

Rare Earth-Transition Metal Compounds: Magnetism and Applications

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The rare-earth or yttrium (R) – transition metal (M) compounds form closely packed structures which may be regarded as arrangement of spheres having different dimensions. The necessity of maximum packing, taking into account geometrical and energetic restrictions, leads to an ordered arrangement, with well defined stoichiometry, in which the atoms are distributed on specific crystallographic sites. For example in Sm-Co series, Sm_3Co , Sm_9Co_4 , SmCo_2 , SmCo_3 , Sm_2Co_7 , SmCo_5 and $\text{Sm}_2\text{Co}_{17}$ compounds, were reported. In the corresponding iron system only SmFe_2 , SmFe_3 and $\text{Sm}_2\text{Fe}_{17}$ were shown [1]. Ternary compounds, as example $\text{R}_2\text{Fe}_{14}\text{B}$ or $\text{R}_{n+1}\text{Co}_{3n+5}\text{B}_{2n}$, are also of interest. Substitutions at the rare-earth and transition metal sites are possible, in a certain amounts.

From magnetic point of view, when transition metals and R are magnetic, the magnetic moments of the two sublattices are parallelly aligned, while in case of heavy rare-earths (Gd to Tm), there is an antiparallel coupling. From this general rule, there are exceptions as in cerium compounds. In case of SmCo_5 , there is a change from ferromagnetic behaviour to a ferrimagnetic one as the temperature increase. Spin reorientations are frequently shown, characteristic for systems whose atoms have competing anisotropies (uniaxial and planar). The magnetic interactions between rare-earths and transition metals can be best described by 4f-5d-3d exchange path [2]. The 4f electrons of rare-earths (except Ce) have a small spatial extent and generally one can assume that they are well localized. On the other hand, the M metals show a wide spectrum of magnetic behaviours. This enclose well established magnetism in which the magnetic ordering temperatures are high, up to an exchange enhanced paramagnetism, crossing the situation in which ordered M moments collapse. Thus, the analysis of the magnetic behaviour of the R-M or R-M-B compounds can give very usefull information on the transition metals, whose magnetic properties are not well known. Thus, in first part we discuss the basic properties of these compounds, focusing mainly on the magnetic behaviour of M (M = Fe,Co,Ni) elements and then, their technical uses will be presented.

The exchange enhanced paramagnets as those based on LaNi_5 , YNi_5 , LuCo_2 , YCo_2 , at low temperatures, show on exchange enhanced paramagnetism. At $T > 10$ K, the magnetic susceptibilities χ , can be described by a T^2 dependence $\chi = \chi_0 (1+aT^2)$. At temperatures higher than a characteristic value T^* , the χ^{-1} vs T follows a Curie-Weiss behaviour, similar as in case of localized moments – Fig. 1 [3]. The XPS studies, at RT show the presence of holes in Ni3d band of LaNi_5 -based compounds. The temperature dependences of the magnetic susceptibilities were analysed in $\text{Y}(\text{Co,Ni})_2$ in the model of spin fluctuations [4], assuming a Gaussian distribution – Fig. 1 [3]. Replacing the nonmagnetic rare earth or yttrium by a magnetic R atom, in the above systems, a magnetic moment will be induced on Co or Ni atoms, beginning with a critical value of the exchange field [5] – Fig. 2. Then, the transition metal moments increase linearly with the exchange field and finally saturated, as shown for example in $\text{R}_{n+1}\text{Co}_{3n+5}\text{B}_{2n}$ system [6]. The same behaviour was seen in RCO_2 -based compounds [5,7,8]. Band structure calculations performed on $\text{Gd}(\text{Co,Ni})_2$ system showed, that in a good approximation, a local environment may describe the composition dependence of the transition metal moments in which Co moment is

