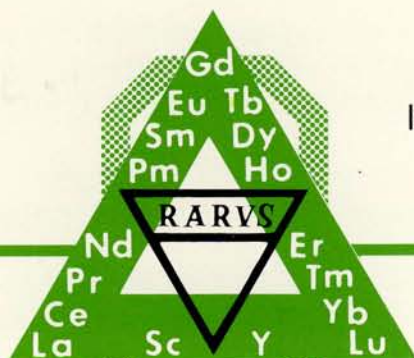


Rare-earth Information Center

INSTITUTE FOR PHYSICAL RESEARCH
AND TECHNOLOGY

Iowa State University / Ames, Iowa 50011 – USA



1787 – 1987

TWO HUNDRED YEARS OF RARE EARTHS

K.A. Gschneidner Jr. and J. Capellen
Editors



NORTH-HOLLAND

AMSTERDAM • OXFORD • NEW YORK • TOKYO

Published by:

Rare-earth Information Center
Iowa State University, Ames, Iowa, USA

North-Holland – Amsterdam, The Netherlands

For further information please contact:

Dr. K. A. Gschneider, Jr.
Ames Laboratory DOE
Iowa State University
Ames, IA 50011-3020, USA

Telephone (515) 294-7931
Telex 269266
FAX (515) 294-3226

PREFACE

The discovery of ytterbite (later called gadolinite) in 1787 was the beginning of the rare-earth chapter in the history of science. Little did Lieutenant Karl Axel Arrhenius realize his place in history when he picked up that black rock near Ytterby, Sweden, and thus brought lasting fame to the town for which many of the rare earths are named.

The Rare-earth Information Center celebrated the 200th anniversary of the discovery of ytterbite by inviting its readers to write stories on what the readers thought were some of the important highlights of the first 200 years of rare earths. Four of these stories were published, in a shortened version, in one of the four quarterly issues of the *RIC News*. All of the stories submitted, including the four published, were to be part of a booklet published by RIC and to be distributed to any one requesting it. RIC decided to include a "letter to the editor" and the editor's response concerning the year Arrhenius made his initial discovery. Also, we have included a 1984 article which was written on the occasion of a special issue commemorating the 100th volume of the *Journal of the Less-Common Metals*. In this paper, K.A. Gschneidner Jr reviews the history and current events of rare earth metallurgy and makes some observations concerning its future – an appropriate concluding paper in this special booklet.

In July of 1987 North-Holland Physics Publishing offered to typeset, print and publish these articles as a joint RIC–North-Holland publication. And this is the result.

CONTENTS

Preface 1

Letter to the Editor, *C.H. Evans* 4

Editor's Reply, *K.A. Gschneidner Jr* 5

How Many REs?, *K.A. Gschneidner Jr* 6

Story of RE Names, *Georg K. Brauer* 7

Necessity is the Mother of Invention, *Werner Fischer* 9

Element 61, *T.V. Swaminathan* 11

Electronic Structure vs. Chemistry, *Christian K. Jørgensen* 12

Nobel Prize 200 Years Later?, *Andrzej Szymanski* 14

Luminescence Applications, *Mel Tecotzky* 17

Powerful New Magnet Material Found, *Arthur L. Robinson* 19

Past, Present and Future of Rare-Earth Metallurgy, *K.A. Gschneidner Jr* 23

LETTER TO THE EDITOR

July 23, 1987

Dear Sir:

I am writing with regard to your designation of 1787 as the year in which rare earths were discovered (*Rare-earth Information Center News*, vol. XXI, No. 4, pp. 1-2). The reason I raise this matter is that I have come across at least four different sources which cite 1788 as the year in which Karl Arrhenius discovered his new mineral, ytterbite. These sources are:

- [1] R.C. Vickery, *Chemistry of the Lanthanides* (Academic Press, New York; Butterworths, London, 1953) p. 1.
- [2] C.V. Banks and D.W. Klingman, Analytical Chemistry of the Rare Earths, in: *The Rare Earths*, eds F.H. Spedding and A.H. Daane (Wiley, New York, 1959) ch. 23, p. 570.
- [3] D.N. Trifonov, *The Rare Earth Elements* (MacMillan, New York, 1963) p. 2.
- [4] G. Magnusson, The Behaviour of Certain Lanthanons in Rats, *Acta Pharmacol. Toxicol.* 20 (1963) 7.

I bring this matter up only through curiosity; a year here or there in two centuries is hardly crucial!

Yours sincerely,

C.H. Evans, Ph.D.
Associate Professor
Department of Orthopaedic Surgery
University of Pittsburgh
Pittsburgh, PA 15261

EDITOR'S REPLY

July 28, 1987

Dear Prof. Evans:

Thank you for your letter of July 23, 1987 concerning the year of the discovery of the rare earths. You may also add to your list the book by S.I. Levy, *The Rare Earths* (Edward Arnold & Co., London, 1924) p. 1.

There are, however, a number of sources which cite 1787 as the year in which Karl Axel Arrhenius found the mineral ytterbite. These are as follows:

- [1] M.E. Weeks, *Discovery of the Elements*, 6th Ed. (J. Chem. Ed., Easton, PA, 1956) p. 695.
- [2] T. Moeller, *The Chemistry of the Lanthanides* (Reinhold, New York, 1963) p. 1; and
- [3] Three books by D.N. Trifonov:
 - (a) *Rare-Earth Elements and Their Position in the Periodic System*, AEC-tr-8675 (Atomic Energy Commission, Washington, D.C., 1970) p. 5.
 - (b) *Problems in the Study of Rare Earths*, AEC-tr-6635 (Atomic Energy Commission, Washington, DC, 1966) p. 3.
 - (c) *The Price of Truth* (MIR Publishers, Moscow, 1984) p. 9, English translation.

The answer to this dilemma is quite simple: the discovery was made in the summer of 1787, but it was not published until 1788, see ref. 12 of item 3a above [Arrhenius, K., *Svenska Akad. Handl.* (1788), 217].

I hope this clarifies the situation. Again, thank you for your interest. We do appreciate our readers taking time out of their busy schedules to write us.

Sincerely yours,

Karl A. Gschneidner, Jr.
Distinguished Professor in
Sciences and Humanities
Senior Metallurgist
Director, RIC

HOW MANY REs?

K.A. Gschneidner Jr

*Rare-earth Information Center, Ames Laboratory and Department of Materials Science and Engineering,
Iowa State University, Ames, IA 50011, USA*

The discovery of the black mineral ytterbite (also known as gadolinite) by Lieutenant Karl Axel Arrhenius in a quarry in the village of Ytterby near Stockholm was the beginning of our 200 year history. The first individual element isolated from this ore was yttrium (in 1794) as an impure oxide. But then things became both complex and confusing because of the great chemical similarity of the rare earths. Many so-called "newly discovered elements" were, in time, found to be mixtures of as many as six different rare earth elements. Furthermore, claims were made of the discovery of a large number of "elements" that were supposed to be members of this series but were not.

Fortunately, other major developments occurred that aided rare earth scientists in their quest for their "holy grail" of isolating these ele-

ments. The application of the spectrograph to chemical determinations by Bunsen in 1859 gave the scientists a powerful tool for following the progress of the fractional separations of the rare earths. The publication of the periodic law of the chemical elements by Mendeleev in 1869, although not of immediate help, pointed the way for the atomic theory of the "aufbau" of the elements spearheaded by Niels Bohr and other quantum theorists in the early 1910s. The prime contribution, however, was the experimental work of H.G.J. Moseley in 1912 on the relationship of the X-ray spectra to atomic number which finally showed exactly how many rare-earth elements should exist. Furthermore, the anomaly that 14 elements with properties similar to lanthanum existed proved to be an extremely important clue in developing our present theory of atomic structure.

STORY OF RE NAMES

Georg Brauer

Institut für Anorganische and Analytische Chemie, Albert-Ludwigs Universität, Freiburg im Breisgau, FRG

The history of baptizing the chemical elements exhibits plenty of curiosities. This especially holds for the rare earths. A look thereon may be amusing.

As already mentioned by Karl A. Gschneidner Jr in the previous story, the discovery and separation of rare earth elements began with the mineral ytterbite found in a fluorspar mine near the Swedish village of Ytterby. Thus, the first name for a trivalent element isolated from this mineral was derived as yttrium. Later on, with growing knowledge of other minerals and improved separation techniques, need arose for names for newly identified rare-earth elements. A comfortable and cheap way seemed to vary the first name by adding or omitting letters. So the names of ytterbium, terbium, and erbium were constructed.

A chemical investigation of other minerals led to defining a group of rare-earth oxides called the "light cerite earths". The name of the dominant element in these ores was chosen as cerium (after the Greek deity of fertility, Ceres) by inspiration from the astronomic detection of the planetoid Ceres (1801) which caused a sensation among scientists of that time.

From the Greek mythology also stems promethium [1] as the element of Prometheus who first brought fire to mankind (it was stolen) and who was therefore severely punished by Zeus. From the old "cerite earth" Carl G. Mosander isolated (1839–1842) two new elements and called them lanthanum (from the Greek *lanthano* meaning I am hidden) and the extremely similar didymium (Greek *didymos* meaning twin). [It is told that Mosander selected the word didymium also in honour to his wedlock which brought birth to twins just at that time.] Similar to lanthanum, the

name dysprosium (from the Greek word *dysprosodos* meaning troublesome accessibility) stems from the painstaking steps required in the separation of the rare earths.

In 1885 the famous Austrian chemist Auer von Welsbach showed that didymium really was a twin: he succeeded in dividing "didymium" into two elements he called neodymium (Greek word which means the new one) and praseodymium (the one with the green compounds; from the Greek word *prason* which means leek-green).

Some of the names of rare-earth elements are given in honour of scientists involved with the development of knowledge of the rare earths. Thus gadolinium was named after the Finnish chemist Johan Gadolin (1760–1852) to honour him for his thorough investigations on the rare earths. Samarium derives its name from a Russian mining officer, V.E. Samarsky, who discovered the rare-earth ore which was eventually called samarskite. Holmium was proposed in honour of Per T. Cleve (born in Stockholm, which in Latin was called *Holmia*) who detected the existence of this element. It is said that the chemist O. Holmberg, who thoroughly investigated the chemistry of holmium and proposed the name, indeed officially honoured Cleve but also tried to fix his own name in history (secret self-advertising!).

There has also been a trend to use geographic terms: europium got its name perhaps in provocation against the so-called supernationalistic named elements germanium (Germany) and gallium (Gaul \equiv France). And thulium, rare and far as it is, refers to the far-off northern mythologic land Thule.

