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CONTRIBUTIONS OF THE RARE EARTHS TO SCIENCE AND TECHNOLOGY

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I was very pleased when the Materials Science division of the ASM, through Dr. Rath, invited me to give the lead-off paper of this symposium in recognition of my long labors in the rare earth field. To me, the rare earths are the most interesting group of elements in the periodic table. They represent roughly 1/6 of the naturally occurring elements and about 1/4 of the known metals. Only recently has it been generally recognized that they possess a very wide range of properties, many unique, in their various compounds and alloys. With careful selection, one can obtain materials which have almost any property one desires.

In discussing what material should be covered in the lead-off paper, Dr. Rath and I thought it might be appropriate if I would give a brief summary of some of the areas of science where the rare earths have already played an important role, and then point out other areas where they are almost certain to be helpful. I shall discuss the alloy field only briefly, since Dr. Gschneidner and other speakers will go into this aspect in greater detail as the symposium progresses.

As you all know, I have spent the past 50 years carrying on a research program in which the rare earths played a major role. When I started working with them, they were not a very popular field of research. It is true that a great many men had spent their lives working with them, but the average chemist, metallurgist or physicist knew very little about these elements, and they believed that these elements possessed properties which were almost the same for all the group. If you looked them up in most inorganic texts of the time you would find them dismissed in a single paragraph as being all alike and having properties similar to lanthanum, if the text mentioned them at all. Even just which elements belonged to the rare earth group was in dispute. The chemists liked to include yttrium and lanthanum along with the elements from atomic number 58 to 71 in the rare earth group, while the physicists preferred to include only the elements from cerium to lutetium in this category. At that time, the new theories of atomic structure predicted that there would be 14 rare earths, starting with cerium and ending with lutetium. Fortunately, this matter has been somewhat clarified when the International Union for Pure and Applied Chemistry recommended, in 1968, that the elements 58 through 71 be referred to as the "Lanthanides", and that the name "Rare earth" be reserved for the elements scandium, yttrium, lanthanum and the lanthanides.

The first of the rare earths, yttrium, was isolated in 1794 from a rare mineral as the oxide, and recognized as a new element. The ancient Greeks believed that all matter was made up of four elements: earth, air, fire and water. The earths were materials which, with the heat sources then available, could not be changed by heating, and the Greek influence was still very strong at the beginning of the Nineteenth Century. Calcium oxide, magnesium oxide and aluminum oxide had not yet been decomposed, and these oxides were assumed to be elements, and were referred to as "common earths". Since yttrium oxide resembled them in its properties, it was called a "rare earth". For the next 125 years, all the rare earth elements except promethium were discovered and isolated in various states of purity. They were all found to be trivalent in their common valency form and in diluted aqueous solutions to be electrolytes which ionized to give trivalent rare earth ions. These trivalent ions strongly attract the water dipoles in solution so that the water forms a tight sheath around the ions. It is, therefore, not surprising that the chemistry of the various rare earth ions in solution do not vary much from one element to another. Prior to 1940, most of the chemistry of the rare earths was carried out in solution, usually aqueous. Consequently, the methods which developed for separating the rare earths one from the other were laborious fractionation processes which produced rare earths of not too high a purity unless thousands of fractionations were performed. The salts were hard to get and very expensive; hence they were thought to be rare.

The development of ion exchange processes after World War II, particularly the band displacement method suddenly made it possible to obtain rare earth salts in very high purity. Industry adopted these methods and the salts and oxides of these elements became available to the average scientist at very reasonable prices. Later, for certain rare earths, liquid-liquid separation processes were developed and the price became even cheaper.

The rare earths are not really rare in nature. Cerium is reported to be more abundant in the earth's crust than lead and tin, and even the rarer elements, europium and lutetium are much more abundant than the platinum group elements. They are found rather evenly distributed in the very deep basalt rocks in a few parts per million concentration. When molten acid silicate rocks come in contact with the molten basalt, rare earths are extracted into the silicates at a somewhat higher concentration, and the extraction is a little bit more efficient for lanthanum than lutetium. In recent years, very accurate analytical methods have been developed for determining the relative abundance of the rare earths when they are present in such low concentrations. This is done by means of the mass spectrograph and by activation analysis. The rare earths are, therefore, of great interest to the theorists and geochemists, because if these workers can get good analytical results of the relative abundances of these elements across the rare earth series, they can work backwards to see whether the rocks at any time have been above a certain temperature or if they have been molten. Further, information can be obtained as to whether the environment in which the extraction took place was a reducing or oxidizing environment. Since europium can be reduced to the divalent form and therefore, separates rapidly from the other rare earths, it will be in low abundance in the series, while if the extraction takes place in an oxidizing atmosphere, cerium will be oxidized to the four-valent state, and again get separated from the system. For these reasons, there was great interest in the rare earth content of the moon rocks. The results showed that the thermal history of these rocks was much more complicated than had been originally believed.

