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Review

Rare-earth elements in permanent magnets and superconducting compounds and alloys (except new high T_c ceramics) as thin films, thin crystals and thinned bulk materials

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Over about 20 years the synthesis of new alloys and compounds has developed greatly. In the field of superconductor and permanent magnet materials one can claim a 'true revolution'. The particular magnetic and electronic properties of the rare earth elements make them very attractive for the fabrication of new permanent magnets, which contain at least one rare earth element, is possibly only a step towards the elaboration of new alloys and/or compounds. This review paper recalls the results and properties relative to super magnets (since 1981) and superconductors (except the new T_c) (since 1960) as thin and thick films, thin crystals and thinned bulk materials up to 1988. This review shows how numerous research teams have followed different and various routes to increasingly improved specimens. Crystallographic and chemical interpretations and conclusions will be compared and discussed. Some applications will be described.

1. Introduction

Supermagnet and superconductor materials will, without doubt, be very important in the future development of electronic, magnetic and recording devices. This review paper is devoted to the history of supermagnets (since 1981) and of superconductors (since 1960) as materials (compounds and alloys) containing at least one rare-earth (R) element. The discussion will be restricted to the physical, chemical and crystallographic properties of thin films, thin crystals and thinned bulk materials. Some applications will be described. It was not possible to compile all the bulk properties, and only some very important papers and special features will be mentioned. A second restriction has also been made. The results from the new high T_c ceramics will not be described. Rather, the discussion of the low T_c alloys and compounds will be directed towards the research which anticipated the great developments concerning the high T_c ceramics.

The following remarks must be made with regard to the abundance of rare-earth elements in minerals, and to the world-wide market in these metals. Two recent papers [1, 2] have shown that the world-wide production of all the lanthanides (scandium, yttrium and lanthanum to lutetium) is increasing continuously and that terrestrial reserves are very abundant [1]. It should also be noted that the rare-earth market, characterized by "volatile performances", has reached a major peak in demand since 1986. This is due to the fabrication of high-magnetic-strength permanent magnets [2]. On the other hand, very recent forecasts (from 1988 to 2005) estimate world-wide consumption of superconductor materials (including low and high T_c alloys and compounds) to reach a value of 2000–10 000 million dollars, according to three different scenarii [3]. Therefore, as rare-earths are "not-so-rare" [1] and easily "available" [2], future research promises to be fruitful.

2. Permanent magnets

Three groups of alloys based on $Nd_2Fe_{14}B$, $SmCo_5$ (and also Sm_2Co_{17}) and Sm–Ti–Fe, are known for their strong permanent magnetic properties (especially their high coercive force). They have been extensively studied. It will be useful to summarize some of their characteristics and discuss some results and interpretations.

2.1. $Nd_2Fe_{14}B$ alloys

Synthesis of this generation of materials was achieved by Croat *et al.* [4] and Sagawa *et al.* [5]. The latter authors claimed that $Nd_2Fe_{14}B$ compounds "are strong candidates for high-performance magnets rivaling Sm–Co magnets" but that an "R–Fe permanent magnet has not been realized yet". This is mainly due to the fact that the Curie temperatures are too

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low, few stable intermetallic phases are formed, and no uniaxial magnetic anisotropy is observed". Crystalline and magnetic properties were refined by various authors [4–9]. Comparisons of these characteristics between different selected materials were performed by Wallace [9], Oesterreicher and Abache (10) and Huang *et al.* [11]. The phase diagram of the ternary compounds was given in detail by Matsuura *et al.* [12]. Hydrogen absorption/desorption phenomena were studied by Cadogan and Coey [13]. Numerous magnetic and crystallographic properties were reviewed by Burzo [14], who emphasized the effect of iron substitution by cobalt and/or nickel. Sagawa *et al.* [15] have recently described the main characteristics of pure and Fe-substitued magnets and reported manufacturing processes and possible improvements and uses of Nd–Fe–B magnets. Extended and detailed papers have also appeared in the proceedings of a workshop [16].