The last story to be mentioned here concerns lutetium. This element had been isolated and characterized quite simultaneously by Auer von

Welsbach who proposed the name cassiopeium and Georges Urbain in France who pleaded for lutetium (in honor of the city of Paris, which in Latin is known as Lutetia). The latter name has been internationally accepted.

The history of detection, isolation and separation of rare earths is full of many more proposals for baptizing elements or oxides believed to be detected from a special ore. But many of these names were dropped later on. So we should be happy to have now our precise and irrevocable list of names of our rare earths in the sequence as we

know it today. However, think about the words of Christian Lichtenberg who told us "He who knows nothing but chemistry, doesn't understand even this right!".

[1] Grace M. Coryell (1945) said "This name not only symbolizes the dramatic way in which the element may be produced in quantity as a result of man's harnessing of the energy of nuclear fission, but also warns man of the impending danger of punishment by the vulture of war!".

NECESSITY IS THE MOTHER OF INVENTION

Werner Fischer

Freiburg im Breisgau, FRG

In 1913 Moseley discovered his rule which states that there are 15 lanthanides and no more. Since separation of these elements was an extremely time consuming task, only a few of them were produced commercially and available through trade channels. Prandtl [1], e.g., employed more than 4000 crystallizations and precipitations to prepare some pure Er_2O_3 . Hönigschmid [2] used 25 g of this to determine the atomic weight. At that time, any chemist who wanted to work with rare earths was forced to hunt for remnants of samples which had been prepared by experts such as Auer von Welsbach, Urbain, and others; experimentation with such priceless rarities was a nerve-racking task.

During the early 1930s this author was in charge of a small group of graduate students. Our financial resources were barely adequate to buy a few test tubes. We decided to examine the basis of qualitative analysis in solution, particularly methods for the separation and enrichment of single elements. Studying the literature we were surprised to find that the separation of inorganic materials by partition between two immiscible solvents had been described only for a few cases, even though such a method appeared to offer a number of fundamental advantages, namely, no slow steps such as filtration and crystallization, no absorption effects, room-temperature operation, convenient and automatic repetition of single steps, so that even substances with similar distribution coefficients could be handled effectively. We therefore decided to apply the liquid-liquid extraction separation technique to the trivalent rare earths, assuming we could find suitable conditions. If this could be achieved, the preparation of pure rare earths and their exploration should be greatly facilitated.

In 1937, we found [4], indeed, that it is possible

to separate rare earths by liquid-liquid extraction with many systems. Let me mention only two examples [3,5]:

- (1) A 25-stage separation process employing partition of a 90/10 mixture of gadolinium and samarium nitrates between an aqueous lithium nitrate solution and diethyl ether resulted in Gd_2O_3 of 99.5% purity and Sm_2O_3 of 90% purity. This corresponds to a separation factor of $\beta(\text{Gd}/\text{Sm}) = 1.5$ per stage.
- (2) Example 5 of our first patent [3] described the use of thiocyanate to substantially enhance the separation of the heavy lanthanides, the separation of scandium from all the other rare earths, and also the separation of zirconium from hafnium. Detailed studies later confirmed all of these initial findings [6].

Our early investigations were interrupted by World War II and the destruction of our laboratories. In the meantime, the separation of rare earths by ion exchange was thoroughly explored [7] in the United States. The separation by partition, however, did not receive much attention. Some reports [8] between 1940 and 1951 gave more examples but did not add anything basically new, and only the use of tributylphosphate [9] finally resulted in a breakthrough. During the ensuing years the literature was flooded with publications dealing with the liquid-liquid extraction of rare earths. Pure compounds of rare earths were produced on a commercial scale and became readily available. Since then, our knowledge of the chemistry and physics of the rare earths has expanded substantially.

This account demonstrates the following points:

- Fundamental research without an economic goal can open new opportunities for industry.
- Not only plentiful financial resources can be-

nefit research, but even the lack of such can be beneficial because it forces us to develop new ideas.

References

- [1] W. Prandtl, *Z. Anorg. Allg. Chem.* 198 (1931) 157.
- [2] O. Höningschmid and W. Kapfenberger, *Z. Anorg. Allg. Chem.* 214 (1933) 97.
- [3] W. Fischer, W. Dietz and O. Jübermann, DR Patent 752 865 (10.4.1937). The most important results of this patent are reported in reference [5].
- [4] W. Fischer, W. Dietz and O. Jübermann, *Naturwiss.* 25 (1937) 348.
- [5] *Science and Medicine in Germany 1939–1946 (FIAT Review of German Science)* Vol. 23, *Inorg. Chem. Section* 1.1.2.
- [6] See for instance:
W. Fischer and R. Bock, *Z. Anorg. Allg. Chem.* 249 (1942) 146.
W. Fischer, W. Chalybaeus and M. Zumbusch, *Z. Anorg. Allg. Chem.* 255 (1948) 277.
- W. Fischer and K.-J. Bramekamp, DB Patent 1 052 968 (20.7.1956).
- W. Fischer et al., *Z. Anorg. Allg. Chem.* 329 (1964) 44.
- W. Fischer and H.-P. Pohlmann, *Z. Anorg. Allg. Chem.* 328 (1964) 252.
- W. Fischer et al., *Angew. Chem. (International Edition in English)* 5 (1966) 15.
- E. Greinacher, W. Fischer and M. Dähne, US Patent 3 715 424 (filed 3.6.1971).
- W. Fischer and F. Schmitt, US Patent 3 721 692 (filed 22.7.1968).
- [7] See F. Spedding et al. and G.E. Boyd et al., *J. Am. Chem. Soc.* 69 (1947) 2769–2881.
- [8] D.B. Appleton and P.W. Selwood, *J. Am. Chem. Soc.* 63 (1941) 2029.
C.C. Templeton and J.A. Peterson, *J. Am. Chem. Soc.* 70 (1948) 3967; 71 (1949) 2187.
G.F. Asselin, L.F. Audrieth and E.W. Comings, *J. Phys. Coll. Chem.* 54 (1950) 640.
Th. Moeller and D.E. Jackson, *Anal. Chem.* 22 (1950) 1393.
- [9] J. Warf, *J. Am. Chem. Soc.* 71 (1949) 3257.
D.F. Peppard, J.P. Faris, P.R. Gray and G.W. Mason, *J. Phys. Chem.* 57 (1953) 294.

ELEMENT 61

T.V. Swaminathan (Manager QC&R)

Indian Rare Earths Ltd, India

The rare earths probably can claim the distinction of having had the attention of the largest number of scientists, not only during the historical development starting in 1787 when Arrhenius discovered gadolinite, but to this day when Dr. Karl A. Gschneidner Jr thought of celebrating the Bicentennial!

Because of the inherent complex nature and the involvement of a large number of scientists, the historical development of rare earths has had more than its share of controversies. The most notorious of all these controversies was that surrounding the discovery (or otherwise?) of element 61. Element 61 was the subject of great polemics during the 1920s.

Ever since Brauner in 1903 predicted the existence of one element between neodymium and samarium attempts were made to isolate it. Originally it was Eder who found some lines in an arc spectrum of samarium supposed to belong to this element. This was confirmed in 1922 by Hadding. However, some confusion was created by Prandtl and Grimm in 1924; after some X-ray spectra studies they suggested that this element might be a homologue of manganese rather than a rare earth.

The most important work on element 61 was done by Hopkins, Yntema and Harris. They claimed the discovery of it in 1926 and named it "illinium" in honour of the University of Illinois where their work was carried out. They cited the presence of some lines in the red, infrared and violet spectral regions in some neodymium and samarium preparations which became more intense in fractions where element 61 was expected. They also cited absorption bands in solution ob-

tained from fractions as evidence for the existence of this element. These lines were said to become stronger as the bands of neodymium and samarium became weaker. They also revealed lines in X-ray emission spectra in places corresponding to the theoretical positions of element 61.

Publication of the work of Hopkins et al. stirred a hornet's nest. Some German workers, notably Mayor, Schumacher and Kotowski, came forward with claims of previous discovery. But the most vehement claims were put forward by Rolla and Fernandes from Italy. They insisted that they had discovered this element earlier as a result of X-ray and absorption spectra work carried out at the University of Florence, and that this element should rightly be named "florentium". Rolla and Fernandes claimed to have placed a sealed record of this work in a vault in the Academy of Lincei in 1924. (Why such a discovery should have been kept secretly in a vault eludes comprehension!) History does not give us any clue as to whether Rolla and company ever met their counterparts Hopkins and others face to face, but judging by the heat of the controversy it is pretty certain they would have come to blows on this account.

Bibliography

- [1] R.C. Vickery, Chemistry of the Lanthanons (Butterworths, London, 1953).
- [2] N.E. Topp, Chemistry of the Rare Earth Elements (Elsevier, Amsterdam, 1965).
- [3] D.M. Yost, H. Russell Jr and C.S. Garner, The Rare Earth Elements and their Compounds (Wiley, New York, 1947).

ELECTRONIC STRUCTURE vs. CHEMISTRY

Christian K. Jørgensen

Section de Chimie, University of Geneva, Geneva, Switzerland.

Yttrium and the lanthanides provide many interesting (and slightly troublesome) paradoxes. Most solid inorganic compounds do not contain separate molecules, but bridged crystal structures, since the coordination number N usually is considerably higher than the oxidation state (when positive). Like Ca(II) and Th(IV), the rare earths add the complication of indifferently showing $N = 6, 7, 8, 9, 10, 11, 12$ (and in organometallic compounds from 4 to 16). There is no feature (like in partly filled d-shells) stabilizing a definite stereochemistry for a given N , and the intercalation of nearly all the chemical properties of Y(III) between those of Dy(III) and Ho(III) is determined by ionic size, disregarding the partly filled 4f shell.

