

RARE EARTH MINERALS AND 21ST CENTURY INDUSTRY

Detailed Written Responses to Subcommittee's Questions

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QUESTION 1: RARE EARTH SCIENCE AND TECHNOLOGY AT THE AMES LABORATORY

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1. Introduction

The Ames Laboratory (AL) is the smallest of DOE's (Department of Energy) seventeen national laboratories. It is a single-program laboratory with about 78% of DOE's funding from the Office of Basic Energy Sciences (BES). Additional non-DOE income of about \$7M is derived from contracts, grants, Cooperative Research and Development Agreements (CRADAs) and Work for Others (WFO) arrangements.

The AL is fully integrated with Iowa State University (ISU) and its buildings are right on the campus and several are directly connected with ISU buildings. All AL personnel are ISU employees, and many of the lead scientists (23) have joint appointments with various academic departments. There are about 140 scientists and engineers, 260 graduate and undergraduate students, another 240 visiting scientists, facility users, and associates, and 180 support personnel, for a total of about 440 employees (or about 300 full-time equivalent employees) and 410 associates (non-payroll). Of the scientific staff about 20% are directly involved in rare earth research and development activities, including materials science, condensed matter physics, and materials chemistry.

2. A Brief History – How Did Rare Earths get to Ames?

Many persons may wonder how the Mecca of rare earths^a ever ended up on the picturesque ISU campus – an oasis amongst the corn and soy bean fields of central Iowa. The story begins in late 1930s when Frank H. Spedding was searching for a permanent academic position after receiving his Ph.D. from the University of California in 1929 under G.N. Lewis. His Ph.D. thesis dealt with the physical properties of rare earth materials at low temperature. He spent a number of years in temporary jobs, including two years in Europe, where he worked with several Nobel prize winners, including Niel Bohr. In 1937, while he was occupied at Cornell University working with a future Nobel prize winner, Hans Bethe, he was offered a permanent position at ISU^b as an associate professor, and he remained at ISU until he retired in 1972. Frank Spedding was primarily a spectroscopist, but he had to separate and purify his rare earth samples from the other rare earth elements in order to carry out his optical measurements, which are very sensitive to the presence of other rare earth impurities. Based on his experience with rare earth (or 4f) chemistry he was asked by A.H. Compton of the University of Chicago to work with actinide (or 5f) materials to assist the team of physicists to build the first nuclear reactor under the stands of Stagg Field at the University of Chicago. Spedding was appointed the Director of Chemistry in the Chicago Project. One of the main goals of the Project was to purify uranium from its ores and then to convert the oxide to the metal – six tons were needed, which seemed like mission impossible since only a few grams of uranium metal had been produced before World War II. By late summer in 1942 the delivery of the uranium was behind schedule and Frank Spedding offered to use a different approach to make the metal via a metallothermic reduction of uranium tetrafluoride, UF₄. It was successful, and as an added bonus it was purer than the metal produced by other organizations. By November, the ISU team sent two tons of

^a Coined by *Chemical and Engineering News* in the 1970s.

^b At that time ISU was known as Iowa State College, but I will use ISU in this presentation. The name change officially occurred in 1959.

uranium cylinders (2" diameter x 2" long) to Chicago. The addition of these two tons to the four tons delivered previously allowed the reactor to go critical on December 2, 1942. This stellar contribution to the Manhattan Project was recognized when ISU and Spedding's team were awarded the "Army and Navy E for Effort with four stars" pennant on October 12, 1945; the only university (college) in the country to receive this prestigious honor. Since the Ames ingots were purer and less expensive to produce, the Manhattan District asked three companies to take over the Ames fluoride process and make large amounts of uranium for the Oak Ridge and Hanford reactors. But since it took time to get the facilities up and running the ISU group was asked to continue to produce uranium metal. More than two million pounds were produced by the end of World War II, and by December 1945 industry took over. The Ames process, albeit somewhat modified, is still in use today [1].

Soon thereafter, a new requirement arose in the war effort. Thorium metal was needed for another type of reactor, and Spedding and his co-workers were asked to develop a process for making thorium metal. Again they were successful and the Ames thorium process was turned over to industry. In the meanwhile, 600,000 pounds of thorium were produced [1].

During the late war years, research on developing methods of separating the rare earth elements was begun at several Manhattan District laboratories because some of the rare earth elements were among fission products which would absorb neutrons because of their high neutron capture cross-section and eventually would cause the reactor to shut down. Also the pure rare earth elements were needed to study their chemical and metallurgical behaviors to help actinide chemists and physicists understand the trans-uranium elements because of the expected similarities in the properties of the two series of elements. It was during these years that Spedding and co-workers developed the ion exchange method for separating rare earths, which was in commercial use for many years after World War II, until displaced by liquid-liquid extraction procedures. The ion exchange process is still in use today to obtain the very highest purity rare earth elements (99.9999% pure), which are primarily used in optical applications such as lasers and optical signal multipliers [1].

On May, 17, 1947 the Ames Laboratory became one of the Atomic Energy Commission (AEC) laboratories to promote the peaceful uses of atomic energy and to do research to increase our understanding and knowledge of the chemistry, physics, and nuclear behavior of the lesser known and uncommon elements, including the rare earths [1].