2.1.1. Thinned bulk materials

2.1.1.1. Microstructure. Determination of the microstructural characteristics was one of the most difficult problems which has been encountered. The $Nd_2Fe_{14}B$ alloy is tetragonal with $a = 0.880$ and $c = 1.218$ nm. Depending on the different preparation methods, other phases are detected by X-ray and electron diffraction, high resolution electron microscopy (HREM) and energy dispersive X-ray spectroscopy (EDX) analysis. From X-ray and conventional transmission electron microscopy (CTEM) studies, Sagawa *et al.* [17] inferred the formation of the $Nd_2Fe_7B_6$ compound (tetragonal with $a = 0.712$ and $c = 0.391$ nm) and of a strange fcc structure ($a \sim 0.520$ nm). From HREM studies Hiraga *et al.* [18, 19] observed that, after annealing at 870 K, or quenching from 1350 K, there was formation of a bcc phase (with $a = 0.290$ nm) either at grain boundaries, or as an overlayer, or as thin platelets inside the $Nd_2Fe_{14}B$ grains. It was concluded that this phase controlled the coercivity mechanism, but it was not possible to determine if it was ferromagnetic (in the form α-Fe, bcc with $a = 0.286$ nm) or not. (The two lattice parameters are similar (difference of about 1%), i.e. the intrinsic accuracy relative to electron diffraction indexation. Sagawa *et al.* [20], from X-ray spectra, reported the lattice value as $a = 0.287$ nm). On the other hand, other areas, located at grain boundaries, revealed the presence of an Nd-rich phase. Thinned flakes annealed at 983 K were studied by CTEM and EDX by Hadjipanayis *et al.* [21, 22]. They noticed the coexistence of the $Nd_2Fe_{14}B$ alloy (tetragonal with $a = 0.709$ and $c = 2.740$ nm), and Fe magnetic phases, and of two high-Nd-content non-magnetic phases (one as bcc with $a = 1.020$ nm). Mishra *et al.* [23, 24], with samples prepared by ion milling and annealed between 903 and 1223 K, studied by CTEM, observed the formation of a $Nd_{1.14}Fe_4B_4$ polycrystalline phase and of Nd-rich zones (as fcc structure with $a \sim 0.560$ nm) at the $Nd_2Fe_{14}B$ grain boundaries. This enrichment was confirmed by EDX, whereas Auger electron spectroscopy (AES) detected boron and oxygen at the grain boundaries. Unfortunately, the intense oxygen edge was not taken into account in the discussion. Instead, the authors speculated on the formation of the fcc high-pressure phase of Nd (fcc with $a = 0.460$–0.480 nm at 5×10^9 Pa). Ramesh *et al.* [25] have also reported the formation of an Nd-rich fcc phase (with $a = 0.524$ nm).