Among the instructive surprises, the most striking is the discrepancy between the electron configuration to which the ground state of the gaseous atom belongs, and the almost invariant Ln(III) chemistry in nonmetallic compounds. Stoner (1924) * connected atomic spectroscopy with the chemical Periodic Table [1] by suggesting that the f shell can accommodate at most 14 electrons (like 10 in one d shell). It remains true that chemical homologs (oxygen, sulfur, selenium, tellurium; fluorine, chlorine, bromine, iodine; ...) have closely similar atomic spectra, and that not only beryllium, magnesium, calcium, strontium, barium, radium, but also zinc, cadmium, ytterbium, mercury, undoubtedly nobelium, and helium (but not the other noble gases) are alkaline-earth atoms, spectroscopically speaking. One might have expected the 54 electrons in closed shells (known from xenon) to be supplemented by $4f^9 5d 6s^2$ with

$q = Z - 57$. We know since 1973 that this is the case for only four lanthanide atoms: lanthanum (Russell and Meggers 1932), cerium (Smith and Spalding 1961, Martin 1963), gadolinium (Albertson 1935), and lutetium (Meggers and Scribner 1930). The remaining eleven atoms are "barides" without the 5d electron and $q = Z - 56$: praseodymium (Lew 1953, Zalubas and Borchardt 1973), neodymium (Schuurmans, 1946), promethium (Reader and Davis 1967), samarium (Albertson 1935), europium (Russell and King 1934), terbium (Klinkenberg and Van Kleef 1970), dysprosium (Cabezas et al. 1961, Conway and Worden 1971), holmium (Childs and Goodman 1961, Blaise et al. 1972), erbium (Cabezas et al. 1961, Marquet and Davis 1965), thulium (Meggers 1942) and ytterbium (Meggers and Scribner 1937). The numerous J -levels belonging to definite electron configurations were tabulated in 1978 by Martin, Zalubas and Hagan [2] extending the three-volume *Atomic Energy Levels* series by Charlotte Moore. When two citations are given for the references above, the first refers to a measurement of the g (gyromagnetic factor) of the ground state, rendering its J value and thus making its electron configuration highly plausible, and the second refers to the analysis of the spectrum. It is an awfully close shave in the terbium atom, where the first excited J -level, belonging to $4f^8 5d 6s^2$, is only 285 cm^{-1} above the ground state. This energy difference is less than 1% of the ionization energy, 47300 cm^{-1} (5.86 eV), which is again smaller than the (calculated) total width of both the $4f^9 6s^2$ and $4f^8 5d 6s^2$ configurations. For the chemist, the major conclusion is that the low-lying electron configurations of the gaseous atom are not particularly relevant for the chemical behavior of the lanthanides, any more than for chromium,

* All references given in "Harvard style" may be found in ref. [2].

rhodium, palladium, platinum, uranium, plutonium, berkelium, and several other atoms.

The oxidation state of lanthanides in translucent compounds can be determined from the narrow absorption bands due to the excited J -levels of $4f^q$ supplemented, if needed, by broad intense electron transfer bands of Ln(IV) and Eu(III), and transitions to $4f^{q-1}5d$ of Ln(II) and Ce(III) [3]. However, molar volumes (unit cell parameters), magnetic and other properties of metallic solids (elements, alloys and stoichiometric compounds) allow the evaluation [4] of the conditional oxidation state Ln(II) for $q = Z - 56$ or Ln(III) for $q = Z - 57$. It turns out that the shorter the Ln-Ln internuclear distances are, the more pronounced is the tendency to go to the Ln(III) state. From 11 Ln(II) species among the gaseous atoms, only six in the LnI₂ phase (neodymium, samarium, dysprosium, thulium, ytterbium) are still in the Ln(II) state; and in the tellurides there are three Ln(II) states (SmTe, EuTe and YbTe) and one compound (TmTe) which shows the simultaneous presence of comparable amounts of Tm(II) and Tm(III) on an instantaneous picture, according to photoelectron spectra. Among LnS, only Sm(II), Eu(II) and Yb(II) persist at ordinary pressure, and among the metallic elements only the last two. In some alloys with heavy metals, only Eu(II), or no lanthanide at all, may remain Ln(II).

The concept derived from atomic spectroscopy of the distance (which may be up to 10 eV) from the lowest J -level of $4f^q$ to the average energy (barycenter) of all states of this configuration, has been highly helpful in rationalizing the stability of the three possible oxidation states when varying Ln, since a chemical reduction is the increase of q by one.

Among the most important applications of lanthanides, subjects such as ferromagnetic SmCo₅ and Nd₂Fe₁₄B seem rather unpredictable, but the transitions between J -levels provide the red cathodoluminescence of Eu(III) in color television, and the Nd(III) glass terawatt lasers [5], and represent an unexpected inheritance from atomic spectroscopy.

References

- [1] C.K. Jørgensen, in: *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 11, eds K.A. Gschneidner Jr and L. Eyring (North-Holland, Amsterdam, 1988) ch. 75.
- [2] W.C. Martin, R. Zalubas and L. Hagan, *Atomic Energy Levels, the Rare Earth Elements*, NSRDS-NBS 60 (National Bureau of Standards, Washington, DC, 1978).
- [3] R. Reisfeld and C.K. Jørgensen, *Lasers and Excited States of Rare Earths* (Springer, Berlin, 1977).
- [4] K.A. Gschneidner Jr, *J. Less-Common Met.*, 17 (1969) 13.
- [5] J.F. Holzrichter, E.M. Campbell, J.D. Lindl and E. Storm, *Science* 229 (1985) 1045.

NOBEL PRIZE 200 YEARS LATER?

Andrzej Szymanski

Institute of Electronic Materials Technology, Warsaw, Poland

In 1787, K.A. Arrhenius discovered the mineral ytterbite, $(\text{Ce, La, Nd, Y})_2\text{Fe}^{2+}\text{Be}_2\text{Si}_2\text{O}_{10}$, now called gadolinite. He had no idea of the new possibilities of development he was opening (not even in his wildest imagination), especially in electronics, a then unknown science. The full brilliance of this science would only be achieved 200 years later, when mankind mastered the control of electronic phenomena in industrial technologies.

Before any growth could take place, geochemists and crystallographers had to understand the specifics of distribution of the rare-earth elements (really not as rare as some think) in the Earth's crust. Thanks to a constant outer electronic shell and completion of subatomic 4f electronic shell, the 15 elements occupy one elementary place in the classical periodic system. Due to similar and low chemical activity in the natural environment, they rarely created unique minerals but must be extracted from poor raw materials. The location of RE elements in the periodic system is more clearly illustrated in the spiral periodic table [2] as shown in fig. 1.

The poor chemical raw materials necessitated the perfection of hydrometallurgical processes for extraction and purification of the rare-earth elements. This is especially true for electronics applications, where purities as high as 99.999% must be achieved. While the specific atomic structure of the rare earths is troublesome in their production, it is this same specific atomic structure that makes

them basic elements for structural stabilization or modification of many metallic or ceramic materials of today's electronic or nucleonic technologies. Some examples are single crystals, polycrystalline ceramics, glasses, glazes, cast iron, steel, stainless steel, other alloys, and permanent magnets based on, or doped with rare-earth elements. Electronic microtechnology, which is first of all crystal engineering, has seen the development of an ever increasing number of materials with various electronic properties created, stimulated, or stabilized by small amounts of rare-earth dopants. It is difficult to say if the most important development in electronics was the discovery of the transistor in 1949, or the succeeding number of rare-earth applications in electronic technologies. The range of these applications can be seen in fig. 2.

Speculation leads one to wonder what Arrhenius would have thought if he could have foreseen the future that rare earths would have in electronics in the 2nd half of the 20th century.

References

- [1] R.B. Sosman, *The Properties of Silica* (Chemical Catalysis Company, New York, 1927).
- [2] A. Szymanski, Spiral Version of Periodic System, *Mat. Elektron.* 3 (1986) 55. In Polish.
- [3] A. Szymanski, *Technical Mineralogy and Petrography* (Elsevier, Amsterdam, 1988) in print.

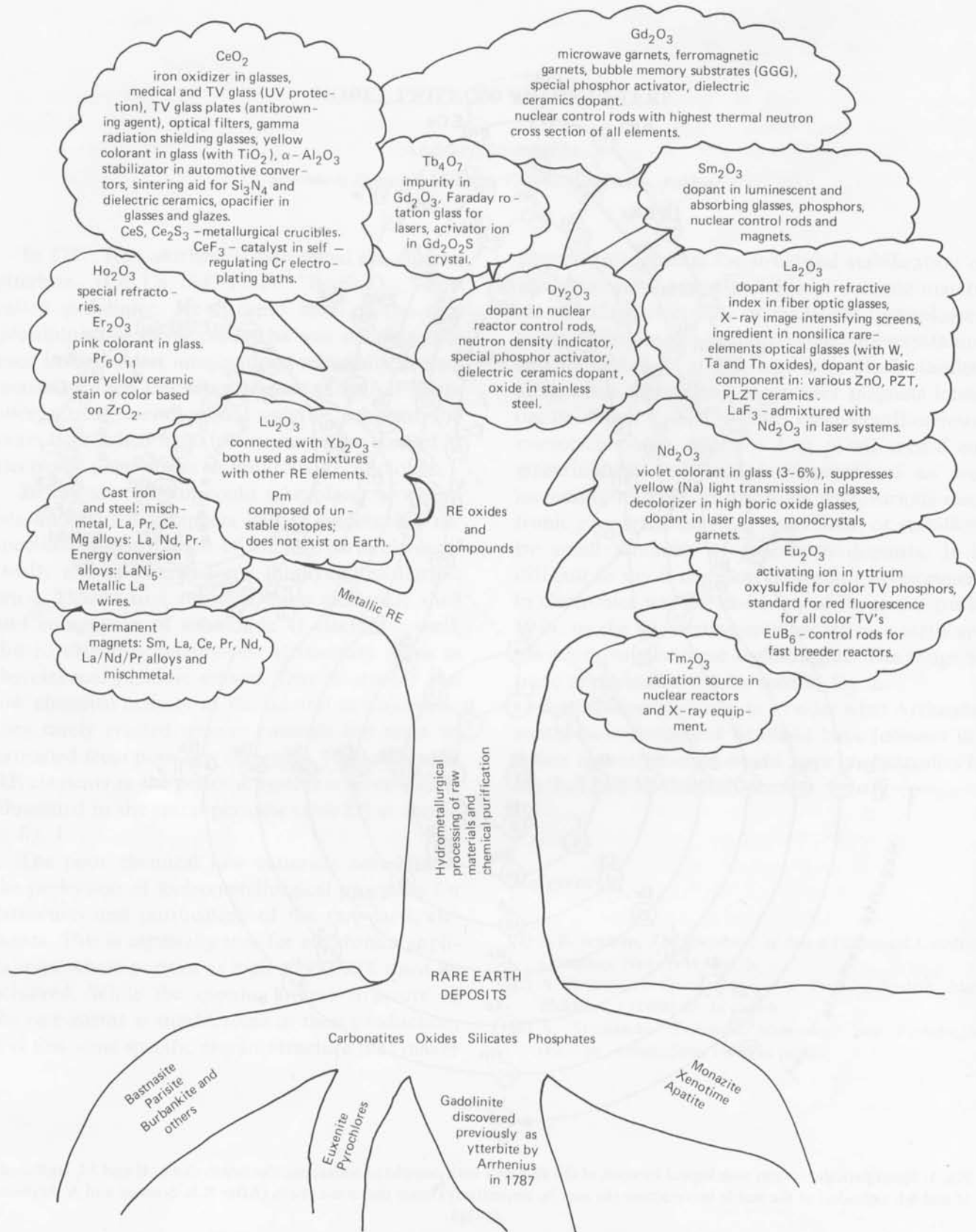


Fig. 2. Rare-earth family in electronic materials.