Additional information about the Ames Laboratory and Frank H. Spedding during World War II and the early post-World War II years can be found in several articles authored by I.E. Goldman [2,3,4] and papers by J.D. Corbett [5] and by S.R. Karsjen [6].

3. The Golden Age of Rare Earth Research

The time span of the 1950s through the 1970s was the golden age of rare earth research at the Ames Laboratory. At that time there was a very wide spectrum of research being carried out ranging from separation chemistry to analytical chemistry to process and physical metallurgy to solid state experimental physics to theoretical first principle calculations.

3.1 Separation Chemistry

The discovery of using ion exchange chromatography to separate and purify the rare earths was further refined and improved in the 1950s through the 1960s. A large pilot plant was set up to supply researchers at the Ames Laboratory and other organizations, including many of the AECs national laboratories, with high purity individual rare earths, to carry out fundamental and applied research on various chemical compounds and the pure metals (see §§3.3-3.6). In addition these ion exchange columns were used to separate the other rare earths from yttrium (also a rare earth element) which was to be used in the nuclear aircraft (see § 3.3).

3.2 Analytical Chemistry

In order to verify the chemical purity of the separated products new and more sensitive chemical and physico-chemical analytical methods were developed to detect impurities of both rare earth and other non-rare earth elements at the part per million level. This included wet chemistry, atomic emission and atomic absorption spectroscopy, laser ion mass spectrometry, vacuum and inert gas fusion, and combustion analysis. This research also led to the development of inductively coupled plasma (ICP)-atomic emission (AE) in the late 1970s, and ICP-mass spectrometry (MS), which occurred in the early 1980s. The ICP-MS technology was turned over to industry and today is still one of the most versatile and utilized analytical techniques, see § 5.

3.3 Process Metallurgy

This was one of the strengths of the Ames Laboratory in this time period. The pure rare earth elements, after separating them on the ion exchange columns, were converted to their respective rare earth oxides. The oxide was converted to the fluoride which was then reduced to the pure metal by calcium metal. These two processes were the critical steps for preparing high purity metals with low concentration of interstitial impurities, especially oxygen, carbon, nitrogen, and hydrogen. The reduced metals were further purified by a vacuum casting step and for the more volatile rare earth metals further purification was carried out by distillation or sublimation. Generally, kilogram (2.2 pounds) quantities were prepared at the Ames Laboratory. Industry adopted the Ames process with some minor modifications to prepare commercial grade rare earth metals, and it is still in use today. This method is still being carried out at the AL under the auspices of the Materials Preparation Center (MPC), see § 6.1.

In the late 1950s the AEC asked the Ames Laboratory to prepare pure yttrium metal for the proposed nuclear aircraft. A nuclear reactor would be used to heat gases to propel an airplane much like a jet engine. This aircraft would carry atomic weapons for months at a time without landing. The yttrium was to be hydride to form YH_2 which is used to absorb the neutrons produced by the fission of uranium protecting the crew from radiation. As part of this project the AL produced 65,000 pounds of YF_3 and 30,000 pounds of yttrium metal. The yttrium metal was cast into 85 pound, 6 inch diameter ingots to ship to the General Electric Co. facilities in Cincinnati, Ohio.

In the mid-1950s, Spedding and A.H. Daane and their colleagues developed a new technique for preparing high purity metals of the four highly volatility rare earths – samarium, europium, thulium, and ytterbium – by heating the respective oxides with lanthanum metal and collecting the metal vapors on a condenser. This process has also been turned over to industry and is used by AL's Materials Preparation Center today (§ 6.1).

3.4 Physical Metallurgy

Research in the physical metallurgy area encompassed: determining melting points, crystal structures, vapor pressures, low temperature heat capacities, elastic constants, and magnetic properties of the pure metals and various intermetallic compounds; and phase diagram and thermodynamic properties studies; crystal chemistry analyses; and alloying theory of rare earth-based materials. This was another strong focus area in the AL in the 1950s-1970s era which is still active today but at reduced level.

Closely related, but not strictly physical metallurgy, was research on the mechanical behavior (tensile and yield strengths, ductility, and hardness) of the metals and some of their alloys, and also oxidation and corrosion studies, especially yttrium in conjunction with the nuclear aircraft project. From the information gained from the mechanical property measurements, processes were developed to fabricate the rare earth metals and their alloys at room and elevated temperature into a variety of shapes and forms, e.g. rolled sheets.

3.5 Materials and Solid State Chemistry, and Ceramics

The chemical activity, in addition to separation and analytical chemistry (§3.1 and §3.2) was another area in which the AL was considered to be world class, even though the manpower levels were smaller than above noted areas of analytical chemistry, process and physical metallurgy. Research was focused on the sub-stoichiometric rare earth halides, and interstitial impurity stabilized compounds including the halides. X-ray crystallography was an important tool in this focus area to characterize these compounds. John D. Corbett was the lead scientist and is still active today.

Investigations of ceramic materials were important in many of the studies and advances in process and physical metallurgy, not only for their refractory properties, but also because of the need to contain the molten metals without contamination. Rare earth oxides and sulfides, because of their intrinsic stability, were candidate materials to contain the molten rare earths, uranium, thorium and other non-rare earth metals.