In fact, the Nd-rich phase observed by Sagawa *et al.* [17], Hadjipanayis *et al.* [21, 22], Mishra *et al.* [23, 24] and Ramesh *et al.* [25] is, the C–Nd_2O_3 compound (bcc with $a = 1.050$ nm) easily formed after annealing above 600 K. The lattice parameter of the sesquioxide is either close to that of the bcc phase, or near twice that of the fcc structures, mentioned above. The indexation as an fcc cell is often linked to the absence, on the electron diffraction patterns (EDP), of the (2 1 1) reflection of the bcc lattice of the C–Nd_2O_3 compound. This leads to confusion between the (1 1 1) and (2 2 2) spacings of the two lattices [26]. In this way, Chang and Qian [27], from HREM studies, deduced the coexistence of three phases: $Nd_2Fe_{14}B$ (major contribution) and $Nd_2Fe_7B_6$ (one-dimensional incommensurate structure) and Nd-rich (reported as fcc unit-cell) (minor contributions). But the reported EDP from the Nd-rich phase corresponds to the classical patterns of the C–R_2O_3 compounds. The Nd, fcc high-pressure phase, could only be formed in very special conditions [26]. Sehrey [28] has shown that strongly oxidized zones exhibited the coexistence of the α-Fe and A–Nd_2O_3 phases (A–Nd_2O_3 is hexagonal with $a = 0.383$ and $c = 0.600$ nm). Likewise, Ramesh *et al.* [25], from CTEM and EDX analyses, inferred the formation of the A–Nd_2O_3 compound in the case of samples with low coercivity values. Fidler *et al.* [29] reported that, depending on the chemical composition and heat treatment, four different phases occurred in the $Nd_2Fe_{14}B$ matrix: $Nd_2Fe_{14}B$, Nd_2Fe_{14}, α-Fe and Nd-rich. In another paper Fidler [30] observed the coexistence of the $Nd_2Fe_{14}B$, $NdFe_4B_4$, $Nd_2Fe_7B_8$ and Nd-rich phases (dhcp form as isolated inclusions). This dhcp phase was claimed to be fcc (with $a = 0.520$ nm) in another paper [31]. Unfortunately, the EDX analysis did not include the oxygen absorption edge. Lastly, Chen [32], in microstructural investigations of thinned ribbons, found an essentially single-phase material characterized by very fine grains. Croat *et al.* [4] observed small particles and spherical crystallites homogeneously scattered, they concluded that the coercivity mechanism was of the single-domain particle type.

Electron microscopy bright-field studies showed either equiaxed or faceted crystals [21], or high-density defects and planar faults (anti-phase boundaries and/or stacking faults [29, 30]). In general, HREM revealed the presence and the localization of the different compounds throughout the studied samples.

2.1.1.2. Domain pattern. For sintered $Nd_2Fe_{14}B$ magnets, domain patterns were observed by means of the Kerr effect or using the Bitter technique [33–35]. In the case of thermally demagnetized conditions the majority of the grains were revealed as multidomains.

Magnetic domain patterns change in applied fields and at elevated temperatures [35]. Also domain walls were characterized by Lorentz microscopy [21–24]. It was concluded that the domains were pinned at grain boundaries. Mistra *et al.* [24] added that wall motion was identified as a magnetization reversal mechanism. Suzuki *et al.* [36] have described and discussed the formation of 180° walls (Bloch walls) in an $Nd_2Fe_{14}B$ grain with the *c*-axis parallel to its surface. They also observed typical stripe and bubble domains.

2.1.1.3. Substitution by other elements. Such materials can undergo Nd substitution by another rare-earth and iron substitution by cobalt and/or addition of other elements.

(i) Croat *et al.* [4] have prepared various $R_2Fe_{14}B$ magnets (with R = Ce, Pr, Nd, Sm, Gd, Tb, Dy, Er and Ho) and found a great homogeneity in their structural properties. Sagawa *et al.* [17] also concluded that La cannot form the basal alloy. They also studied the rare-earth series (from Ce to Tm and Y) and reported that the highest anisotropies were obtained in the case of $[Nd, Dy\ (or\ Tb)_2]Fe_{14}B$ alloys for which the coercive force was greatly enhanced. Tokunaga *et al.* [37] have studied the characteristics of (Nd, Dy)–Fe–B alloys. They observed the coexistence of $(Nd, Dy)_2Fe_{14}B$ (as the matrix phase) with an $(Nd, Dy)_{1.14}Fe_4B$ phase, an R-rich phase, and a b c c structure (with $a = 0.290$ nm). The latter was characterized by small platelets, which were not explained. Dickenson *et al.* [38] have analysed the different phases formed during heat treatment of (Tb or Pr) FeB alloys.

(ii) Substitution of various elements (Si, C, Al, Ge and P) for iron led to the formation of the Nd_2Fe_{14} alloy [4]. Substitution of cobalt for iron increased the Curie temperature and decreased intrinsic coercive force and anisotropy fields [17, 39]. Ma and Narasimhan [39] noticed that addition of nickel was detrimental to the intrinsic coercivity of NdFeCoB alloys.