LUMINESCENCE APPLICATIONS

Mel Tecotzky

Matrix, Palo Alto, CA 94303, USA

One of the most significant discoveries in rare earth technology is the commercial and medical application of rare earth luminescence. Even though Urbain reported on the cathodoluminescent properties of $Gd_2O_3:Eu$ in 1907, no significant applications appeared until the middle 1960s.

In the 1960s, $YVO_4:Eu$, $YVO_4Eu:Bi$, $Y_2O_3:Eu$, $Gd_2O_3:Eu$ and $Y_2O_2S:Eu$ were introduced as red phosphors for color television. These technological advances had a profound influence on the rare earth industry. There was now commercial justification to build large separation plants to prepare tonnage quantities of high-purity rare earth oxides.

With the introduction of the red emitting CRT phosphor, we saw a \$125.00 a pound product capture the market from a \$28.00 a pound zinc cadmium sulfide:silver phosphor. The TV industry has now settled on $Y_2O_2S:Eu$ as the red phosphor of choice. Other important rare earth phosphors for specialty CRT's followed: $Gd_2O_2S:Tb$ for avionics, $Y_2O_2S:Tb$ a one-component black and white phosphor for special displays, and terbium- and cerium-activated rare earth garnets for high current density and rapid decay displays.

The luminescent properties of the rare earths have also improved the quality of fluorescent lamps. There are now blue, green, and red rare earth phosphors used in fluorescent lamps which produce energy-efficient fluorescent lamps with improved color rendition.

The CRT and fluorescent lamp applications of rare earth phosphors are important and have expanded rare earth production. However, the most significant application of rare earth luminescence is in medicine.

Calcium tungstate was the only significant X-

ray phosphor for 70 years. In the early 1970s, rare earth phosphors were introduced as X-ray phosphors for intensifying screens. Through the use of these phosphors, which have excellent conversion efficiency, and X-ray photon absorption in the medical range, it is possible for a patient to get an X-ray with *half* the dose and *equivalent* image quality. Further cuts in dosage are possible depending on the type of examination. Medical X-rays are the greatest source of radiation we receive, and through the use of rare earth X-ray phosphors we have thus been able to decrease the amount of radiation a patient receives. The rare earth X-ray phosphors in current commercial use are: $Gd_2O_2S:Tb$, $LaOBr:Tb$, $LaOBr:Tm$, $Y_2O_2S:Tb$, $BaFCl:Eu$, yttrium tantalate:Nb, and yttrium tantalate:Tm. These phosphors are used in general diagnostic radiology for many types of examinations; in addition, $Gd_2O_2S:Tb$ is also used for mammography.

Some of the important benefits of rare earth phosphor intensifying screens are:

- (1) Dose reduction for the patient and X-ray staff.
- (2) Extended X-ray equipment life owing to decreased dose.
- (3) Decreased exposure time, reducing loss of image detail or blurring due to patient motion. This can reduce the need for re-takes, especially for children.
- (4) Increased brightness or speed, permitting the use of small focal spot X-ray tubes for improved geometric sharpness.
- (5) Increased phosphor brightness, permitting the use of less silver in X-ray film.

The commercial applications of rare earth luminescence have provided us with:

- (a) Less radiation from medical X-rays.
- (b) Improved cathode ray tubes for home and industry.
- (c) Improved lighting.
- (d) Economic windfall for the rare earth industry

and justification for plant expansion and improved separation techniques.
 One significant and major application of rare earth luminescence not mentioned is the laser.

POWERFUL NEW MAGNET MATERIAL FOUND *

Arthur L. Robinson

Center for X-ray Optics, Lawrence Berkeley Laboratories, Berkeley, CA 94720, USA

If a person thinks of a material for a permanent magnet at all, it is likely to be of something with lots of iron in it. In fact, however, for many years the best permanent magnets have contained little or no iron. Now iron is back.

In 1983, several research groups in Japan and in the United States announced the discovery of a new compound – probably of composition $R_2Fe_{14}B$, where R is a light lanthanide (usually neodymium) – that has some of the best magnetic properties ever.

The impact of the breakthrough will depend on both technological and economic factors. Magnets made of the compound tend to lose their desirable properties at elevated temperatures. If this fault can be cured – there is evidence that it can – and if the cost drops, as it should when volume production begins, the new material could push aside all but the most inexpensive alternatives and dominate the magnet market, the most optimistic observers say.

Permanent magnets have a number of parameters that measure their performance. The two most important are the coercivity and the energy product. The coercivity is the strength of the external field needed to demagnetize the material. A high coercivity is needed to prevent the demagnetization of permanent magnets when they encounter fields produced by other sources. The energy product is a composite parameter determined by both the strength of the magnet and the coercivity and is the most frequently cited figure of merit.

Until the new iron-based compound popped up, the materials that most closely satisfied re-

quirements for high values of these parameters were compounds principally comprising samarium and cobalt. The original compound, $SmCo_5$, was discovered in the mid-1960s by Karl Strnat (now at the University of Dayton) and his co-workers at the Air Force Materials Laboratory, Wright-Patterson Air Force Base, and the General Electric R&D Center, Schenectady. This compound has an energy product of 143 kilojoules per cubic meter (kJ/m^3), more than six times that of the widely used ceramic or ferrite materials. Subsequent development led to more complex materials containing limited amounts of copper, zirconium and iron, which have energy products up to 239 kJ/m^3 .

The high price of samarium-cobalt magnets has limited their use in large volume, however. For example, starter motors in automobiles now rely on battery-driven electromagnets. Samarium-cobalt permanent magnets could make smaller, more reliable starters, and General Motors once considered them for that purpose. But the company decided against them partly because of their cost.

Fluctuations in the price and availability of cobalt made General Motors even more nervous. Cobalt is a by-product of copper and nickel mining, and the main source for the United States is southern Africa, Zaire in particular. When fighting broke out there in 1978 and the copper mines were at risk, the price of cobalt on the spot market rocketed up by a factor of 8 and was still up by a factor of 5 a year later.

Cobalt is also an essential ingredient of high-temperature superalloys for aircraft and is therefore classified as a strategic material. Both for economic reasons and to relieve any possible drain on cobalt resources required for strategic applica-

* Excerpted from *Powerful New Material Found*, by A.L. Robinson, *Science (Research News Section)* 223 (2 March 1984) pp. 920–922. Copyright 1984 by the AAAS.

tions, the 1978 cobalt crunch precipitated a search for cobalt-free permanent magnet materials.

Metallurgists searching for new magnetic materials face a formidable task. The strength of the ideal magnet depends on the elements making up the material. Each atom has a magnetic moment due to the orbital and spin angular momenta of its electrons. The macroscopic magnetization of a material is the resultant sum of the moments of each atom, which would all be aligned in the fully magnetized state. Transition elements such as iron and cobalt have large moments, so one likes to put large amounts of these elements into the mix. However, the coercivity depends first on the crystal structure of the compound and then on the metallurgical microstructure of the final material.

Magnetic materials resist demagnetization when it takes a large energy to rearrange the aligned magnetic moments of the atoms in the material. Crystal structures come into play because, with respect to ease of magnetization, some crystallographic directions are easy (do not take much energy) and some are hard. A high coercivity requires a crystal structure with very hard directions separating the easy ones so that it takes a great deal of energy to reorient the magnetic moments from one easy direction to another.

Transition metals such as iron and cobalt do not have what researchers call high magnetocrystalline anisotropy energies. Metallurgists therefore add rare earths to transition metals because the compounds they form sometimes have structures with the required high anisotropy energies. The trick is to achieve this without losing the high magnetization through dilution of the magnetic moments.

The actual mechanism by which the direction of the magnetization changes is not one in which the atomic moments flip simultaneously throughout the material. Instead, entities called domain walls that separate regions of different directions of magnetization move through the material, reorienting moments only where they pass. The highest coercivity, therefore, requires the inhibition of domain wall motion. In general, this is done by adjusting the composition of the material so that two phases form with different magnetic properties, one the magnetic compound

and the other something else. The second phase must be very finely distributed (for example, scattered throughout the magnetic phase). It then pins or traps the domain walls and thereby raises the strength of the magnetic field needed to demagnetize the material.

Research in the United States sprang from two primary sources. The Office of Naval Research sponsored work at several industrial and academic laboratories, while the General Motors Research Laboratories in Warren, Michigan, mounted an independent effort. All the groups apparently used for their starting point the 1973 work of Arthur Clark of the Naval Surface Weapons Center in White Oak, Maryland. The 1960s studies of Strnat's group, as well as the studies of a number of others, had shown that binary rare earth-iron compounds were few in number and had unimpressive magnetic properties. Clark found, however, that compounds of the form RFe_2 , where R is terbium, dysprosium, or samarium, had much improved coercivities, provided they were first prepared in a noncrystalline or amorphous state.

With no long-range crystal structure and hence no anisotropy, amorphous materials would not seem to be candidates for permanent magnets. However, amorphous materials provide a nice starting point from which to prepare crystalline materials with unusual metallurgical microstructures or to make crystalline nonequilibrium (metastable) phases with novel properties. Clark's results had suggested the possibility that annealing amorphous materials could give rise to magnetically active materials composed of very fine crystallites or grains.

The investigators who followed Clark's lead in looking at rare earth-iron compounds used a technique called melt spinning in which a stream of molten material is blown out through the orifice of a crucible onto a spinning copper wheel. For example, at the Naval Research Laboratory in Washington, D.C., Norman Koon and Badri Das started from the well-known observation that the presence of boron enhances the likelihood of rapidly cooled materials being amorphous. They studied terbium-lanthanum-iron-boron mixtures in the hope that magnetically active compounds with optimized microstructures would form upon

annealing the amorphous material. Upon annealing at successively higher temperatures, they found the coercivity rose sharply, then decreased.