little modified if there is at least a critical number ($n_c = 3$) of atoms in a cluster. Values of $H_{cr} \cong 70$ T were estimated for transition from nonmagnetic to magnetic state of cobalt. In case of nickel, a value of $H_{cr} \cong 40(10)$ T was suggested [9]. The high field measurements on YCo_2 [10] evidenced the same type of transition [10]. Also, a linear dependence of the cobalt moment on the exchange field of $(3 \cdot 10^2)^{-1} \mu_B/T$ was shown [11] and confirmed by high field measurements [12]. Iron shows a more localized behaviour. The dependence of the iron moment on the exchange field is of $(18 \cdot 10^2)^{-1} \mu_B/T$. As seen in Fig. 3, there is a rather good agreement between the computed values according to the above relation, and the variation of iron moments. The exchange splitting of M3d band is proportional to the exchange field.

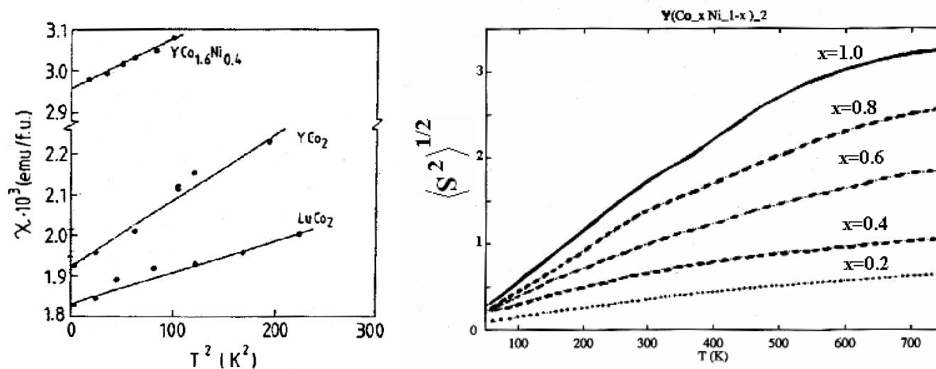


Fig.1

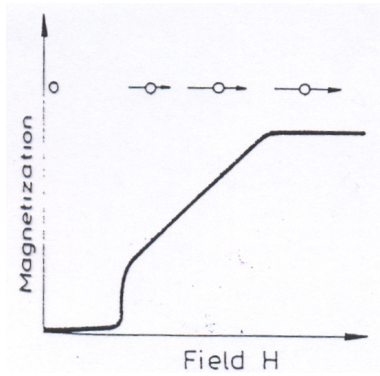


Fig. 2

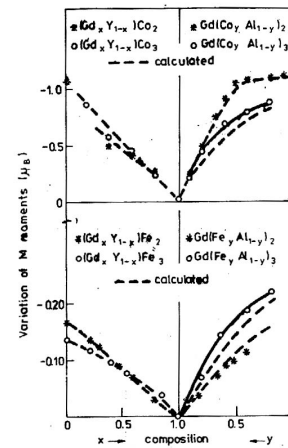


Fig.3

The measurements made in a large temperature range, including the paramagnetic one show that there are large differences in the ratio $r = S_p/S_0$, between the number of transition metals spin determined from Curie constants, S_p , and those obtained from saturation data S_0 , as previously evidenced by the Rhodes-Wohlfarth curve. The ratio r , as a function of the reciprocal of exchange fields acting on M atoms, decreases as the exchange fields increase, approaching $r = 1$, a value characteristic for a localized moment – Fig. 4. This behaviour can be analysed considering the effect of exchange field on M atoms as well as the partial quenching of spin fluctuation by exchange field.

The band structure calculations showed that the R5d band polarizations can be described by a linear relation $M_{5d} = M_{5d}(0) + aG$ where G is the De Gennes factor and $M_{5d}(0)$ is the value of R5d band polarization at $G = 0$. As an example, in Fig. 5 are given the data obtained in RM_2 compounds. The first term is due to short range exchange interactions of R atoms with the M

ones situated in the first coordination shell, while the second is due to 4f-5d interactions. In compounds where there are lattice sites, having different environments, the $M_{5d}(0)$ is determined by the number of atoms (and their moments) situated in the first coordination shell – Fig. 6.