The individual rare earths, with the possible exception of scandium, are never found pure in nature, but only as rare earth mixtures. They do occur, however, as minerals very rich in rare earth content. We find deposits of such materials as monazite, xenotime, bastnaesite, gadolinite, samarskite, etc., and these minerals were probably precipitated from either the molten rocks or from superheated brines under pressure. It is known that the molten magma is welling up under the mid-ocean mountain ranges, and comes in contact with sea water at very high pressures and temperatures. Brines also come in contact with the hot rocks under pressure deep in volcanos and in the deep ocean trenches where the ocean plates reenter the molten magma. In these areas, the rare earths are extracted from the molten rocks and at other temperatures and pressures are redeposited. While information under these conditions at present is sketchy, the presence of rare earth materials can tell us something about the earth's earlier history, and we can already draw some conclusions from the information now available. As we learn more about the phase systems and solubilities of these rare earth compounds under conditions of high temperature and pressure, much more precise information can be deduced as to previous history of the rock formations in which they occurred.

When organic matter derived from many living specimens is calcined, the ashes contain rare earths at a concentration of a few parts per million. This phenomena is very widespread, but it is not known whether these trace elements play an essential role in the living process. Further research in this area should be interesting.

The rare earth elements have already played a major role in the development of our present understanding of atomic structure and the periodic table. When Mendeleev first published a periodic table, he found it was necessary to leave a space now occupied by scandium, and he predicted a new element would be discovered and what properties it would possess. Later, scandium was discovered and helped establish general acceptance of his table. As more and more rare earths were discovered, they did not fit well into his table, and it seemed to the early chemists that they were finding a new type of element, which had properties which we now attribute to isotopes. Many of the ideas concerning the fact that isotopes should exist were developed during this period. Finally, Moseley showed that there were only 14 rare earths and the spectroscopists showed that the electrons in the atoms existed in subshells, and the existence of the 4f subshell was extremely important in establishing our present concept of atomic structure.

It was found that as one proceeds across the rare earth series, the increased charge on the nucleus pulls the electron shells in closer, so that the radii of the atoms or ions get smaller with increasing atomic number. This is known as the "lanthanide contraction". The charge on the nucleus increases with atomic number, and at this point in the periodic table, the extra electrons which enter the atom to balance the increased charge on the nucleus start entering an inner subshell (4f). This subshell is well protected from the fields of the neighboring atoms by the completed $5s^2$--$5p^6$ subshells. It is well known that the chemical and physical properties of a material are essentially determined by the electrical and magnetic fields, which the neighboring atoms sense. These fields are mainly determined by the valency or conduction electrons of the materials. The 4f electrons, which are so strongly shielded from the fields of the neighboring atoms, play only a minor role in influencing the field set up by the valency electrons. Therefore, all the rare earth elements usually have only three electrons taking part in their valency shell, or conduction bands. The energy of formation of various compounds, alloys or solutions may be such that it can promote one of these 4f electrons to the valency or conduction shell so as to produce the most stable configuration. In this case, the rare earth becomes 4-valent and cerium, praseodymium and terbium can exist in some solid compounds in the 4-valent form. The crystal fields may also cause a valency or conduction electron to enter the 4f shell, and in this case, the divalent rare earth ions exist in the compound. Thus, in aqueous solution, one can oxidize cerium to the 4-valent form and reduce samarium, europium, and ytterbium to the divalent form. In fused salts mixtures, it is possible to oxidize or reduce other members of the rare earth series and if the rare earth ions are introduced into divalent or quadrivalent lattices, the anomalous valencies become much more frequent. This "doping" of crystals with rare earths is proving to be a very fruitful field, since it produces materials with very unique properties.

The electric and magnetic field set up by the valency electrons in any series of compounds shift in predictable ways due to the lanthanide contraction as one goes across the rare earth series. Many of the rare earth salts are very soluble in water, and they form strong electrolytes which in very dilute solutions are completely ionized, but in more concentrated solutions first form outer complexes with a water layer intervening, and then inner complexes with their anions. While as a first approximation, the behavior of these solutions is much alike, accurate measurements of the thermodynamic properties show significant differences as information concerning these properties is obtained over a wide concentration, temperature and pressure range. Such information should prove invaluable in helping to develop better theories concerning the nature of water and electrolytic solutions. This is extremely important since much of our chemistry deals with electrolytes. Oceans are electrolytic solutions, and electrolytes play a vital role in most life processes.