During the same 1980 to 1982 period, reports from John Croat's group at General Motors described experiments on melt-spun praseodymium-cobalt, praseodymium-iron, and neodymium-iron materials. Neodymium-iron was the most interesting. A series of specimens was prepared by spinning the wheel at different speeds. In general, one would expect faster cooling at higher speeds and hence an increased tendency toward the formation of amorphous material. However, the coercivity of unannealed specimen increased dramatically with spinning speed at first, then dropped off more gently. Croat's interpretation was that at the lowest speed a magnetically active phase did not form. At higher speeds one did, and the coercivity rose. At still higher speeds, the grain became so small that their properties deteriorated.

It is clear that these investigations formed the background for the development of the new rare earth-iron-boron permanent magnets. But the line of thinking that led the various participants to their goal is not so clear. Nearly everyone missed a 1979 report in a Soviet journal by crystallographers at the Lvov Ivan Franko State University in the Ukraine. During their study of the neodymium-iron-boron phase diagram they found an equilibrium ternary compound, which turned out to be the one that makes the new magnets possible. They did not report its structure or magnetic properties.

One American scientist who did notice the report was Hans Stadelmaier of North Carolina State University in Raleigh, who was investigating rare earth-transition metal-boron systems. Stadelmaier was only beginning work on permanent magnets, however, and did not immediately follow up on the discovery. He and his colleagues later found an identical samarium-cobalt-boron compound and gathered some structural information.

Things began moving faster in April 1983. Spurred by new results from a group comprising George Hadjipanayis and Robert Hazelton of the Kollmorgen Corporation in Radford, Virginia, and K.R. Lawless of the University of Virginia in Charlottesville, ONR program director Donald

Polk suggested his contractors compare notes prior to an international magnetic materials meeting in Philadelphia. Hadjipanayis discussed some of the results obtained by the group and later sent some data and samples to Stadelmaier. Stadelmaier immediately identified the Kollmorgen material (which consisted of a praseodymium-iron-boron-silicon mixture that was annealed following rapid solidification by the melt-spinning technique) as containing a compound with the same composition as that reported by the Ukrainians. In June 1983 an unexpected announcement from Japan set magnetics people buzzing. The Sumitomo Special Metals Company of Osaka revealed that it had made magnets from a new compound based on neodymium and iron that had an energy product of 290 kJ/m^3 , higher than the best samarium-cobalt material. Moreover, the company was making the material by conventional powder metallurgical techniques of the type used to manufacture samarium-cobalt magnets. Sumitomo said it would begin making samples of the material available to prospective customers in the fall.

In November 1983 at the 29th Annual Conference on Magnetism and Magnetic Materials held in Pittsburgh, all the players were called to lay their cards on the table. Researchers from General Motors, NRL, General Electric, Kansas State University, to which Hadjipanayis had migrated, and North Carolina State summarized their findings. Koon from NRL, for example, reported that he and Das had made, by annealing melt-spun praseodymium- and neodymium-iron-boron material, magnets with energy products up to 103 kJ/m^3 .

Similarly, GM's Croat discussed praseodymium-iron-boron and neodymium-iron-boron compounds that had energy products of up to 120 kJ/m^3 that were produced by the same method that his group had been using before. Croat also revealed that the laboratory had found a way to double this value, but did not say how it had been done.

In contrast, Sumitomo's Masato Sagawa was forthcoming in his presentation at the conference. Lyman Johnson of General Electric said "it was explicit and so well done that anyone who knows

how to make samarium-cobalt could make rare earth-iron-boron in a week".

Late in January 1984, Crucible's Research Center in Pittsburgh announced publicly that it had made by a powder-metallurgical method the highest energy product material yet, 341 kJ/m^3 . Crucible's Kalatur Narasimham said that the company's search for a cobalt-free magnet had been going on for about 2 years.

The powder method begins with an ingot solidified from the melt in the ordinary way so that mainly the magnetic compound of composition $\text{Nd}_2\text{Fe}_{14}\text{B}$ forms. The ingot is ground in several stages to small particles a few micrometers in diameter. The particles are aligned and pressed together in a magnetic field so that they are all magnetized in the same direction; that is, the compacted body has some of the anisotropy of the crystal structure. Then the particles are sintered to form a dense solid. During the sintering at high temperature, the particles lose their magnetization, so the sintered material must be remagnetized.

One interesting question is, with all the early emphasis on rapid solidification, why is it possible to make the rare earth-iron-boron compound by ordinary methods? Part of the answer is that the boron stabilizes the new compound. The resulting crystal structure is tetragonal, an anisotropic structure that contributes to the high coercivity. The relatively small concentrations of light rare earths and boron allow the magnetization to remain high.

Somewhat conjectural still is the nature of the

metallurgical microstructure that enhances the coercivity. Those making the new compound by the powder metallurgy method find that the overall composition must differ slightly from that of the compound to allow the formation of one or more additional phases that are richer in rare earth or boron than the magnetic compound and that are seen near the grain boundaries. The General Motors group has stuck to its original explanation that the grains are so small that they contain no domain boundaries and that it takes a lot of energy to nucleate any.

The main limitation of the new magnetic compound is that it has a low Curie temperature, 585 K (312°C) as compared to over 1000 K (727°C) in samarium-cobalt compounds. Since magnets lose their magnetization above the Curie temperature, the magnet strength and the coercivity of the new material drop off severely when it is heated to only 100°C above room temperature. But researchers have found that the addition of cobalt raises the Curie temperature, and that addition of heavy rare earths enhances the coercivity, rendering it less sensitive to temperature effects.

If cobalt is needed to make the rare earth-iron-boron compound useful, can one still speak of cobalt-free magnets? The literal answer is no, but the concentration of that element is nonetheless greatly reduced. Strnat says the likeliest outcome is the development of a large family of magnets of varying composition. Rare earth-iron-boron and rare earth-cobalt will be extremes at each end of the family.

PAST, PRESENT AND FUTURE OF RARE EARTH METALLURGY *

K.A. Gschneidner Jr

Ames Laboratory, and Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011, USA

Summary

Advances in the field of rare earth metallurgy and solid state physics in the last 157 years (the years since the first rare earth element was prepared in the metallic state) have gone hand in hand with the purity of the available metals. The scientific and technological developments have been grouped into three ages or eras: the Dark Ages, the Age of Enlightenment and the Golden Age. A glimpse of the future is also given.

1. Introduction

At the outset of this paper I must, unfortunately, define the term "rare earths" since so many scientists still incorrectly use these two words to mean the "lanthanides" [i.e. the elements with atomic numbers $Z = 57$ (lanthanum) to $Z = 71$ (lutetium)]. The correct terminology as defined by the International Union of Pure and Applied Chemistry is that the *rare earths* comprise the elements scandium ($Z = 21$), yttrium ($Z = 39$) and the lanthanides [1], and this definition will be used in this paper.

As the title implies I shall present a brief historical summary of the events that have occurred in the field of rare earth metallurgy, including the role that the Journal of the Less-Common Metals (JLCM) has played over the past 25 years. The emphasis will be on the basic and applied research aspects, but important events concerning industrial and commercial applications will also be noted.

The history of rare earth metallurgy can be divided into three eras or ages, based more or less on the availability and purity of the metals (a similar division of the development of and discoveries in solid state physics was presented by

Mackintosh [2]). These are the Dark Ages (before 1950), the Age of Enlightenment (1950–1969) and the Golden Age (1970 to present). The important events in these three eras will be discussed separately below.

2. The Dark Ages (1787–1949)

The Dark Ages began with the discovery of the rare earths by Arrhenius in 1787 in the Swedish town of Ytterby, but as far as the field of metallurgy is concerned they began about 40 years later (table 1) when Mosander [3] prepared cerium by reduction of $CeCl_3$ with sodium or potassium. The resultant product was a highly contaminated cerium powder. About another 50 years passed before Hillebrand and Norton [4] first successfully applied the electrolytic method to reduce the metal salts. Their metal was also highly contaminated, particularly with the electrode materials carbon and/or iron. It was over 50 years later before scientists were able to prepare metals which were sufficiently pure to determine some of their physical properties.

As is noted in table 1 the existence of both ferromagnetism (gadolinium) [10] and superconductivity (lanthanum) [12] in a rare earth metal was discovered about the time that these metals became available in a reasonably pure form [9,11].

* From *Journal of the Less Common Metals* (Elsevier Sequoia 100 (1984) 1.

Table 1
Major events in the Dark Ages (1787–1949)

1827	Preparation of the first rare earth metal (Ce) [3]
1875	Electrolytic method used for the first time to prepare rare earth metals [La, Ce and didymium (1Pr–3Nd)] [4]
1908	First major metallurgical application of the rare earths: mischmetal–iron lighter flints (von Welsbach, in ref. [5])
1911	First rare earth metal binary phase diagram study reported (Ce–Sn system) [6]
1912	X-ray spectra confirm that only 15 lanthanides are to be expected plus the two closely related metals Sc and Y (Moseley, in ref. [7])
1925	The term “lanthanide contraction” is coined [8]
1931	Preparation of “reasonably pure” light lanthanides by electrolysis (bulk metals) [9]
1935	Discovery of ferromagnetism in a rare earth metal (Gd) [10]
1937	Preparation of “reasonably pure” powder lanthanide metals (essentially all of them) and determination of their crystal structures (many for the first time) [11]
1937	Discovery of superconductivity in a rare earth metal (La) [12]
1947	First successful separations of adjacent lanthanides by ion exchange: Spedding and coworkers (Ames) and Boyd and coworkers (Oak Ridge) (see ref. [13])
1948	Beginning of the utilization of Ce (mischmetal) additions to procedure nodular cast irons (Morrogh and Williams, in ref. [14])

By “reasonably pure” I would estimate that the metals were about 90 at% pure with the major impurities being the interstitial elements (hydrogen, carbon, nitrogen and oxygen); however, metallic impurities as high as a few atomic per cent could also be expected. It is interesting to note that Mendelssohn and Daunt [12], who discovered superconductivity in lanthanum, stated that their metal contained 1% Fe (probably wt%, and if so then the lanthanum contained 2.5 at% Fe). It is amazing that their sample was still superconducting ($T_c = 4.7$ K), but this probably arose from the insolubility of iron in lanthanum.