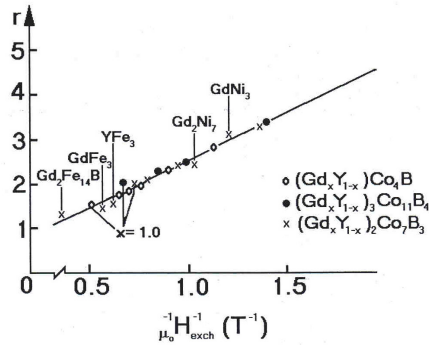


Fig.4

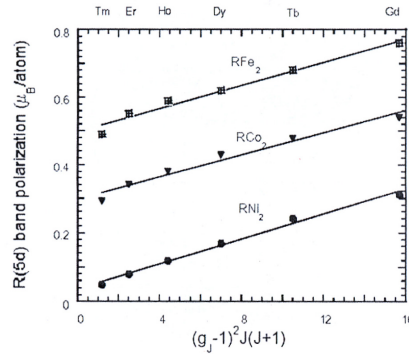


Fig.5

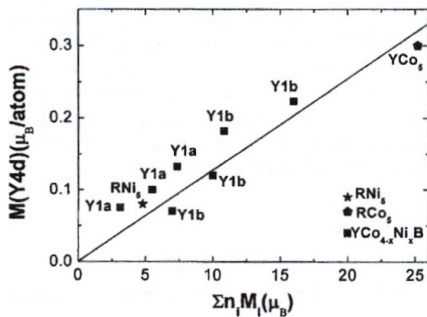


Fig.6

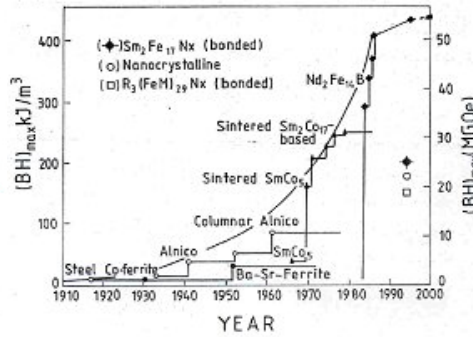


Fig.7

The rare-earth-transition metal compounds have interesting physical properties involving technical applications. Some of them will be surveyed:

Permanent magnets. The evolution of the maximum energy product in the last century showed an exponential increase, described by the relation $(BH)_{max} = 9.6 \exp [(year-1910)/\delta]$ with $\delta = 20$ years – Fig. 7. The remarkable evolution has been determined by the use of R-M or R-M-B intermetallic compounds where R is generally a light rare-earth. The $SmCo_5$ and $Sm(Co,Fe,Zr,Cu)_7$ permanent magnets have a good thermal stability determined by their high Curie temperatures ($T_c > 1000$ K) [13]. Since both Sm and Co are expensive, the researches have been directed for development of cheaper permanent magnets, based on iron, as Nd-Fe-B [14]. Since of the low Curie temperatures, of $Nd_2Fe_{14}B$, hard magnetic phase, many studies were developed to improve their thermal stability, as alloying and changing microstructure. The nanocomposite magnets based on Nd-Fe-B were also realized. These are formed from two magnetic phases one hard, as $Nd_2Fe_{14}B$ and another soft as α -Fe or Fe_3B [15]. The remanent induction and coercive fields of $Nd_5Fe_{70.5}Co_5M_1B_{18.5}$ nanocrystalline alloys are given in Fig. 8. Certain M additives, in combination with Co, significantly improves the squareness of the hysteresis loops and the intrinsic coercivity [16]. Nanocrystalline metastable alloys $SmFe_{9-y}Si_yC$ show also high coercive fields [17] – Fig. 9. The high coercivities of these samples originate from the P6/mmm type structure of the 1/9 metastable phases.