3.6 Condensed Matter Physics

The AL was very strong in this area from the very beginning and still is today. Research under the leadership of Sam Legvold was concentrated on the magnetic behavior of the metals and the intra-rare-earth alloys. This work was strongly coupled with neutron scattering studies at both the Ames Laboratory and Oak Ridge National Laboratory, and also with the theorists. The theoretical efforts included first principle calculations (Bruce

Harmon) and phenomenological approaches (Sam Liu). Superconductivity was also another active topic of research, but most of the effort was concentrated on non-rare-earth compounds.

3.7 Interdisciplinary Research

Two of the main strengths of the Ames Laboratory are magnetism and X-ray crystallography of rare earth and related materials. In part this is due to cooperative research efforts that cut across the disciplines of physics, materials science, and chemistry. Frank Spedding was one of the leaders in this approach to scientific research, which was rare in the 1950s.

4. Interactions with Industry

As mentioned above in §3 much of the research and development efforts were turned over to industry – the uranium and thorium metal production, the ion exchange separation processes, and the analytical techniques (especially ICP-MS). In addition, K.A. Gschneidner, Jr. established the Rare-earth Information Center (RIC) in 1966 with the initial support of the forerunner of BES, and later by industry (starting in 1968), which totaled about 100 companies world-wide in 1996. RIC's mission was to collect, store, evaluate and disseminate information about new scientific discoveries, industrial developments, new commercial products, conferences, books and other literature, honors received by rare earthers, and to answer information inquiries. RIC published two newsletters – a quarterly (available free) and a monthly (available to supporters of RIC), and occasional reports. In 1996 the directorship was turned over to R.W. (Bill) McCallum. But RIC ceased operation in August 2002 – when industry support dwindled significantly as China forced many companies out of the rare earth markets with extreme price reductions and, simultaneously, a down-turn in the economy dried up state and federal support.

Because of the expertise of individual AL scientists and/or some unique AL analytical or processing capability, many organizations, including industrial companies, asked the AL to perform applied research as Work for Others projects or CRADAs. Many of these non-DOE projects include the rare earths. One of these cases is discussed in more detail in § 6.5. In addition to these individual interactions, the AL established the Materials Preparation Center (MPC) in 1981 to provide unique metals, alloys and compounds to worldwide scientific and industrial communities; and to perform unusual processes for fabricating materials which could not be done elsewhere, see § 6.1. The functions carried out by the MPC over the nearly 30 years of its existence are an outstanding example of AL-industry interactions.

Over the years various industrial organizations have sent their staff scientists and engineers to work at Ames Laboratory getting firsthand experience on a particular technology. These arrangements may be part of CRADAs or Work for Others projects.

In 2009 ISU became a research member of the Rare Earth Industry and Technology Association (REITA) to implement rare earth technology and promote commercialization of the rare earths for military and civilian applications.

5. Technology Transfer and Patents

The Ames Laboratory (AL) has been awarded 300 patents, of which about 45 are concerned with rare earth materials. Ten patents deal with the rare earth-base permanent magnets and four with magnetic refrigeration materials. Before the passage of the Stevenson-Wydler Technology Innovation Act of 1980 (P.L. 96-480) and the Dayh-Dole Act of 1980 (P.L. 96-517) all patent rights were turned over to the U.S. Government. After the Acts became law, the AL (a GOCO - government owned, contractor operated laboratory) began to license the various technologies developed at the AL via the Iowa State University Research Foundation (ISURF).

The combination of inductive coupled plasma with atomic emission spectroscopy in 1975 and later with mass spectrometry in 1984 was a quantum jump in increasing the sensitivity for detecting and determining trace elements in various materials. The two analytical methods were developed at the AL to improve the speed and lower the limits of detecting various rare earth impurity elements in a given rare earth matrix. This technique was soon applied to other impurities in a variety of non-rare-earth materials, e.g. detection of poisons such as mercury and arsenic in drinking water. The ICP-MS and ICP-AE technologies were turned over to industry and are now a standard analytical tool in over 17,000 analytical laboratories worldwide. It is a rapid and accurate method for 80 elements, and in some cases allows the detection of an impurity down to the parts per trillion level. Today there are at least six companies that manufacture ICP-MS instruments.

In addition to the various technology transfers noted in the previous paragraph and in sections 2, 3.1-3.3, one of the more recent success stories is concerned with Terfenol. Terfenol is a magnetic iron-rare-earth (containing dysprosium-terbium) intermetallic compound which has excellent magnetostrictive properties. When a magnetic field is turned on Terfenol will expand and when the magnetic field is removed it relaxes to its original shape and size. There are many applications for this material including sonar devices for detecting submarines, oil well logging, vibration dampers, audio speakers, etc. The magnetostrictive properties were discovered in the early 1970s at the Naval Ordnance Laboratory in Maryland. Shortly thereafter the Navy contracted the AL to grow single crystals and Terfenol samples with preferred orientations. The AL was successful and designed a procedure for making the orientated material to maximize the amplitude of the magnetostrictive effect. Patents were issued and in the late 1980s ISURF licensed the processing technology to Etrema, a subsidiary of Edge Technologies, Inc. in Ames, Iowa. Today Etrema is a multimillion dollar business.

6. Where We are Today 1980-2010

With the Ames Laboratory's successes, some of the golden-age research was no longer deemed to be basic research and funding dried up. In addition key personnel started to retire. As a result of these two events a number of AL capabilities were phased out completely. These include: analytical chemistry, separation chemistry, process metallurgy, and ceramics. The excellent analytical capabilities were slowly reduced and completely lost by the 2000s,

except for inert gas fusion and combustion analysis. The rare earth research activities in physical metallurgy and condensed matter physics areas have also suffered some downsizing to about half the level of what it was in the pre-1980 era, but what is left is still first class state-of-the-art basic research.