The first rare earth metal binary phase diagram (Ce–Sn) was reported by Vogel [6] in 1911, but we know now that many parts of this diagram were in

error. A few more systems were studied by Vogel over the next two decades, but the 1930s were the real beginning of phase diagram studies, at least of the binary systems of lanthanum, cerium and praseodymium. However, because of the impure nature of these rare earth metals, all phase diagrams published in this era should be considered to be wrong unless verified by more recent experimental measurements. It is quite likely that many of these “binary” phase diagrams may actually quite accurately represent a section cut through a ternary or quaternary system. Unfortunately only the two elements which make up the “binary” alloys are known. The third (and fourth in the case of quaternaries) element(s) is (are) unknown, but since carbon or iron were used as electrode materials these two elements would be prime candidates. Indeed, lanthanum metal stocks used in some phase diagram studies were reported to have a melting point in the range 800–810 °C, which overlaps the lanthanum-rich eutectic temperature of 806 °C in the La–C system [15].

The dramatic discovery (published in 1947) by scientists and engineers working on the U.S. Manhattan Project that adjacent lanthanide metals could be separated from one another, at least on a laboratory scale, by ion exchange quickly brought an end to the Dark Ages. Subsequently Spedding and coworkers improved the ion exchange method so that kilogram quantities of the individual elements were obtained, and commercial production soon followed [13]. These developments ushered in the Age of Enlightenment.

Before we turn to the next age, we should note that there are several developments, discoveries etc. which were not discussed above but are listed in table 1 as major milestones. The X-ray spectra studies of Moseley [7] and the observation of the lanthanide contraction [8] greatly contributed to our knowledge of these metals, while use of lighter flints in 1908 was the beginning of the metallurgical portion of the rare earth industry [5]. Most of the other commercial metallurgical applications were not realized until later eras. However, the earliest use of rare earth metal additives had its beginning just as the Dark Ages closed, but major tonnage amounts were not realized until 10–15 years later [14].

3. Age of Enlightenment (1950–1969)

With the availability of high-purity rare earth oxides, there was a large upswell of scientific studies of these unique elements. Concurrent with the improvements and scaling-up of the ion exchange separation techniques new methods were developed for preparing high-purity rare earth metals in kilogram quantities. At the beginning of this era the metals were 95–98 at% pure, the major impurities being the interstitial impurities, but by the end of the 1960s the routinely prepared metals were attaining purities close to 99 at%. Furthermore, by the end of the era methods of producing selected rare earth metals with purities approaching 99.99 at% had been developed and were successfully tested. These advances greatly aided scientists in their investigations of the rare earth metals and their alloys, and as a result we uncovered many surprises in their unique natures and behaviors (several of the more important ones are listed in table 2).

One of the first surprises was the discovery that the large volume of transformation in cerium which had been observed in the early 1940s on cooling or under pressure at room temperature was an isostructural transformation (fcc $\gamma \rightarrow$ fcc α). Zachariasen, who analyzed the high pressure results of Lawson and Tang [16], and Pauling, who analyzed the low temperature results of Schuck and Sturdivant [17], independently suggested that this large volume change was due to the promotion of the 4f electron in γ -Ce to the valence band. This was the beginning of the subject which today is called "valence fluctuations" and is one of the most exciting current research topics. Continued studies of cerium led to another major surprise in about the middle of this era: the discovery of a solid–solid critical point, i.e. near T_c – P_c (the critical point) the γ and α phases of cerium are indistinguishable from one another [22].

At about this time two major developments took place and they greatly enhanced the spreading of the gospel of the rare earths: the founding of the JLCM in 1959 and the commencement of the Rare Earth Research Conferences in 1960. The first paper which appeared in the JLCM concerning the rare earth elements was by Hellowell [31]

Table 2

Major events in the Age of Enlightenment (1950–1969)

1949–1950	Beginning of valence fluctuations; discovery of a valence transformation in cerium ($\alpha \rightleftharpoons \gamma$) at low temperature or high pressure [16,17] (independent research)
1951	Discovery of the high thermionic emissivity properties of LaB_6 [18]
1953	Development of the metallothermic reduction of R_2O_3 method for preparing the high vapor pressure metals ($\text{R} \equiv \text{Sm, Eu, Tm and Yb}$) [19]
1953–1954	Determination of the unique structure of Sm [20,21] (independent research)
1958	Discovery of a solid state critical point (Ce) [22]
1959	First issue of the <i>Journal of the Less-Common Metals</i> published; a major journal for reporting rare earth metallurgical research
1960	First Rare Earth Research Conference, held at Lake Arrowhead, CA, USA
1961	Discovery of the unique beautifully complex magnetic structures of the heavy lanthanide metals [23]
1962	Discovery of the existence of the Sm (δ) phase in intra rare earth binary alloys [24]
1963	Last rare earth element to be prepared in the metallic state: radioactive Pm [25]
1966	Establishment of the Rare-earth Information Center at Iowa State University, Ames, IA, USA
1966	First successful application of solid state electrolysis to purify a rare earth metal (Y) [26]
1966	Discovery of the high-strength rare earth–cobalt permanent magnets YCo_5 [27,28]
1967	Reporting of the superior permanent magnet properties of SmCo_5 [28,29]
1967	First direct Fermi surface measurements (de Haas–van Alphen oscillations) on a rare earth metal (Yb) [30]

and dealt with the effect of scandium and yttrium on the fcc \rightleftharpoons bcc transformations in manganese and iron. The number of papers published on the rare earth metals slowly increased from an average of about two in the first three volumes (Vols. 1–3) to about six in Vols. 4–6 and about 12 in Vols. 7–9. This latter number of 12 papers per volume

(approximately 33% of each volume) has remained reasonably constant since then (Vols. 10–90), but the number of volumes per year had increased to six by 1982. In 1983 the JLCM and the Sixteenth Rare Earth Research Conference combined their efforts, resulting in the appearance of the conference proceedings as Vols. 93 and 94 which were the first volumes of the JLCM devoted entirely to rare earth research and technology.

The Rare Earth Research Conferences have served as an important vehicle for announcing new discoveries and major advances. The most important of these, in my opinion, was the presentation by Koehler et al. [23] at the First Rare Earth Research Conference describing the first neutron diffraction measurements on the heavy lanthanide single crystals which revealed their unique and fascinating magnetic structures. To date there have been 16 such conferences in the USA, and future plans are to hold one yearly, beginning in 1985, alternating between Europe (1985) and the U.S.A. or Canada (1986). It is hoped that the JLCM will continue to publish the proceeding of future conferences.

Another important source of information on the rare earths – the Rare-earth Information Center (RIC) – was founded in the last quarter of the Age of Enlightenment. The RIC was initially supported by the US Atomic Energy Commission, but 2 years later (1968) the world-wide rare earth industry became the major source of financial support and today the RIC lists about 50 companies as its benefactors. It publishes a quarterly publication called the *RIC News* * (the circulation is about 5500) and answers slightly more than one information inquiry per working day.

The development of new and improved methods for preparing pure rare earth metals for research purposes was a major goal of these two decades. Early in the period Daane et al. [19] developed a new method for preparing the high vapor pressure lanthanide metals (samarium, europium, thulium and ytterbium) by reduc-

tion of the respective oxides with lanthanum or cerium metal. Because of either their high vapor pressures or their divalent states it was difficult (almost impossible for samarium) to prepare these elements in the metallic state by the usual technique of calcium reduction of the fluoride (chloride). However, because of the large difference between the vapor pressure of lanthanum and these four volatile lanthanides (a factor of 10^{10} between lanthanum and ytterbium) these metals were the first to be prepared with purities greater than 99.9 at%. This development in turn led to several important advances in this era: the structure of samarium metal, the SmCo_5 permanent magnet (to be discussed later) and the first Fermi surface measurements on a rare earth metal. The determination of the structure of samarium was important for two reasons: (1) its structure, a nine-layered hcp structure, is unique among the elemental structures; (2) the knowledge of its structure permitted us to close the chapter on the room-temperature equilibrium structures of the naturally occurring rare earth metals. By the end of the Age of Enlightenment, ytterbium metal had been prepared of a sufficiently high purity and quality that the first direct Fermi surface measurements ever made on a rare earth metal were accomplished by observing the Haas-van Alphen oscillations [30] in a single crystal.

The next major step that occurred in the research on developing or improving processes for purifying rare earth metals took place in 1966 when Carlson et al. [26] demonstrated for the first time that significant improvements in the interstitial content could be achieved by solid state electrolysis (also called electrotransport purification). This step and subsequent improvements in the techniques and equipment played a substantial role in making available high-purity rare earth metals for research in the next era: the Golden Age.

The growth in the number of nuclear reactors in 1950s and early 1960s accounted for the increased availability of fission products, which meant that researchers finally had sufficient amounts of promethium oxide from which the metal could be prepared and studied. Thus, with the report of the preparation of promethium metal

* The RIC News is available free and can be obtained from the Rare-earth Information Center, Energy and Mineral Resources Research Institute, Iowa State University, Ames, IA 50011, USA.

by Weigel [25] in 1963, all the rare earth metals had been prepared in their elemental state and at least some of their properties had been characterized.

Although the unique structure of samarium had been determined in 1953–1954, this structure was to make its presence felt again about eight years later when Spedding et al. [24] reported the existence of the samarium structure (called the δ phase) as an intermediate phase when a trivalent light lanthanide metal is alloyed with a trivalent heavy lanthanide or yttrium metal. This discovery spurred many theoretical papers and other alloying and high pressure experimental studies of this phase, which can be considered to be composed of nine layers, two-thirds of which have hexagonal symmetry and one-third of which have fcc symmetry.

Before closing the discussion of the Age of Enlightenment I should like to review several important developments or discoveries which took place and have significant technological and commercial implications. Early in this age, in an investigation of the thermionic properties of metal borides, carbides and nitrides, Lafferty [18] found that LaB_6 had superior properties to any materials then known. As a matter of fact this statement is still valid today, nearly 35 years later. This material is currently being used in electron microscopes, television and cathode ray tubes, electron guns etc. where enhanced brightness or high electron emission is required.

The major industrial development in this Age involving the rare earth metals occurred in the late 1960s when Strnat and coworkers discovered the fantastic permanent magnet properties of the RCO_5 series of materials, first with YCo_5 (in 1966) and then with several of the light lanthanides, especially SmCo_5 (1967) [27–29]. This development grew rapidly in the 1960s and 1970s, and the commercial market was saturated in the late 1970s when the available supply of inexpensive samarium metal was consumed as fast as it could be produced. Today this is still an important market, but developments in the early 1980s (see below) may be a harbinger of its demise.