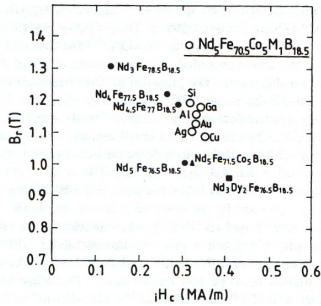


Fig.8

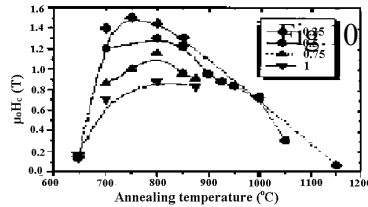


Fig.9

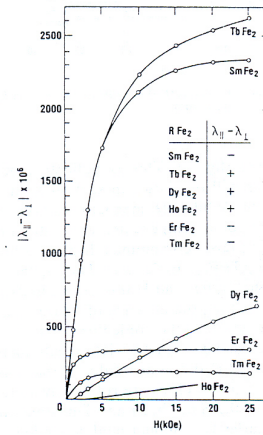


Fig.10

Magnetostrictive materials. The non-S state rare-earths at low temperatures, have high magnetostriction, λ . The λ value, at 4.2 K, are $\cong 9 \cdot 10^{-3}$ for Tb and $2.5 \cdot 10^{-3}$ for Ho. Since of low Curie temperatures of R metals, these cannot be used in magnetostrictive devices working at RT. In the RFe₂ Laves phase compounds, on the support of exchange interactions involving iron, the Curie temperatures increase up to 600-700 K. Thus, the large magnetostriction, characteristic to R metals at low temperatures, are translated at higher temperatures as shown in Fig. 10 [18].

Magnetocaloric materials. Magnetocaloric effect (MCE) has been evidenced in rare-earth compounds. Under adiabatic conditions, the change in magnetic entropy is compensated by an equal and inverse change in lattice entropy which causes a variation in the temperature of materials. A variety of intermetallic compounds were studied in order to achieve alloys having a large MCE, at RT, for magnetic refrigerators or at smaller temperatures for liquefaction of nitrogen, hydrogen or helium. The large MCE can be obtained for materials having large magnetic moment and also a sharp drop of the magnetization with increasing temperature, associated with the magnetic phase transition. Some examples are given in Fig. 11 [19].

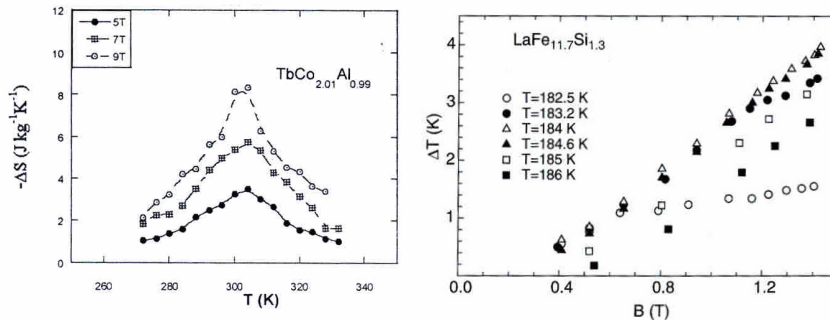


Fig.11

Hydrogen storage. Some intermetallic compounds can absorb a huge hydrogen content as shown in Fig. 12, for LaNi₅. Pure LaNi₅ – shows an absorption plateau pressure of a few bars at ambient. There is a complete reversibility between formation and decomposition with a hysteresis between the corresponding equilibrium pressures. An α -phase solid solution precedes the β -LaNi₅H₆ hydride. The system requires an activation stage which involves decrepitation into small particles [20]. One of the most interesting use of intermetallic hydrides has been as a carrier of hydrogen fuel for motor vehicles.

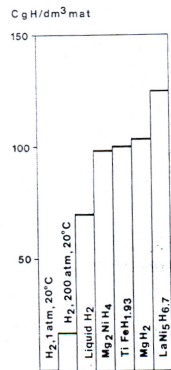


Fig.12

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