

R A R E M E T A L S
< blue skies ahead >

HIDEO KANEKO
Director of the Society of Non-Traditional Technology
1-2-8 Toranomom Minato-ku Tokyo, 105 Japan

A B S T R A C T

This contribution discuss the changing nature of the field related to the development of novel metals, especially rare earth metals and their intermetallic compounds. I believe that this will be able to transmit some of the enthusiasm of materials scientists for the development of advanced materials.

I N T R O D U C T I O N

This contribution is a general discourse or overview of research and development of advanced materials, discussing the changing nature of the field and the development of novel rare earth alloys.

Materials science is entering a new and exciting period and the next century will bear witness to completely new types of materials. Rare metals, especially rare earth metals and their alloys are example of these materials.

Challenges are going on not only in relation to the never ending demand for superior materials, but also for new and sophisticated materials for microelectronic, magnetic, opto-electronic and superconducting applications. Besides these new materials, you may notice some quite new manufacturing processes or uses of these materials.

However, this contribution will describe only a few of the many advances made recently in materials technology, and mention some of the challenges ahead. It is not intended to be comprehensive, nor to introduce detail, but rather to capture the spirit of today's renaissance in the field of materials. Therefore materials experts will find that a number of potentially important materials have been omitted. This is partly due to

the limitation of pages. But I hope that the materials discussed here are those that particularly excite you and seem most likely to become prominent in the near future.

F U N D A M E N T A L S O F R & D

The prediction mentioned above in the chapter of introduction are not the results into of gazing a crystal ball, but are based on an appraisal of current research in leading laboratories around the world. However, in discussing the likely materials or processes, it is not enough to consider current research only. In a dynamic world of changing political frontiers, shrinking distances, widening information net-works and growing environmental concern, attitudes to the production and uses of materials will also radically change. This transformation has come about quite suddenly. As you know, it is only a few-years since you were considered to be a very new and specialized field with few applications. What has caused this situation? At least two factors seem to have been involved.

First is an increased need for higher performance materials. The market demand has resulted from increasingly vigorous international competition. This has been the response of materials scientists and engineers to challenges to their creativity.

A second factor is our recently enhanced capability for producing inovative materials with specified properties. For instance, it is possible to build up a structure literally atom layer by atom layer using molecular beam epitaxy. In addition, none-equilibrium concentrations of elements can be introduced by ion bombardment and laser annealing.

Another example is rapid solidification technology. By this method amorphous or fine crystalline materials can be produced. The great advantage of this approach is that the metals has a very high alloy content which can not be obtained by traditional technologies.

C R O S S - D I S C I P L I N A R Y I N R & D

An important change of the situation would relate to some significant breakthrough in understanding of research and development. Formerly, the inter-disciplinary approach has been evaluated as a fundamental idea, but now a days, this idea is becoming old fashioned, and a new idea the - cross-disciplinary approach taking its place.

The old concept inter-disciplinary means that different fields of specialists co-operated with each other in recognizing the boundary of each field. But what seems to have happened is the cross-disciplinary research development now being conducted in industry. Cross-disciplinary is a new concept, meaning the overlapping of different fields, eliminating their border lines; that is to say a borderless idea. Earlier distinctions between basic and applied, metals and polymer, since and engineering are breaking down and are being replaced by the cross-disciplinary teams forced on an emerging technology.

It is evident that today's highly competitive environment is bringing science and practice closer together then ever before. Consequently, in today's laboratories, it is not unusual to see a theoretical physicist and

a technical engineer gathered together in front of a blackboard, discussing production or performance of some new materials. Fig.1 shows the relationship between inter-disciplinary and cross-disciplinary.