(iii) Co and Al substitution for iron increased effective magnetic hardness [40]. The intrinsic coercivity increased while the Curie temperature decreased strongly [39].

2.1.2. Thick and thin films

2.1.2.1. Structural and magnetic properties of thick films. Important results were reported by Cadieu and co-workers (41–46). The films were deposited by means of r.f. selectively thermallized sputtering. During sputtering, a magnetic field ($160\ kA\,m^{-1}$) was applied in the plane of the substrates. The film thicknesses were approximately 1–2 μm. In the case of substrates kept at 293 K the as-deposited films were amorphous with a mirror-like aspect. Complete crystallization was achieved after annealing of the substrate to a suitable temperature. Films deposited on to heated substrates were crystallized and dark in appearance. In general, the samples were single phase. The first experiments [41] indicated that films deposited on to substrates held at 873 K were textured, with the *c*-axis considerably out of the film plane. For a substrate temperature of 973 K the *c*-axis was better aligned. X-ray spectra clearly showed the texture change (in the second case the (0 3 1) diffraction line was more intense than the (2 2 2)). In the case of films deposited at 1023 K, the room-temperature intrinsic coercive force was $1280\ kA\,m^{-1}$. Cadieu *et al.* [42] later showed that low-rate sputtering produced perpendicular anisotropy in $Nd_2Fe_{14}B$ films and that high deposition temperatures produced a high coercive field. X-ray spectra and hysteresis loops clearly indicated the film properties for different sputtering rates. In another paper [43] these authors noticed that, as their samples could not be crystallized below the Curie temperature, no appreciable in-the-film-plane anisotropy was observed. Magnetic films with special anisotropies were studied elsewhere [46]. Lastly electron energy loss spectroscopy (EELS) experiments [45] have shown that, compared to the $SmCo_5$ alloy, Nd4f electrons were less localized than Sm4f. In contrast, the iron in $Nd_2Fe_{14}B$ was more localized than the cobalt in $SmCo_5$. This implied a better anisotropic field in the $SmCo_5$ lattice and to a lower Curie temperature for the $Nd_2Fe_{14}B$ compound. Similar results were obtained by Sellmyer *et al.* [47] in the case of $Nd_2(Fe, Co)_{14}B$ thick films. Other samples, such as $Nd_{15}Fe_{77}B_9$, were also synthesized by r.f. sputtering [48]. The as-deposited films were amorphous. The crystallization and the Curie temperature were studied as a function of the B content. The sample possessed a coercivity less than $0.08\ kA\,m^{-1}$ and a uniaxial anisotropy less than $10^{-10}\ J\,m^{-3}$.

2.1.2.2. Thin films. Few papers have been published in this field of research. Zasadzinski *et al.* [49, 50] and Segre *et al.* [51] have widely studied thin-film morphology after deposition on to different substrates by means of d.c. triode sputtering. The morphology is dependent on the temperature of the single-crystal sapphire substrate. At 873–973 K the films are textured with the *c*-axis predominantly perpendicular to the film plane. At 293 K the easy axis is along the *c*-axis. Electrical transport measurements revealed a high resistivity of $(350 \pm 35)\ 10^{-8}\ \Omega m$ and displayed a change of slope near 150 K, which was interpreted as a consequence of the spin reorientation. Kerr rotation indicated an intrinsic anisotropy consistent with the preferred orientation. The coercive field was $120\ kA\,m^{-1}$. Some results relative to $Sm_2Fe_{14}B$ and $Er_2Fe_{14}B$ thin films are also given. The intrinsic anisotropy field was estimated at $1500\ kA\,m^{-1}$, whereas it is more than $4800\ kA\,m^{-1}$ in the case of single crystals [52]. Ingots evaporated in a tungsten crucible led to the formation of amorphous thin films, as shown by Gasgnier *et al.* [53]. Lorentz microscopy revealed the formation of two kinds of domain wall: the fine magnetic domain and ripple types. Application of the magnetic induction of the objective lens, or heating by means of the e-beam, generated new magnetic domains. All the contrast was characterized by an in-plane magnetization. Boron was only detected by ion mass spectroscopy. Annealing at high temperatures by means of the e-beam led to the disproportionation of the amorphous matrix with formation of the α-Fe and A–Nd_2O_3 phases. At very high temperature, the $NdFeO_3$ compound was formed.