4. The Golden Age (1970 to date)

The basic and applied research of the late Dark Ages and the Age of Enlightenment has provided the fundamental background and the high purity materials necessary to fuel the Golden Age to (1) new heights of knowledge and understanding, (2) advanced technological achievements and (3) many new surprises. Early in the 1970s several important discoveries were noted (table 3), and most of these have had some limited commercial utilization by the 1980s and offer much promise for growth in the near future. These include the ability to absorb large amounts of hydrogen [32], the preparation of the first amorphous rare earth materials [33] and the observation of giant magnetostrictions at room temperature in the rare earth–iron Laves phases [35].

The ability of LaNi_5 -base materials to absorb

Table 3
Major events in the Golden Age (1970 to date)

1970	Discovery of the unique hydrogen absorption properties of the LaNi_5 family of materials [32]
1970	Preparation of the first rare-earth-containing amorphous alloys [33]
1970	Initial commercial realization of mischmetal additions to steels to achieve shape control of metal sulfide inclusions [34]
1971	Discovery of giant magnetostrictions in RFe_2 phases [35]
1976	Demonstration of a rare-earth-based magnetic heat pump [36]
1976	Kondo scattering observed in a pure element (Ce) [37–39]
1978	First volume of the <i>Handbook on the Physics and Chemistry of Rare Earths</i> published
1979	First Frank H. Spedding Prize awarded at the Fourteenth Rare Earth Research Conference, Fargo, ND, USA, to W.E. Wallace
1980	Successful application of PrNi_5 in ultralow temperature refrigerators [40]
1981	Discovery that spin fluctuations could be quenched in magnetic fields of less than 10 T (LuCo_2) [41]
1981	Discovery of the high-strength iron–rare earth permanent magnets [42]

copious amounts of hydrogen (more hydrogen per unit volume than liquid hydrogen at 20 K) at room temperature and modest pressure (below 10 atm) make these alloys excellent candidates for hydrogen storage, hydrogen separation and/or purification, heat pumps, refrigeration etc., especially in view of the reversible absorption and desorption of hydrogen [43]. The plateau pressures can be altered by appropriate alloying, but except on rare occasions alloying usually reduces the hydrogen storage capacity of the prime candidate LaNi_5 .

The work of Bates et al. [33] on amorphous Gd–Ag alloys was the beginning of a large ground swell which has developed into one of the most active areas of rare earth research today. In the past 15 years the properties and behavior of many materials have been characterized and several interesting and unusual phenomena have been observed [44–46], but no major applications have yet developed.

The discovery in 1971 of giant magnetostrictions [35] has many high technology implications, but commercial utilization has only recently begun to be realized. This is rather surprising since the magnetostrictions observed in the RFe_2 phases (primarily TbFe_2 -based materials) are about three orders of magnitude larger than those observed in the best known material (nickel) prior to that time.

The demonstration that the magnetic properties of rare earth materials can be used to pump heat (or to cool) [36] has generated considerable interest in the past few years, but it is too early to know how practical this approach will be and whether a commercial market will develop.

The most recent discovery of the excellent permanent magnet properties of the Nd–Fe–B alloys (approximately $\text{Nd}_2\text{Fe}_{14}\text{B}$) has generated considerable excitement in the permanent magnet technology area. Shortly after the initial report by Croat [42] of the large energy products of amorphous Nd–Fe alloys, researchers at the Naval Research Laboratory [47] reported that the addition of boron to iron-rich lanthanide alloys improved the coercivity and energy product. The importance of alloy chemistry and metallurgical processing in producing these “super”-permanent

magnets cannot be emphasized enough and is quite evident in the recent summary given by Robinson [48] concerning the developments in this area since 1981. To date the highest energy product reported for an Nd–Fe–B alloy is more than 40% larger than the best value attained for an Sm–Co magnet, and at this early state of development this value should easily be exceeded. Thus it appears that the SmCo_5 – $\text{Sm}_2\text{Co}_{17}$ permanent magnets will become passé because the Nd–Fe–B alloys have higher energy products and are made of much cheaper materials.

The utilization of rare earths in the form of rare earth silicides or mischmetal additions to control the shape of sulfide particles in steels grew explosively in the early 1970s and peaked around 1975. Since then, however, this commercial market for rare earth products has dropped off slowly at first and more rapidly in the early 1980s. The major reasons for this reversal are competition by other cheaper shape-control processes and materials and the decline of the steel industry from 1981 to 1983 owing to the world-wide recession. The outlook for a strong steel market involving rare earths in the remainder of this decade is dim.

The remaining milestones of this Golden Age do not seem to have as strong a commercial bent as the items discussed above. As has been noted, throughout the two earlier ages cerium has had a dominant share of the honors, but this is understandable considering its unique position in the Periodic Table (it is the first element to have a 4f electron). Again in this age cerium has another claim to make. Although Kondo scattering had been observed for many years, first in dilute systems (from 1000 at ppm to 2 at%) and then in concentrated systems (i.e. 33 at%), it was discovered in 1976 that Kondo-like behavior occurs in a pure element: naturally cerium [37–39]. Today it is the only pure element known to exhibit Kondo scattering, but if another pure element does show similar behaviour it will probably be a metal from the early part of the actinide series.

One of the greatest surprises in this era was the discovery that spin fluctuations could be quenched in fields of 5–10 T instead of fields of 100 T or more as predicted by theory. Since the initial work by Ikeda and Gschneidner [41] on LuCo_2 the

quenching of spin fluctuations has been observed in about ten other materials, not only by these researchers and their coworkers but also by other scientists [49]. Furthermore, the quenching or non-quenching of spin fluctuations seems to depend quite critically on the presence or absence of certain impurities, the chemical composition and the chemical ordering of the component metal species in the intermetallic compound. Careful metallurgical processing will play an important role in our understanding of this phenomenon. Our present ideas on the occurrence of quenching of spin fluctuations suggest that these materials have an unusual Fermi surface with small areas of extremely high density of states. Continued research in this area will be quite fruitful in our understanding of the nature of the magnetic materials which lie between normal paramagnets and strong ferromagnets and also in our understanding of superconductivity.

Although scientists had suggested almost 20 years ago [50] that temperatures of 10^{-5} K might be attained by adiabatic demagnetization using lanthanide materials, it was not until 1980 that Pobell and coworkers [40] successfully demonstrated that useful working temperatures of about $40 \mu\text{K}$ could be obtained by using a two-stage nuclear demagnetization refrigerator. The first stage consisted of several moles of PrNi_5 and the second stage consisted of copper metal. In early 1983 the Japanese team headed by Ishimoto [51] claimed a new world record for a working temperature of $27 \mu\text{K}$ using the same type of refrigerator.

Other notable events of the golden era include the inauguration of the Frank H. Spedding prize at the Rare Earth Research Conferences and the serial publication *Handbook on the Physics and Chemistry of Rare Earths*. The winner of the first Spedding prize in 1979 was W.E. Wallace from the University of Pittsburgh. Subsequent winners were G. Busch, Eidgenössische Technische Hochschule, Zürich, in 1981, and S. Legvold, Iowa State University, and W.C. Koehler, Oak Ridge National Laboratory, who shared the 1983 prize. The first volume of the *Handbook on the Physics and Chemistry of Rare Earths*, which is edited by K.A. Gschneidner Jr and L. Eyring, was published in 1978 and since then five more volumes have ap-

peared, the latest (Vol. 6) in 1984. It consists of timely, authoritative and comprehensive reviews of various aspects of rare earth research written by experts in the various fields.

The end of the golden era is nowhere in sight but, in the first decade plus, a number of notable advances and discoveries have been duly noted. However, because of my limited vision and wisdom there are probably a few more achievements which occurred in the early 1980s and were not obvious to me. Undoubtedly these will need to be added to table 3 at a later date.

5. The future

The future is here, but all we can do is to speculate on what might be, and I hope history will not judge my views of the future too harshly. Some things are clearly obvious, but most hide as if in a morning fog, a few faintly visible as shadowy forms and many not to be seen until sufficient time has passed to allow the sunshine of knowledge to penetrate and disperse the foggy air.

The future of the rare earths will be glorious, in its science, its technology and its commercial utilization, and the JLCM will play a major role in bringing the rare earths to new heights and adventures. That much is clear, but the details are nebulous.

The application of alloy chemistry and metallurgical processing will be essential in the research and development of rare earth amorphous and thin film materials, especially with respect to their electrical and magnetic properties. I foresee expanded efforts on these materials and metastable phases in both short- and long-term time scales, and some notable achievements will be realized. Most of the research on equilibrium alloys will be concentrated on ternary and higher-order systems, but some unexpected developments will be found in the binary systems.

Exciting developments in the next 10 years will occur in our studies of mixed valent materials and other narrow electron energy band systems involving the lanthanide metals. Both non-magnetic and magnetic impurities and sample perfection are known to have pronounced effects on the various

phenomena observed in these materials. In order to understand these phenomena the metallurgist, chemist, physicist and materials scientist will be sorely tested to provide the required well-characterized samples. The characterization techniques will need to be improved by an order of magnitude over what is possible at present if substantial progress is to be realized in our knowledge of this exciting class of materials.

Some surprises will be found in superconducting rare earth systems involving at least one non-metallic element (such as boron, carbon, nitrogen, phosphorus etc.) and another metallic element (preferably a middle transition metal such as vanadium, niobium, molybdenum etc.). I expect that the current highest superconducting transition temperature of about 17 K for a rare earth material will easily be exceeded by 1995.

Continued studies of the magnetic behavior of the rare earth metal compounds and alloys will reveal some new and exciting phenomena, and new records will be established. Research being carried out at the extremes of laboratory experimental variables, such as low temperatures, high magnetic fields and high pressures, have the highest probability of success.

Surface studies will also receive much greater attention in the future, not only as studies in themselves but also because many of the techniques involved in characterizing samples utilize surface-sensitive measurements. As a result of these surface science studies some new commercial applications and novel surface behavior can be expected.

These are the shadowy forms that we can dimly see in the morning fog. The rest are unseen, unheard and unthought of, but they will come at the appropriate time in their full glory to take their places as milestones of the Golden Age.