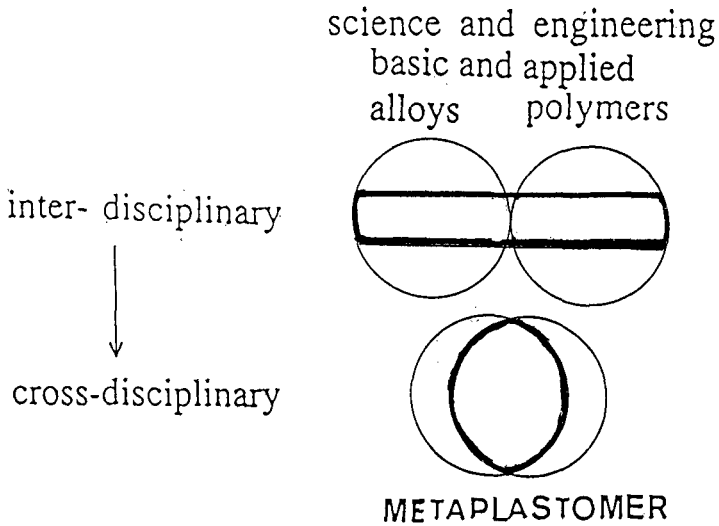


Fig.1 Inter-disciplinary and cross-disciplinary

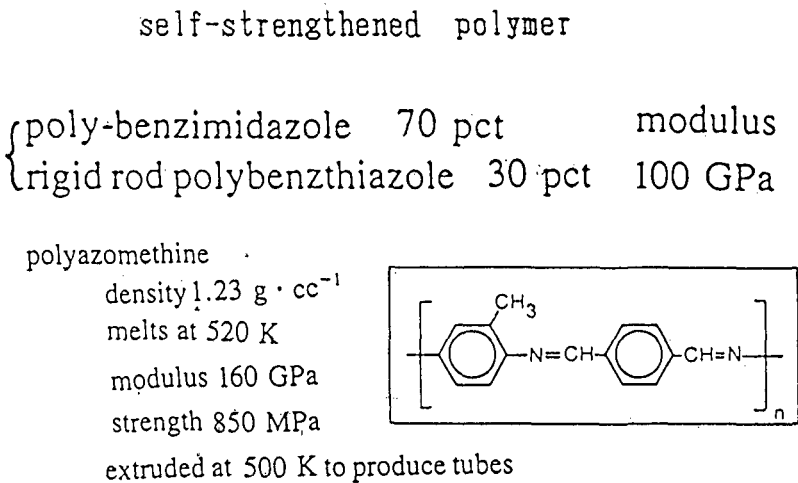


Fig. 2 An example of metaplastomer

As a consequence of this new idea. Japanese laboratories and universities are being built in abroad and some industrial plants of foreign countries are being built in Japan. These are good examples of the cross-disciplinary or borderless idea.

A typical example of cross-disciplinary of metals and polymers is metaplastomer, one of which is shown in Fig.2. This new material has the highest specific strength of any kind of material, as can be seen in Fig.3.

