applications. Some fascinating properties of the hydrides were reported. For example, LaNi$_5$H$_6$, when formed, rapidly turns to a powder. Nd$_2$Fe$_{14}$B$_2$, also a powder, has a significantly higher Curie temperature than the Nd$_2$Fe$_{14}$B, a suitable material for permanent magnets. Peculiar electronic properties of hydrides with metal to semiconductor transitions, core hole screening, H-sorption, surface reactions, and catalysis were discussed. Other presentations on rare earth hydrides are listed in Table 4.

Prediction of Properties

Several presentations and posters were related to the prediction of
properties and structures of rare earth compounds. All presentations on this subject generated a considerable amount of discussion. C. Görller-Walrand (University of Leuven, Belgium) first discussed the principles of MCD. Then MCD theory was adapted to rare earths by considering the mechanisms which account predominantly for the intensity in the spectra: the magnetic dipole and the induced electric dipole mechanisms. The coordination symmetry can be predicted in cases where rare earths are present in media where this symmetry is unknown or difficult to determine by classical methods. Faucher used a simplified procedure to predict crystal field parameters by considering nearest neighbors distances and by using an off-diagonal expression.

W. Paszkowicz (Institute of Atomic Energy, Poland) in a poster presented a pseudo-atom model to predict the stability of intermetallic compounds. The model offers a way to calculate different variants of first coordination-sphere compositions and to indicate possible compositions of binary intermetallic compounds. Where the atoms may be treated as hard spheres, the model is constructed by the symmetry of the coordination sphere and their filling. The model, which was applied to selected rare-earth-transition-metal binary systems, should be applicable to systems such as the intermetallics formed in electrochemistry where a mercury electrode is used. Paszkowicz said he was currently extending the model to tertiary systems.

Summary
IREC 85 was successful in bringing together physicists, chemists, and engineers to discuss a broad range of topics centered around the rare earth elements. The blend of solid state and solution chemistries marked a first for the conference and provided an excellent stage for many fruitful discussions on the use of the rare earths in glasses, ceramics, alloys, and catalysts. The conference had a good balance of physics, chemistry, theory, and application.
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