In the following sections important activities that are still ongoing are described. Other research that had been completed in the 1980s and may play an important role in the future activities of a new national rare earth research center, is also noted.

6.1 Materials Preparation Center

As an outgrowth of the Ames Laboratory's interactions with industry, other DOE laboratories, universities, other research organizations, the Materials Preparation Center (MPC) was established in 1981 to provide high purity metals (including the rare earths, uranium, thorium, vanadium, chromium); and intermetallics, refractory, and inorganic compounds, and specialty alloys; none of which are available commercially in the required purity or form/shape needed by the requestor on a cost recovery basis. The MPC is a BES specialized research center with unique capabilities in the preparation, purification, processing, and fabrication of well-characterized materials for research and development. The Center is focused on establishing and maintaining materials synthesis and processing capabilities crucial for the discovery and development of a wide variety of use-inspired, energy-relevant materials in both single crystalline and polycrystalline forms, spanning a range of sizes with well-controlled microstructures. There are four functional sections within the MPC: (1) high purity rare earth metals and alloys; (2) general alloy preparation; (3) single crystal synthesis; and (4) metallic powder atomization. Each area is provided scientific and technical guidance by a Principal Investigator (PI) whose individual expertise is aligned with the function of each section. The original director was F. (Rick) A. Schmidt who retired in 1993 and turned over the directorship to Larry L. Jones.

In 2008 the MPC filled 183 external materials requests from 111 different scientists at 88 academic, national and industrial laboratories worldwide. Internally the Center provided materials, and services for 53 different research projects that totaled 1092 individual requests.

6.2 Nd₂Fe₁₄B Permanent Magnets

The announcement of the simultaneous discovery of the high strength permanent magnet materials based on Nd₂Fe₁₄B by scientists at General Motors in the USA and at Sumitomo Special Metals. Co., Ltd. in Japan in November of 1983 set off a flurry of activities everywhere. The lead scientist at General Motors was John Croat (an ISU graduate), who was Frank Spedding's last graduate student. DOE/BES funding for research on these materials at the AL started in 1986 and lasted through 1998. U.S. Department of Commerce (DOC) funding for gas atomization processing work on Nd₂Fe₁₄B alloys, through the ISU Center for Applied Research and Technology, was received from 1988 through 1993. Funding was renewed at the AL in 2001 under the auspices of DOE/EERE's Vehicle Technology (formerly FreedomCar) program.

Notable achievements in the BES funded project included: (1) demonstrating that the $\text{Nd}_2\text{Fe}_{14}\text{B}$ compound can be prepared by a thermite reduction process that is competitive with other methods of the permanent magnet material; (2) developing methods for controlling the solidification microstructure of melt spun $\text{Nd}_2\text{Fe}_{14}\text{B}$ which leads to large energy products (the larger the energy product the better the permanent magnet properties); (3) proposing a model for the rapid solidification of a peritectic compound to explain the solidification microstructure of melt spun $\text{Nd}_2\text{Fe}_{14}\text{B}$; and (4) developing a model for hysteresis in exchange coupled nanostructure magnets. In 1996 the AL team headed by R.W. (Bill) McCallum^c received the DOE Materials Science Award for “Significant Implications for DOE Related Technologies, Metallurgy and Ceramics” (items 2 and 3 above). A year later this same team won an R&D-100 Award for Nanocrystalline Composite Coercive Magnet Powder (see § 7.1). In the DOC funded project, an alternative rapid solidification process, gas atomization, was developed for making fine spherical $\text{Nd}_2\text{Fe}_{14}\text{B}$ powders, for which the AL (Iver Anderson and Barbara Lograsso) received an R&D-100 award in 1991 (see § 7.1). They also received the Federal Laboratory Consortium Award for Excellence in Technology Transfer for gas atomization processing of $\text{Nd}_2\text{Fe}_{14}\text{B}$ to enable improved molding of bonded magnets. The AL thermite reduction process (item 1), which was developed by F. (Rick) A. Schmidt, J.T. Wheelock and Dave T. Peterson under MPC research, was selected for one of the 1990 IR-100 (changed to “R&D 100” in 1991) Awards for new innovative research for potential commercialization.

The Vehicle Technology research funded by EERE is on-going and includes design of improved $\text{Nd}_2\text{Fe}_{14}\text{B}$ permanent magnets which can operate at high temperature, enabling more powerful and more efficient motors. This project also is developing further the high temperature RE magnet alloys for powder processing, intended for injection molded bonded magnets for mass production of hybrid and electrical vehicles. Based on initial success with both aspects of the RE magnet project, in 2009 EERE expanded their support into the high risk task of identifying non-rare-earth magnet alloys with sufficient strength for vehicle traction motors.

6.3 $\text{Nd}_2\text{Fe}_{14}\text{B}$ Scrap Recovery

As manufacturers began to make the $\text{Nd}_2\text{Fe}_{14}\text{B}$ material, it soon became apparent there was a great deal of waste magnet material being generated because grinding, melting and polishing the magnets into a final form/shape. Much of the magnet material is mixed with oils and other liquids used in these operations – this material is known as “swarf”. The team of scientists at AL headed by F. (Rick) A. Schmidt developed two different processes to recover the neodymium metal: a liquid metal extraction process to treat the solid materials; and an aqueous method for treating the swarf. Both processes were patented, but the patents have since expired.