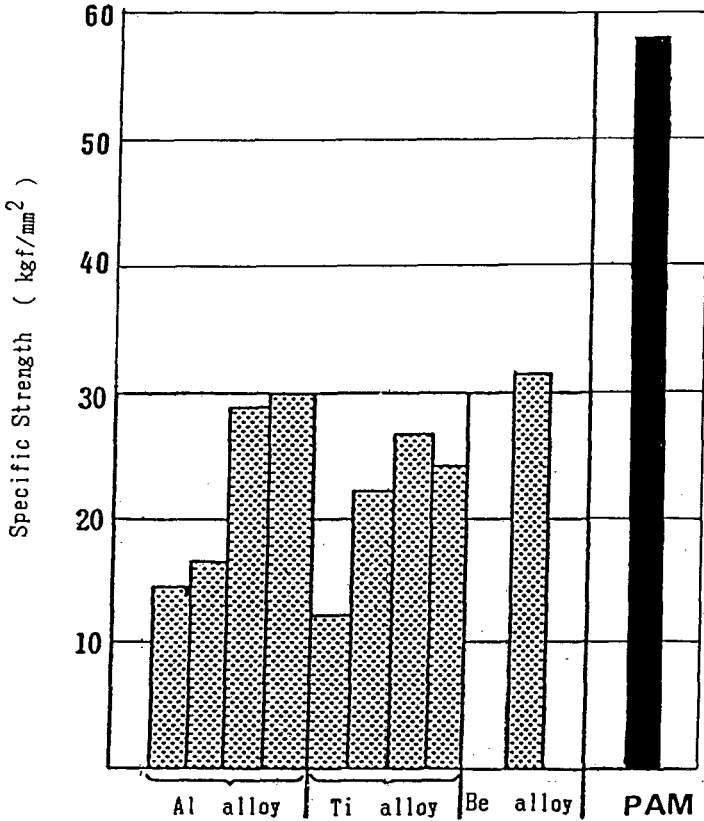


Fig. 3 Specific strength of light materials

4 f - METAL BASED MAGNETIC MATERIALS

The 3d metal based magnetic materials can now be said to have been older materials, because they have the electron structure shown in Table.1, and therefore are being replaced by newer magnetic materials.

Table 1 Electron structure and magnetic moment of 3d metals

Electron structure		Magnetic Electron							Conduction Electron	
		1s	2s	2p	3s	3p	3d	4s		
22	Ti	2	2	6	2	6	2	2	} ferro	
23	V	2	2	6	2	6	3	2		
24	Cr	2	2	6	2	6	5	1		
25	Mn	2	2	6	2	6	5	2		
26	Fe	2	2	6	2	6	6	2		
27	Co	2	2	6	2	6	7	2		
28	Ni	2	2	6	2	6	8	2		
29	Cu	2	2	6	2	6	10	1		
30	Zn	2	2	6	2	6	10	2		
Magnetic Moment ($\mu\text{B}/\text{atom}$)										
							Fe	Co	Ni	
	atom						6	6	5	
	crystal						2.2	1.7	0.6	

what are these newer magnetic materials? It can be said that they are 4f metal-based materials. Then, what are these 4f metals? For what reason were these new materials developed. Here we have an explanation, which initially refers to the reasons and finally to the practical materials available. Though the close relationship between the newer magnetic materials and the periodic table will immediately be revealed.

The 4f metals are generally known as the rare-earth metals, and in a narrow sense, they are the fifteen elements from La, the No.57 in the periodic table, to Lu, the No.71. However, from the practical viewpoint, Sc and Y, which belong to the III a group, are usually included in the 4f metals. Then, why can these 4f metals develop as newer magnetic materials? Let's determine the reasons by studying the periodic table.

This can be done by referring to Table.2 to examine the electron structures of the 4f metals, as has been done for the 3d metals. The structures show that the number of electrons is gradually increased on the outer sides of the 4f level with vacancies left on it. Thus, with the rare-earth metals, the 4f-level electrons serve to provide the magnetic properties. The structures given in Table.2 can be represented by the following general expression:

$$(Xe \text{ electron shell}) + 4f^n 5s^2 5p^6 5d^1 6s^2$$

When atoms with such an electron structure constitute a crystal, the electrons on the outer two levels, 5d and 6s, will be emitted as free electrons. Consequently, the rare-earth metals are generally trivalent. The 4f-level electrons, which are responsible for the magnetic properties, are protected by the outer two orbits, 5s and 6p. Therefore, when a crystal is formed, the magnetic properties of the atom are maintained without any change; this is an outstanding feature of the 4f metals. The previously described 3d metals have a disadvantage in that the 3d level is fully exposed to the outside field when a crystal is formed. Fig.4 compares the 4f atom with the 3d by means of model illustrations.