Thermoelectric power measurements of amorphous $Nd_{0.04}Fe_{0.94}B_{0.02}$ films were carried out by Litai *et al.* [54]. The power is reported as positive and non-linear, exhibiting a broad peak as the temperature is varied.

Magnetization of GdFeB and GdCoB amorphous films (0.4–1 μm) was reported by Taylor [55] and Taylor and Gangulee [56]. The results obtained in the case of a large number of compounds were discussed in terms of the noncollinear (sperimagnetic) alignment behaviour of the Fe magnetic sublattice in amorphous ferrimagnetic alloys.

2.1.2.3. Thin film applications. $Nd_2Fe_{14}B$ alloys, as fine particles or thin films, are potential candidates as a perpendicular recording medium [49, 57]. Such an application seems peculiarly enhanced when, at room temperature, the easy axis in $Nd_2Fe_{14}B$ is along the *c*-axis as demonstrated by Kerr hysteresis loops [49]. Suitable microstructures and low coercivities are also two fundamental parameters [57]. Thin films for surface acoustic wave devices were studied by Hietala [58].

2.1.2.4. Rapid survey of R–Fe (or Co, or Ti) thin films. Perpendicular magnetic anisotropy of r.f. sputter-deposited Nd (or Pr)–Fe and NdFeCo alloy thin films was recently investigated by Susuki [59–62] and Suzuki and Katamaya [63]. The authors concluded that the magneto-optical properties were close to those of the classical Gd–Fe and TbFeCo alloys. In the same way Carey *et al.* [64–66] noticed that r.f. sputtered films prepared at very high deposition rates exhibited unusually large coercivities and it was shown, without ambiguity, that the samples presented a marked perpendicular anisotropy. Nd–Fe–Ti alloy r.f. sputtered films with perpendicular anisotropy were prepared by Tsutsumi and Sugahara [67]. The magneto-optical properties were discussed mostly in terms of the film microstructure. All these results indicate that the above-mentioned assertion of Sagawa *et al.* [5] is invalid. The fabrication of Nd (or R)–Fe(Co)–Ti thin films or thin particle alloys with high coercivity, high Kerr rotation angle, etc., for magneto-optical devices as recording medium, has led to various patents [68–73].

2.2. RCo_5 alloys

In the last 15 years the study of the R–Co and R–M–Co (M = other different metals) alloys as permanent magnets has been widely extended. Three kinds of materials emerge. It is not possible here to discuss all the literature, only the more interesting papers will be reviewed.

2.2.1. First class

The first class of materials includes the following alloys: $SmCo_5$, $Sm(Cu, Co)_5$, Sm_2Co_7, $Sm[(Co, Fe, Cu)Sr$ and/or Ti and/or $Hf]_7$, Sm_2Co_{17} and $Sm_2(Co, Cu, Fe)_{17}$. The aim of most of the studies was to determine the microstructure of thin flakes (defects, grain boundaries, compositions, precipitates, etc.) and its influence on the magnetic properties. Lorentz microscopy and Kerr and Bitter techniques have been used to determine the magnetic domains. To gain a wide view of the problems (both microstructure and magnetic properties), the reader should refer to the papers of Fidler [74], Fidler and Stalicky [75], Fidler *et al.* [29], Livingston [76] and to a series of proceedings [77].