6.4 High Temperature Ceramic Oxide Superconductors

In the mid-1980s another major discovery occurred and had an enormous impact on the rare earths as well as science and technology in general – the discovery of the oxide

^c Other team members were K. Dennis, M. Kramer and Dan Branagan, who moved to DOE’s INEEL laboratory.

superconductor with transition temperatures greater than that of liquid nitrogen 77 K (-195°C). One of the key superconductors was $\text{YBa}_2\text{Cu}_3\text{O}_7$, also known as “1:2:3”. It is utilized today in electrical transmission lines, electrical leads in low temperature high magnetic field apparatus and other superconducting applications. The AL had a strong tradition in superconducting research well before this discovery, and when they learned of it the condensed matter physicists and materials scientists immediately began research on these ceramic oxide superconductors. A National Superconducting Basic Information Center was established at AL in 1987 with financial support from DOE’s BES. It was headed by John R. Clem, a theorist who continues to consult with American Superconductor. The experimentalists worked diligently on various aspects of the 1:2:3 and other oxide superconductors to understand the processes by which they are formed and to prepare high purity well characterized materials for physical property studies, which would assist the theorists to understand the fundamental nature of these superconductors. This work laid the ground work for the development of a method of fabricating the rare earth 1:2:3 materials into filaments and flexible wires. Most of the research on these oxide superconductors at AL has stopped and most of the know-how has been turned over to industry. However, AL scientists are still at the forefront of the field studying the new high temperature superconductors: the rare-earth-arsenic-iron-oxide-fluoride and the MgB_2 materials.

6.5 Magnetic Cooling

Magnetic cooling is new, advanced, highly technical, energy efficient, green technology for cooling and climate control of buildings (large and homes), refrigerating and freezing food (supermarket chillers, food processing plants, home refrigerator/freezers). The AL team headed by K.A. Gschneidner, Jr. and V.K. Pecharsky has been involved with magnetic cooling since 1990, when Astronautics Corporation of America (ACA) asked Gschneidner to develop a new magnetic refrigerant material to replace the expensive GdPd refrigerant they were using for hydrogen gas liquefaction (a DOE sponsored research effort). The AL team was successful and showed that a $(\text{Dy}_{0.5}\text{Er}_{0.5})\text{Al}_2$ alloy was about 1000 times cheaper and 20% more efficient than GdPd. A patent was issued for this new magnetic refrigerant material. This work was recognized as the best research paper presented at the 1993 Cryogenic Engineering Conference. A few years later AL teamed up with ACA and designed, constructed and tested a near room temperature magnetic refrigerator. In 1997 they demonstrated that near room temperature magnetic refrigeration is competitive with conventional gas compression cooling technology and is about 10% more efficient, and is a much greener technology because it does not employ ozone depleting, or greenhouse, or hazardous gases [7]. This work was funded by BES’s Advanced Energy Project program. Additional research on magnetocaloric materials was supported by BES after the Advanced Energy Project ended in 1998. But in 2005 BES funding for this research was terminated because they thought it was no longer basic research, i.e. it was too applied. Since then some work has continued on magnetocaloric materials under a work for others subcontract with ACA who has a Navy contract to build shipboard cooling machines, and a few SBIRs which are being funded by EERE.

This research on magnetic cooling is a good example of AL’s response to a problem encountered by industry which was successfully solved, and then later, this work led to a

whole new cooperative AL-industry project on near room temperature magnetic refrigeration.

6.6 Neutron Scattering

Neutron scattering is a powerful tool in determining magnetic structures of magnetic materials and it compliments magnetic property measurements made by standard magnetometers. The rare earth research at AL has benefited from interactions with the neutron scatterers. In the early 1950s Frank Spedding and Sam Legvold of the AL had a close relationship with the neutron scattering group headed by Wally Koeller at Oak Ridge National Laboratory neutron scattering facility and furnished single crystals of the rare earth metals. Recognition and demand for neutron scattering resulted in a 5MW reactor being constructed locally for Ames Laboratory. Scientists used this reactor for extensive measurements of the electronic interactions in rare earth and other magnetic materials. Because of a large jump in the cost of operating and fueling this reactor, it was shut down in 1978. The relationship with the neutron scattering effort at Oak Ridge was enhanced and continued for many years up to about 1980, shortly before the death of the three scientists in 1983-84. To this day a dedicated neutron scattering facility, run by AL scientists, operates at the Oak Ridge High Flux Isotope Reactor (HFIR). It is still of great benefit to AL scientists studying rare earth materials.

6.7 X-ray Magnetic Scattering

X-ray magnetic scattering is a fairly new tool, which was developed in the early 1990s, to study magnetic structures. It is fortunate that this new tool became available because a few of the rare earth elements, especially gadolinium, readily absorb neutrons and neutron scattering measurements are very difficult if impossible to make. Thus, X-ray magnetic scattering has been especially useful in determining the magnetic structures of gadolinium compounds.