While the properties of aqueous electrolytes and the equilibrium constants of the various complexes formed in solution vary slowly as one proceeds across the rare earth series, the differences in the properties and equilibrium constants change much more rapidly if the water sheath is removed from the rare earth ion. If the rare earth ion is surrounded by an organic molecule, such as a chelate, most of the water is displaced and advantage of this is taken in developing separation processes such as ion exchange or liquid-liquid extraction procedures. If all water is removed, such as in molten salts, the property difference for adjacent rare earth elements is considerably larger. Finally, in the case of metallic alloys, the properties of adjacent rare earths can be quite marked, and the difference in properties across the rare earth series is at least as great or greater than in the case of other natural series in the periodic table, such as Na, K, Rb, Cs; or Be, Mg, Ca, Sr, Ba; or Cu, Ag, Au; or iron, cobalt and nickel. For example, the melting point of lutetium is about twice that of lanthanum.

The 4f electrons which are well shielded from the fields of the neighboring atoms do have magnetic moments, and in general, these moments do not cancel. Most materials containing rare earths are therefore magnetic and the materials can be paramagnetic, antiferromagnetic, ferrimagnetic, or ferromagnetic, depending on the temperature. Some of the rare earth metals and alloys form stronger permanent magnets than iron, cobalt and nickel. Further, in many of the alloys, and compounds, the magnetism is highly anisotropic. The magnetic properties of the rare earth metals and compounds have already greatly influenced our present understanding of magnetism, and I am sure that as more basic research is done on these substances we will get a much better understanding of magnetism, and will find many unique properties which will have commercial applications. Already permanent magnets, electronic devices, transformer cores, etc. containing rare earths are on the commercial market.

The rare earths possess extremely complex spectra. The unbalanced magnetic moments of the inner shell combine in many ways with the unbalanced moments of the valency shell or conduction shells, and give rise to many metastable states, a considerable number of which occur close to the basic state. This means that the magnetic properties of these materials are very sensitive to temperature because a magnetic moment of one of the metastable states which can be populated with increasing temperature can be very different from that of the basic state.

The existence of many metastable states make these materials a rich source for laser materials, fluorescent screens, such as television screens, intense sources of light, such as street lights, and perhaps in the future, even for intense panel lighting. The spectra is also of considerable interest to the theorists, since these inner electrons give rise to sharp absorption and fluorescent spectra. These spectra offer a precise probe for exploring the magnetic and electric fields which exist in the condensed state.

The nuclear properties of the rare earths also are of great interest to scientists. The even numbered rare earths are rich in stable isotopes, posessing from three to seven each; while the odd numbered rare earths have few: Pm has 0, five have 1 and 2 have 2. Radioactive rare earths are formed in fission in considerable abundance, and this is not only true for uranium, but for the actinides in general. They can also be formed by accelerators and by radioactive decay from other radioactive isotopes. The rare earth elements appear in that part of the periodic table where the number of isotopes, radioactive and stable, are the most numerous. Already, from 10 to 20 radioactive isotopes for each element have been identified. It is also in this part of the periodic table where the nuclei show anomalies, some of them being quite ellipsoidal Several of the isotopes belong to the "magic number" group, where all the neutrons are in completed shells. A careful study of the nuclear properties of the rare earths has already played a very important role in helping establish the shell model of the nucleus, and I am sure that in the future, as the properties of these isotopes are better known and understood, a great deal more will be learned about nuclei. The relative abundance of the rare earths, elements and isotopes is of great interest to the cosmologists in developing the theories of how the universe, galaxies and stars formed; how they obtain their energy, and how they decay in cosmic time.

Some of the rare earth nuclei have very small capture cross-sections for neutrons, and some have extremely large capture cross-sections. From the practical viewpoint, since the rare earths are formed in fission, such information plays an important role in nuclear energy considerations. A knowledge of the cross-section lifetimes and chemical behavior of the isotopes is extremely important in the design of reactors, control rods, "nuclear poisons" and reactor waste disposal processes.

In closing, I would again like to point out that the rare earth metals comprise almost one-fourth of the known metals, and their alloy systems contain a third of the possible alloys, since a number of metals elsewhere in the periodic table are so scarce that they cannot be used to make useful alloys. As one moves up or down the rare earth series in the alloy system, the properties can be changed in known ways so materials can be found to give almost any property desired.

One can state that the rare earth materials, alloys and compounds, possess such a wide variety of properties that one can find some rare earth material which can be substituted for most other materials. Unfortunately for the commercial use of rare earths, if the other materials give satisfactory results for the use intended, the rare earths are seldom used, since they are more expensive than the common materials, but they do furnish good substitutes when the usual materials become scarce, and they do find wide commercial applications where the rare earth properties are particularly unique. However, it is unfortunate from a commercial viewpoint that many of these unique properties which would make the use of the individual rare earths essential also, all too frequently, use very small amounts of the material to supply the necessary ingredients. Never the less, I am convinced that as time goes on, the specialized use of rare earths will steadily increase, and that the rare earth industry will continue to grow, both in volume and in total dollar sales.