Table 2 Electron structure of 4f metals

		Magnetic Electron						Conduction Electron											
		K	L	M	N			O			P								
					4s	4p	4d	4f	5s	5p	5d	5f	5g	6s	6p	6d	6f	6g	6h
55	Cs	2	8	18	2	6	10		2	6				1					
56	Ba	2	8	18	2	6	10		2	6				2					
57	La	2	8	18	2	6	10	0	2	6	1			2					
58	Ce	2	8	18	2	6	10	1	2	6	1			2					
59	Pr	2	8	18	2	6	10	3	2	6	0			2					
60	Nd	2	8	18	2	6	10	4	2	6	0			2					
61	Pm	2	8	18	2	6	10	5	2	6	0			2					
62	Sm	2	8	18	2	6	10	6	2	6	0			2					
63	Eu	2	8	18	2	6	10	7	2	6	0			2					
64	Gd	2	8	18	2	6	10	7	2	6	1			2					
65	Tb	2	8	18	2	6	10	9	2	6	0			2					
66	Dy	2	8	18	2	6	10	(10)	2	6	(0)			2					
67	Ho	2	8	18	2	6	10	(11)	2	6	(0)			2					
68	Er	2	8	18	2	6	10	(12)	2	6	(0)			2					
69	Tm	2	8	18	2	6	10	13	2	6	0			2					
70	Yb	2	8	18	2	6	10	14	2	6	0			2					
71	Lu	2	8	18	2	6	10	14	2	6	1			2					

Unpaired Electron

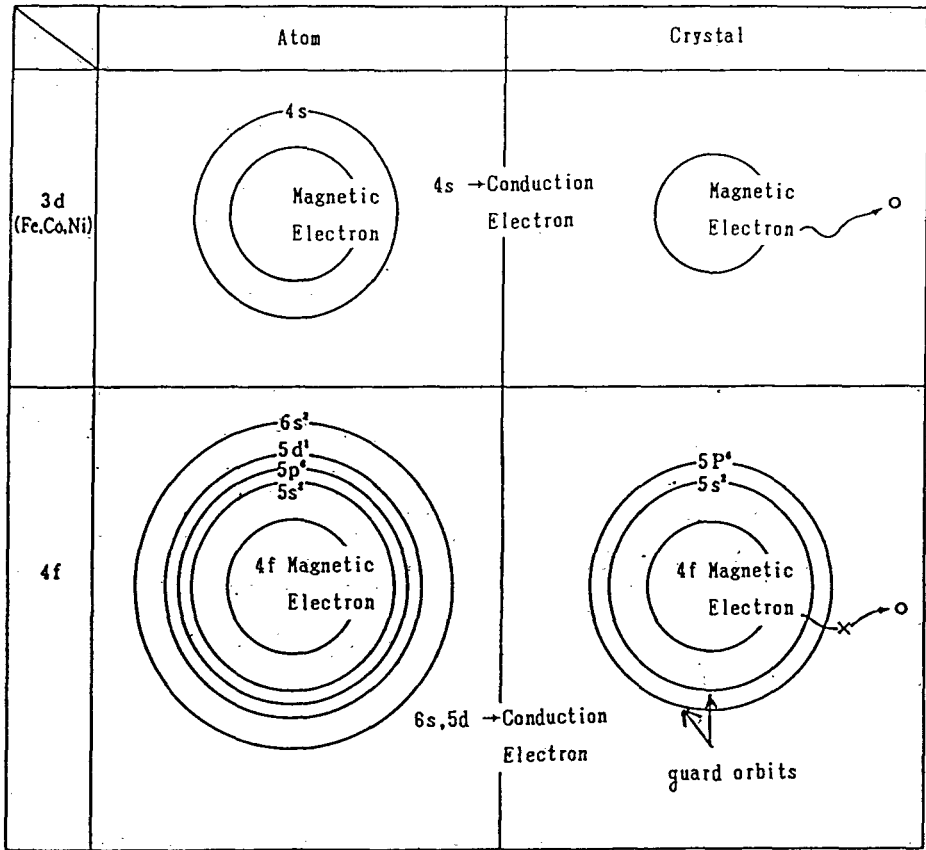


Fig.4 Model illustration of 3d and 4f atoms

Now, let's discuss the magnetic properties of the atom of an rare-earth metal. As stated above, the 4f-level electrons are protected by the outer two orbits, 5s and p, and thus, stable as if they are in a castle equipped with outer and inner moats. Consequently, the 4f-level electrons generate a magnetic moment through the orbital motion (L) and spin (S). The total magnetic moment (J) for an atom is the vector sum of (L) and (S) as expressed by the following equation:

$$J = L + S$$

where, when $n < 7$, the negative sign must be taken, while, when $n > 7$, the positive sign must be used, and "n" is the number of electrons.