In more recent years scientists have improved the X-ray magnetic scattering technique, which is called X-ray magnetic circular dichroism (XMCD). The AL scientists have been on the forefront by applying the latest experiments and theoretical tools to help elucidate complex electronic interactions underlying bulk magnetic properties. The AL team, led by Alan Goldman (experiment) and Bruce Harmon (theory), has been pioneers in the development and application of XMCD on rare earth materials. This tool gives valuable and direct information about the itinerant electrons responsible for coupling the individual localized magnetic moments of each rare earth atom in a solid. The stronger the microscopic coupling the stronger the bulk magnet, and the more useful it can be in applications. Such experiments and powerful computers are essential for helping AL scientists in their latest “materials discovery” initiative to accelerate the discovery of new magnetic materials for industry.

6.8 Emerging Technologies

One of the new and exciting, ongoing developments at Ames Laboratory is a revolutionary method of preparing rare earth-based master alloys for energy and other applications. In addition to lowering costs of the starting material, the processing technique also reduces energy consumption by 40 to 50% and is a very green technology. The work on preparing $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnet material began about a year ago with financial support from AL patent royalties, and it has been reduced to practice – we have prepared a state-of-the-art permanent magnet on February 5, 2010, see attached figure. It is a one step process going from the neodymium oxide to the neodymium master alloy, and since the end-products are completely utilized, there are no waste materials to dispose of. The conventional process also starts with the neodymium oxide but takes two steps to obtain the neodymium metal, and there are waste products associated with both steps which need to be disposed of in an environmentally friendly manner. The step to prepare the $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnet material is essentially the same in either case. This processing technique was invented by F. (Rick) A. Schmidt and K.A. Gschneidner, Jr. A provisional patent has been filed.

A modification of this process should enable us to prepare a lanthanum master alloy to prepare lanthanum nickel metal hydride batteries, which are used in hybrid and electrical vehicles. Likewise, we believe this process can be used to make magnetic rare earth refrigerant alloys (see § 6.5).

7. Kudos

The Ames Laboratory scientific achievements and their science/engineering leaders have been recognized by several organizations including DOE.

7.1 R&D-100 Awards (former IR-100 Awards)

Industrial Research magazine annually identifies the nation's top 100 technological innovations, called the IR-100 Awards before 1991 and now are called the R&D-100 Awards. These awards are also known as the "Oscars of Science". Over the past 25 years AL has received 17 R&D-100 Awards. Of these three are involved with rare earths, in particular the $\text{Nd}_2\text{Fe}_{14}\text{B}$ permanent magnet materials. These are listed below.

- 1990: "Thermite Reduction Process to Make Rare-earth Iron Alloys"
F. (Rick) A. Schmidt, John T. Wheelock and Dave T. Peterson
- 1991: "HPGA (High Pressure Gas Atomization)"
Iver Anderson and Barbara Lograsso
- 1997: "Nanocrystalline Composite Coercive Magnet Powder"
R.W. (Bill) McCallum, Kevin Dennis, Matt Kramer, and Dan Branagan



FIGURE CAPTION: The first and second $\text{Nd}_2\text{Fe}_{14}\text{B}$ bonded permanent magnet prepared using the new process for making the neodymium master alloy.

Left: Our KAA-1-34 composition. 60/40 by vol. $\text{Nd}_2\text{Fe}_{14}\text{B}$ /PPS (poly(phenylene sulfide)). Hot pressed at 300°C and magnetized with a 2T electromagnet. The second bonded permanent magnet prepared.

Center: Practice magnet of similar composition. The surface is boron nitride coating from the die used to compact the $\text{Nd}_2\text{Fe}_{14}\text{B}$ particles in the polymer.

Right: First Bond permanent magnet. 30/70 by vol. $\text{Nd}_2\text{Fe}_{14}\text{B}$ /diallyl phthalate sample mounting material. Hot pressed and sealed with thin layer of epoxy.

7.2 National Academies Members

Six Ames Laboratory scientists have been named to the National Academy of Sciences and the National Academy of Engineering. Frank H. Spedding was elected in 1952 and John D. Corbett in 1992 to the National Academy of Sciences. The four National Academy of Engineering members are: Donald O. Thompson – 1991, Dan Schechtman – 2000, R. Bruce Thompson – 2003, and Karl A. Gschneidner, Jr. – 2007. Of the six three (Spedding, Corbett and Gschneidner) were heavily involved in the rare earth science and technology of rare earths during their careers. Corbett and Gschneidner are still actively engaged in research and development activities. Spedding died in 1984 but was still active until shortly before his passing.

7.3 Department of Energy Awards

Scientists at AL have won several DOE, (mostly from BES) awards for their scientific achievements. These are listed below.

- 1982 K.A. Gschneidner, Jr. and K. Ikeda for quenching of spin fluctuations
- 1991 I.E. Anderson and B.K. Lograsso received the Federal Laboratory Consortium Award for Excellence in Technology Transfer for high pressure gas atomization of rare earth permanent magnet alloys
- 1994 B.J. Beaudry for thermoelectric materials characterization from DOE's Radioisotope Power Systems Division
- 1995 J.D. Corbett for sustained outstanding research in materials chemistry
- 1995 A.I. Goldman, M.J. Kramer, T.A. Lograsso, and R.W. McCallum for sustained outstanding research in solid state physics
- 1996 D. Branagan, K.W. Dennis, M.J. Kramer, R.W. McCallum for studies on the solidification of rare earth permanent magnets
- 1997 K.A. Gschneidner, Jr. and V.K. Pecharsky for contributions to the advancement of magnetic refrigeration
- 2001 K.A. Gschneidner, Jr. and V.K. Pecharsky received the "Energy 100 Award" for research on magnetic refrigeration as one of the 100 discoveries between 1997 and 2000 that resulted in improvements for American consumers.