As described above our increased knowledge of the science and technology of the rare earth metals has greatly depended upon the availability of increasingly pure materials. However, will this hold true for the future? For example, in the past 10 years we have been able to prepare sufficiently high purity metals that we are able to study their Fermi surfaces [52] and for the first time obtain

reproducible low-temperature (1–20 K) heat capacity measurements (the electronic specific heat constant γ and Debye temperature θ_D) for various samples of the same metal performed by various investigators [53]. Thus it would appear that the driving force for even higher purity is no longer present or is much smaller than in the past. If this is the saturation, then I doubt it will last for long. For example, the only Fermi surface measurement that has been made on a heavy lanthanide metal with a non-zero L (orbital) quantum number is for terbium [54] and there are four more lanthanides (dysprosium, holmium, erbium and thulium) which have not been examined. The main reason for this is the unavailability of ultrapure single crystals of these elements. This lack of availability is in part due to the high vapor pressures of these metals which make electrotransport purification more difficult, but ways will be found to circumvent this problem. Another area of research, that on narrow electron energy band phenomena (Kondo effect, valence fluctuations, spin fluctuations etc.), will more than likely demand purer materials than are currently available so that we can measure their intrinsic properties. Other unexpected research areas will suddenly appear and will demonstrate a need for pure materials. Current examples of this are the nuclear magnetic resonance (NMR) studies involving gadolinium impurities in some rare earth metal hydrides, e.g. YH_2 [55]. Phua et al. [55] have shown that the proton spin–lattice and spin–spin relaxation times are controlled by the gadolinium contents down to 50 at ppm. More recent NMR studies of LaH_3 have indicated that a gadolinium concentration as low as 5 at ppm has an effect on the NMR relaxation times [56].

Even though the driving force (need) may be there, can we make purer metals? The answer is yes. As pointed out by Gschneidner [57] it should be possible by combining zone refining and electrotransport purification techniques to prepare metals approaching 99.999 at% purity with respect to *all* the elements in the periodic table. As yet this has not been demonstrated in practice, but when the need arises it will be done.

Acknowledgements

The author wishes to acknowledge his colleagues B.J. Beaudry and J. Capellen for their helpful comments, and R.G. Barnes for permission to quote some unpublished results.

The Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract W-7405-ENG-82. This work was supported by the Office of Basic Energy Sciences.

References

- [1] J.A. Christiansen, *J. Am. Chem. Soc.* 82 (1960) 5525.
- [2] A.R. Mackintosh, 6th Frank H. Spedding Lecture, Iowa State University, Ames, IA, USA, October 10, 1983.
- [3] G.G. Mosander, *Ann. Phys. (Leipzig)* 11 (1827) 406.
- [4] W. Hillebrand and T. Norton, *Ann. Phys. Chem.* 155 (1875) 633.
- [5] E. Greinacher, in: *Industrial Applications of Rare Earth Elements*, ed. K.A. Gschneidner Jr, *Am. Chem. Soc. Symp. Ser.* 164 (1981) 3.
- [6] R. Vogel, *Z. Anorg. Allg. Chem.* 72 (1911) 319.
- [7] F.H. Spedding, in: *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 1, eds K.A. Gschneidner Jr and L. Eyring (North-Holland, Amsterdam, 1978) p. xv.
- [8] V.M. Goldschmidt, T. Barth and G. Lunde, *Skr. Nor. Vidensk.-Akad. Oslo, I, Mat.-Naturvidensk. Kl.* (7) (1925) 59.
- [9] M. Billy and F. Trombe, *C.R. Acad. Sci.* 193 (1931) 421.
- [10] G. Urbain, P. Weiss and F. Trombe, *C.R. Acad. Sci.* 200 (1935) 2132.
- [11] W. Klemm and H. Bommer, *Z. Anorg. Allg. Chem.* 231 (1937) 138.
- [12] K. Mendelssohn and J.G. Daunt, *Nature (London)* 139 (1937) 473.
- [13] J.E. Powell, in: *The Rare Earths*, eds F.H. Spedding and A.H. Daane (Wiley, New York, 1961) p. 55.
- [14] H.F. Linebarger and T.K. McCluhan, in: *Industrial Applications of Rare Earth Elements*, ed. K.A. Gschneidner Jr, *Am. Chem. Soc. Symp. Ser.* 164 (1981) 19.
- [15] F.H. Spedding, K.A. Gschneidner Jr and A.H. Daane, *Trans. Metall. Soc. AIME* 215 (1959) 192.
- [16] W.H. Zachariasen, cited by A.W. Lawson and T. Tang, *Phys. Rev.* 76 (1949) 301.
- [17] L. Pauling, cited by A.F. Schuck and J.H. Sturdivant, *J. Chem. Phys.* 18 (1950) 145.
- [18] J.M. Lafferty, *J. Appl. Phys.* 22 (1951) 299.
- [19] A.H. Daane, D.H. Dennison and F.H. Spedding, *J. Am. Chem. Soc.* 75 (1953) 2272.
- [20] F.H. Ellinger and W.H. Zachariasen, *J. Am. Chem. Soc.* 75 (1953) 7650.
- [21] A.H. Daane, R.E. Rundle, H.S. Smith and F.H. Spedding, *Acta Crystallogr.* 7 (1954) 532.
- [22] E.G. Ponyatovskii, *Dokl. Akad. Nauk SSSR* 120 (1958) 1021.
- [23] W.C. Koehler, E.O. Wollan, M.K. Wilkinson and J.W. Cable, in: *Rare Earth Research*, ed. E.V. Kleber (Macmillan, New York, 1961) p. 149.
- [24] F.H. Spedding, R.M. Valletta and A.H. Daane, *Trans. Am. Soc. Met.* 55 (1962) 483.
- [25] F. Weigel, *Angew. Chem.* 75 (1963) 451.
- [26] O.N. Carlson, F.A. Schmidt and D.T. Peterson, *J. Less-Common Met.* 10 (1966) 1.
- [27] K.J. Strnat and G.I. Hoffer, Rep. AFML-TR-65-446, May 1966 (U.S. Air Force Materials Laboratory, Dayton, OH), available from National Technical Information Service Springfield, VA 22161, USA.
- [28] J.J. Becker, *Sci. Am.* 223 (6) (1970) 92.
- [29] K. Strnat, G. Hoffer, J. Olson, W. Ostertag and J.J. Becker, *J. Appl. Phys.* 38 (1967) 1001.
- [30] S. Tanuma, Y. Ishizawa, H. Nagasawa and T. Sugawara, *Phys. Lett. A* 25 (1967) 669.
- [31] A. Hellawell, *J. Less-Common Met.* 1 (1959) 110.
- [32] J.H.N. van Vucht, F.A. Kuijpers and H.C.A.M. Bruning, *Philips Res. Rep.* 25 (1970) 133.
- [33] P.A. Bates, J. Popplewell and S.W. Charles, *J. Phys. D* 3 (1970) L15.
- [34] L.A. Luyckx, in: *Industrial Applications of Rare Earth Elements*, ed. K.A. Gschneidner Jr, *Am. Chem. Soc. Symp. Ser.* 164 (1981) 43.
- [35] A.E. Clark and H.S. Belson, in: *Magnetism and Magnetic Materials 1971*, eds C.D. Graham Jr and J.J. Rhyne, *AIP Conf. Proc.* 5 (1972) 1498.
- [36] G.V. Brown, *J. Appl. Phys.* 47 (1976) 3673.
- [37] K.A. Gschneidner Jr, P. Burgardt, S. Legvold, J.O. Moorman, T.A. Vyrostek and C. Stassis, *J. Phys. F* 6 (1976) L49.
- [38] S.H. Liu, P. Burgardt, K.A. Gschneidner Jr and S. Legvold, *J. Phys. F* 6 (1976) L55.
- [39] P. Burgardt, K.A. Gschneidner Jr, D.C. Koskenmaki, D.K. Finnemore, J.O. Moorman, S. Legvold, C. Stassis and T.A. Vyrostek, *Phys. Rev. B* 14 (1976) 2995.
- [40] R.M. Mueller, C. Buchal, H.R. Folle, M. Kubota and F. Pobell, *Cryogenics* 20 (1980) 395.
- [41] K. Ikeda and K.A. Gschneidner Jr, *Phys. Rev. Lett.* 45 (1980) 1341.
- [42] J.J. Croat, *Appl. Phys. Lett.* 39 (1981) 357.
- [43] E.L. Huston and J.J. Sheridan III, in: *Industrial Applications of Rare Earth Elements*, ed. K.A. Gschneidner Jr, *Am. Chem. Soc. Symp. Ser.* 164 (1981) 223.
- [44] J.J. Rhyne, in: *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 2, eds K.A. Gschneidner Jr and L. Eyring (North-Holland, Amsterdam, 1979) p. 259.
- [45] M. Gasgnier, in: *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 5, eds K.A. Gschneidner Jr and L. Eyring (North-Holland, Amsterdam, 1982) p. 1.
- [46] K.H.J. Buschow, in: *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 7, eds K.A. Gschneidner Jr and L. Eyring (North-Holland, Amsterdam, 1984) p. 265.

- [47] N.C. Koon and B.N. Das, *Appl. Phys. Lett.* 39 (1981) 840.
- [48] A.L. Robinson, *Science* 223 (1984) 920 [Excerpted in this booklet.]
- [49] K.A. Gschneidner Jr and K. Ikeda, *J. Magn. & Magn. Mater.* 31-34 (1983) 265; 39 (1983) 320.
- [50] S.A. Al'tshuler, *Pis'ma Zh. Eksp. & Teor. Fiz.* 3 (1966) 177 [*JETP Lett.* 3 (1966) 112].
- [51] H. Ishimoto, N. Nishida, T. Furubayashi, M. Shinohara, Y. Takano, Y. Miura and K. Ono, *Tech. Rep. Inst. Solid State Phys., Univ. Tokyo, Ser. A*, 1357 (August 1983); *J. Low Temp. Phys.* 55 (1984) 17.
- [52] S.H. Liu, in: *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 1, eds. K.A. Gschneidner Jr and L. Eyring (North-Holland, Amsterdam, 1978) p. 233.
- [53] T.-W.E. Tsang, K.A. Gschneidner Jr, F.A. Schmidt and D.K. Thome, *Phys. Rev. B* 31 (1985) 235.
- [54] R.C. Young, S.P. Farrant, D.W. Jones and J.J. Beaudry, *J. Phys. F* 12 (1982) L35.
- [55] T.-T. Phua, B.J. Beaudry, D.T. Peterson, D.R. Torgeson, R.G. Barnes, M. Belhoul, G.A. Styles and E.F.W. Seymour, *Phys. Rev. B* 28 (1983) 6227.
- [56] R.G. Barnes, Iowa State University, Ames, IA, USA (1980) personal communication.
- [57] K.A. Gschneidner Jr, in: *The Rare Earths in Modern Science and Technology*, Vol. 2, eds G.J. McCarthy, J.J. Rhyne and H.B. Silber (Plenum, New York, 1980) p. 13.