Table 3 Magnetic moment of 4f atoms
and 4f metals

	Atom	Crystal
La		
Ce	2.5	2.5
Pr	3.5	3.4
Nd	3.6	3.3
Sm	0.8	1.7
Eu	7.9	8.4
Gd	7.9	7.9
Tb	9.7	9.7
Dy	10.6	10.6
Ho	10.6	10.9
Er	9.5	9.9
Tm	7.5	7.6

Table.3 gives comparison with those for the crystals of rare-earth metals. As can be seen from this table, the value of the magnetic moment for the rare-earth metal crystal is equal to the value of the magnetic moment for the atom, and the values of magnetic moment themselves are very large.

Now, let's go back to Table.1 for comparison. It will be found that the atom of the 3d metals provide large values of magnetic moment, however, with the crystals of the 3d metals, the vales of magnetic moment are very small. Thus, as the base metal of magnetic material, the rare-earth metals are the 3d metal based magnetic materials for practical use are being developed one after another to play a leading role in tommorow's industries.

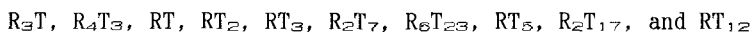
The above description emphasizes only the advantages of the rare-earth metals, however, any advantage is always accompanied by some disadvantage. Recognizing the drawbacks will serve to extend the advantages. Thus, let's discuss the Curle or magnetic transformation points for the rare-earth metals.

Fig.5 shows magnetic transformation points and the effective magnetic moments. From the figures, the following drawbacks can be found. First,

the transformation points are all low; that for Gd. which is the highest, being as low as near room temperature. This is a drawback as the practical material. Secondary, from the viewpoint of practical use, there is no good balance between the magnetic transformation point and the magnetic moment. This is another shortcoming.

Thus, the rare-earth metals offer both advantages and disadvantages. What is the measure to be taken to cover the disadvantages and extend the advantages? Solving these problems will provide the key to the development of practical materials, and the solution will be stated in the next section.

One way to extend the advantages and eliminate the disadvantages of the 4f metals is to combine 4f metals (R) with 3d metals (T). The R and T metals can form a wide variety of intermetallic compounds, as follows: (1) (4)



The magnetic moments acting between the R and R, R and T, T and T metals provide various characteristics. In other words, the exchange interactions occurring between the R and R, R and T, T and T metals in a compound vary in behavior, depending upon the combination. The magnetic moments acting between the R and R, R and T, T and T metals offer various behavior; parallel and anti-parallel, or ferro, ferri, and anti-ferro. Consequently, the materials produced offer a variety of magnetic properties which results in availability of various magnetic materials for use in a variety of applications. Thus, the 4f metal-based functional materials for use in electromagnetic applications are replacing the 3d metal-based ones. It must be emphasized that such replacement can be derived from the periodic law.