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References

1. H.J. Svec, pp. 1-31 “Prologue” in *Handbook on the Physics and Chemistry of Rare Earths*, vol. 11, K.A. Gschneidner, Jr. and L. Eyring Eds., Elsevier Science Publishers (1988).
2. J.A. Goldman, “National Science in the Nation’s Heartland. The Ames Laboratory and Iowa State University, 1942-1965”, *Technology and Culture* **41**, 435-459 (2000).
3. J.A. Goldman, “Mobilizing Science in the Heartland: Iowa State College, the State University of Iowa and National Science during World War II”, *The Annals of Iowa* **59**, 374-397 (Fall 2000).
4. J.A. Goldman, “Frank Spedding and the Ames Laboratory: The Development of a Science Manager”, *The Annals of Iowa* **67**, 51-81 (Winter 2008).
5. J.D. Corbett, “Frank Harold Spedding 1902-1984”, *Biographical Memories* **80**, 1-28 (2001); The National Academy Press, Washington, DC.
6. S.R. Karsjen, “The Ames Project: History of the Ames Laboratory’s Contributions to the Historic Manhattan Project, 1942-1946”, published by Ames Laboratory Public Affairs, Iowa State University, Ames, Iowa (2003).
7. K.A. Gschneidner, Jr. and V.K. Pecharsky, “Thirty Years of Near Room Temperature Magnetic Cooling: Where we are Today and Future Prospects”, *Intern. J. Refrig.* **31**, 945-961 (2008).

QUESTION 2: BASIC RESEARCH PROGRAM

In the 1990s the Chinese flooded the marketplace with low priced raw rare earth products (mixed and separated rare earth oxides) and as a result, not only did the primary rare earth producers in the United States and the rest of the world shut down, but technical personnel with expertise in rare earth mining, refining, extraction, etc. found employment in other industries. Soon thereafter the Chinese began manufacturing higher value rare earth products, including rare earth permanent magnet materials, and in time, all of the Nd₂Fe₁₄B magnet manufacturers in the United States also went out of business. This also resulted in a brain drain of scientists and engineers in this field, and also in all high-tech areas involving other rare earth products, such as high energy product permanent magnet materials, metallic hydrogen storage and rechargeable battery materials. Some of these experts have moved on to other industries, others have retired, and others have died, basically leaving behind an intellectual vacuum.

In the late 2000s the Chinese game plan changed, and they have started to exercise export controls on a variety of rare earth products, and signaled that they intend to consume all the rare earths mined in China internally in the next three to five years. This change will allow the rare earth producers and manufacturers to supply the needed products, but this presents several problems which have been cited by others at this House Committee hearing. One of these is the shortage of trained scientists, engineers, and technicians. Another need is innovations in the high tech areas which are critical to our country's future energy needs. A research center which alleviates both of these problems is the best way to work our way through the rare earth crisis facing the USA. An educational institution which has a long and strong tradition in carrying out research on all aspects of rare earth materials – from mining and purification to basic discovery and applications – over a number of disciplines (i.e. chemistry, materials, physics, and engineering) with a strong educational component (undergraduate, graduate and post doctoral students) would be the ideal solution. A National Research Center on Rare Earths and Energy should be established at such an institution initially with federal and, possibly, state support, and as the US rare earth industry matures in five to ten years, supplemented by industrial financial support. The center would employ about 30 full time employees – group leaders; associate and assistant scientists and engineers; post docs, graduate and undergraduate students; and technicians plus support staff. This research center will be a national resource for the rare earth science, technology and applications, and therefore, it would also provide broad support of research activities at other institutions (universities, national laboratories, non-profit research centers, and industry) who would supply intellectual expertise via subcontracts to complement the activities at the center.

The major emphasis of the center would be goal oriented basic research, but proprietary research directly paid by the organizations that request it would also be part of the center's mandate. The center would have an advisory board to oversee, guide and refocus as needed the research being conducted. The advisory board would be made up of representatives from the university, government, industry and the general public.

I would like to suggest to this House subcommittee that they consider a second national center, the National Research Center for Magnetic Cooling. Cooling below room temperature accounts for 15% of the total energy consumed in the USA. As noted in my response to the first

question, magnetic refrigeration is a new advanced, highly technical, energy efficient green technology for cooling and climate control of buildings, ships, aircraft, and refrigerating and freezing (§ 6.5). We have shown that magnetic cooling is a refrigeration technology competitive with conventional gas compression cooling. Magnetic cooling is 10 to 20% more efficient, and it is a very green technology because it eliminates hazardous and greenhouse gases, and reduces energy consumption. If we were able to switch all of the cooling processes to magnetic refrigeration at once we would reduce the nation's energy consumption by 5%. But there are a lot of hurdles that need to be overcome and the USA needs to put together a strong, cohesive effort to retain our disappearing leadership in this technology, by assembling a National Research Center for Magnetic Cooling. Europe and China are moving rapidly in this area, and Denmark has assembled a magnetic refrigeration national research center at Risø – so far the only one in the world. The US Center should be structured similar to what has been proposed in the above paragraphs for the National Research Center on Rare Earth and Energy. The question is, are we going to give up our lead position and be a second rate country, or will we be leading the rest of the world? I hope and pray that the answer is, we are going to show the world that we are number one.