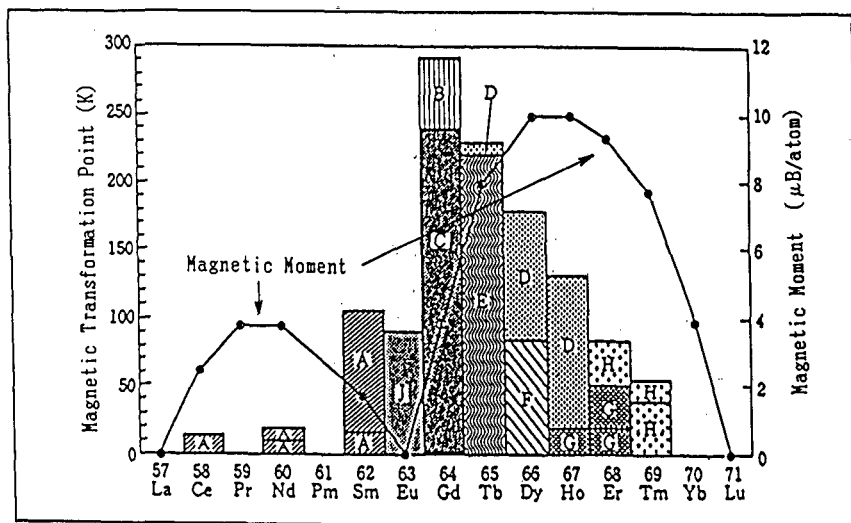


Fig.5 Magnetic transformation point and magnetic moment of 4f metals

f - d ALLOYS AND HEAVY FERMION

One of the new and exciting theories of f-d alloys is the theory of heavy electron and valance fluctuation. The special types of behavior of electronic and magnetic properties of f-d compounds are the reflection of the characteristic features of the f electronic states. A clear-cut example of heavy electron behavior is found in compounds containing f-element. Among these, Ce, Yb and U are the most common elements forming such materials. It is these same elements which are known to be capable of exhibiting the Kondo effect in dilute alloys and the high temperature properties of heavy electron systems appear to be those of a collection of independent Kondo elements. These compounds are called the dense Kondo alloy system. The rare-earth compounds including the nearly trivalent Ce or Yb ions frequently exhibit the dense Kondo behavior. In the magnetic part of the electric resistance, the logarithmic temperature dependence reveals in the high temperature range above the Kondo temperature T_k , where the 4f electrons behave as the isolated ions. At low temperature below T_k , the resistance behaves proportional to T^2 . The specific heat coefficient of dense Kondo compounds are extremely enhanced, which indicate the high states of density at Fermie surface. Therefore, various aspects of the magneto-acoustic effects of valance fluctuation compounds with the unstable 4f electronic state should be studied. And the de Haas-van Alphen effects due to the cyclotron motion of the conduction electron, focusing on the properties of the heavy electron, should be also studied.

				II _B	III _B	IV _B	V _B	VI _B
					B			
					Al			
VI _A	VII _A	VIII		I _B				
←		3d	→	Cu	Zn			
←		4d	→		Cd			
←		5d	→	Pt	Au			
CeAl ₂ UAl ₂				CeAl ₃ GdAl ₃ , UPt ₃				
YbCu ₅ YbAgCu ₄				CeCu ₅	CeZn ₅	CeAlCu ₄		
CeZn ₃ Cu ₂				CeAlZn ₂ Cu ₂				
UPt ₅ UAu ₂ Pt ₃				UAuPt ₄	CeB ₆ , Ce _{0.5} La _{0.5} B ₆			

Fig. 6 Dense Kondo alloys

In Fig.6 I show where binary heavy electron compounds are found in the periodic table. Elements near and to the right of the border of d elements from such compound with f elements. Compilation of these heavy materials suggest that certain crystal structure are better suited to the forming of a heavy electron ground state. (2)

$CeAl_2$ and UAl_2 are examples of C15 cubic Laves phase structure. The $CaCu_5$ structure is a simple hexagonal structure. $CeCu_5$ and $CeZn_5$ are examples of this structure. $CeZn_3Cu_2$ is also found in it. What is interesting is that substituting Al to form $CeAlCu_4$ and $CeAlZn_2Cu_2$ leads to very large specific heat coefficient. In a number of other materials, heavy electron behavior has been found. The examples of these materials are shown in Fig.2. (3)
(4)

C O N C L U S I O N

I trust that I have been able to transmit some of my personal enthusiasm about my field, and some sense of the incredible number and diversity of challenging opportunities it now presents. Many if not most of the technologies will depend, for the foreseeable future, on rare metals. I believe there are blue skies ahead for rare-earth metals.

R E F E R E N C E S

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