QUESTION 3: KNOWLEDGE TRANSFER

Knowledge is transferred from a research organization to industry through two primary routes. The first is the transfer of intellectual property. Research findings carried out at universities, colleges, non-profit organizations, and DOE and other federal laboratories are disseminated as published articles in peer-reviewed journals and in trade journals, presentations at national and international conferences, electronic media, or their organization's web site, and if exciting enough, via news conferences and press releases assuming the new results are not patentable. If, however, the research has some potential commercial value, this new information/data should be made available as soon as feasibly possible after filing a patent disclosure. However, before the patent is filed one could disseminate the results to companies that might be interested by contacting them directly to see: (1) if they are interested, (2) if they would sign a non-disclosure agreement, and (3) if they answer yes to both (1) and (2) then the information could be disclosed to them. However, all the companies must be treated equally and fairly.

The second route is highly effective when the research organization is connected with a university. This is exemplified by Ames Laboratory and Iowa State University. AL employs a significant number of ISU students in part time positions either as graduate research assistants or undergraduate research helpers. These science and engineering students, particularly at the bachelors and masters levels, transfer the skills and process the knowledge gained in working in the laboratory to their employers after they graduate.

QUESTION 4: U.S. RESEARCH ON RARE EARTH MINERALS

Rare earth research in the USA on mineral extraction, rare earth separation, processing of the oxides into metallic alloys and other useful forms (i.e. chlorides, carbonates, ferrites), substitution, and recycling is virtually zero. As is well-known, research primarily follows money; but prestige and accolades are other drivers; or when someone serendipitously comes up with an exciting idea for a research project. The lack of money and excitement accounts for the low level of research on the above topics.

Today some work on rare earth and actinide separation chemistry is directed toward treating waste nuclear products and environmental clean-up of radioactive materials in soils is being carried out at various DOE laboratories. This research may be beneficial to improving rare earth separation processes on a commercial scale.

Some research at various universities might be considered to be useful in finding substitutes for a given rare earth element in a high tech application. But generally the particular rare earth's properties are so unique it is difficult to find another element (rare earth or non-rare earth) as a substitute.

The Chinese have two large research laboratories which have significant research and development activities devoted to the above topics. They are the General Research Institute for Nonferrous Metals (GRINM) in Beijing, and the Baotou Research Institute of Rare Earths (BRIRE) in Baotou, Inner Mongolia. GRINM is a much larger organization than the Baotou group, but the rare earths activity is smaller than what is carried out at BRIRE. The Baotou Research Institute of Rare Earths is the largest rare earth research group in the world. Baotou is located about 120 miles from the large rare earth deposit in Inner Mongolia and is the closest large city to the mine. This is the reason why BRIRE is located in Baotou.

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Karl A. Gschneidner, Jr. was born on November 16, 1930 in Detroit, Michigan, and received his early education at St. Margaret Mary grade school and St. Bernard high school. He attended the University of Detroit, 1948-1952 and graduated with B.S. in Chemistry. He went to graduate school at Iowa State College (became Iowa State University in 1959) and in 1957 obtained a Ph.D. degree in Physical Chemistry studying under Distinguished Professor Frank H. Spedding and Professor Adrian H. Daane. He then worked in the plutonium research group at the Los Alamos Scientific Laboratory from 1957 through 1963. In 1963 he joined the Department of Metallurgy as an Associate Professor, and jointly as a group leader at the Ames Laboratory of Iowa State University. He was promoted to a full professor in 1967, and named a Distinguished Professor in 1979. In 1966 he founded the Rare-earth Information Center and served as its Director for 30 years. He was also the Program Director for Metallurgy and Ceramics at the Ames Laboratory from 1974 to 1979. He taught mostly graduate level courses, including x-ray crystallography, the physical metallurgy of rare earths, and alloying theory.

Gschneidner, sometimes known as “Mr. Rare Earths”, is one of the world’s foremost authorities in the physical metallurgy, and the thermal, magnetic and electrical behaviors of rare earth materials, a group of chemically similar metals naturally occurring in the earth’s crust. His work lately has taken him into the field of magnetic refrigeration, a developing technology that has the potential for significant energy savings with fewer environmental problems than existing refrigeration systems.

Gschneidner has over 450 refereed journal publications and nearly 300 presentations to leading scientific gatherings worldwide to his credit. Holder of more than a dozen patents, he has been honored with numerous awards by governmental, professional, and industrial bodies, including recognition for his Ames Lab team’s research in magnetic refrigeration by the U.S. Department of Energy in 1997 and with an Innovative Housing Technology Award in 2003.

In addition to the National Academy of Engineering, Gschneidner is also a Fellow of the American Society for Materials-International, The Minerals, Metals and Materials Society, and the American Physical Society. In 2005, he was honored for 53 years of outstanding contributions to his field with a symposium at Iowa State that was attended by some of the world’s leading experts in rare earth materials, many of them his former students or collaborators. He maintains an active research program with Ames Laboratory.