2.2.2. Second class

The second class is related to Sm_xCo_y amorphous thin films prepared by various procedures (flash-evaporation, coevaporation, e-beam, plasma spraying, splat-cooling, sputtering, etc.). Gronan *et al.* [78] have listed and compared the main results (structures, coercive field and magnetic anisotropy) obtained for various preparations and compositions. Kullman *et al.* [79] have shown that amorphous materials were promising in recording performances. Few patents were taken out in this field of application [80, 81]. Lee *et al.* [82–84] have studied the galvanomagnetic effects of Sm_xCo_{1-x} layers deposited from two heating sources. They observed a large Hall effect. The results were discussed as a function of the Sm content. An Sm content, close to 15%, led to an initial stage of crystallization.

2.2.3. Third class

The third class is based on ferromagnetic $SmCo_5$ crystalline thick films (1–2 μm). A wide range of studies was carried out by Cadieu and co-workers [43–45, 85–92]. The first experiments have shown that r.f. sputtered films were inhomogeneous (coexistence of the $SmCo_5$ and Sm_2Co_{17} phases [85]). Then [86, 87] a selectively thermalized r.f. trisputtering procedure was used to synthetize directly the $SmCo_5$ compound on a heated substrate (873–1023 K) in the presence of an applied in-plane field. In these conditions the *c*-axis is rapidly aligned into the substrate plane.

The oxygen content was observed, as a contaminant, and was found to affect the film texture [(2 0 0) and (1 1 1) orientation]. Intrinsic coercive force was measured to be 600–720 $kA\,m^{-1}$ depending on the in-plane field angle. In later work the experimental procedure was further refined [88–92] by producing films with a uniform $SmCo_5$ composition. The use of polished Al_2O_3 substrates kept at temperatures between 873 and 923 K produced directly crystallized films. It was also demonstrated that sputtering rates strongly influenced the texture and the coercive force of the films. Higher rates (~ 0.5 $nm\,sec^{-1}$) resulted in the (2 0 0) texture growth, while lower rates (0.05–0.15 $nm\,s^{-1}$) resulted in the (1 1 0) texture. The (1 1 0) textured films were finer in microstructure and magnetically harder than the (2 0 0) films. In the case of films sputtered at 0.15 nm s^{-1} the intrinsic coercive force was 1840 kA m^{-1} and the energy product 144 T kA m^{-1} (at 210 K). Some additional results were given for uniform Sm_2Co_{17} films (with a maximum energy product of 160 T kA m^{-1}) and for $Sm_2(CoFeZr)_{17}$ samples (with a static energy product up to 170 T kA m^{-1}). The higher energy products were attributed to both the high induction and to the squareness of the in-plane hysteresis loops. Amorphous samples exhibited a lower intrinsic coercive force (80 kA m^{-1}) [90]. Munakata *et al.* [93], in the case of r.f. sputtered films with an average composition of Sm_2Co_8, observed the amorphous–crystalline transition at about 500 K. Well-crystallized samples (as a $SmCo_5/Sm_2Co_{17}$ mixture) were obtained after annealing at about 800 K. Maximum coercive force ($\sim$ 880 kA m^{-1}) was obtained for substrates maintained at about 700 K during deposition.

Other studies were carried out using plasma spraying [94] and ion-plasma sputtering [95, 96]. In the case of high substrate temperature (1400 K) the film were textured according to the (0.2) plane of the hexagonal structure [94]. Therefore, the *c*-axis alignment (normal to the plane of the film) was achieved under these conditions. The intrinsic coercive force was 1040 kA m^{-1} and the maximum energy product was 75 T kA m^{-1} [94]. Merkulova *et al.* [95] have briefly described the amorphous–crystalline transition by means of laser annealing in an attempt to fabricate miniature $SmCo_5$ film magnet arrays. They have given some optical properties (R and T). In the case of very thick films [96] it was observed that the as-deposited films were amorphous. After annealing up to 893 K they formed an $SmCo_5$-rich Co alloy, and at 1073 K there was coexistence of the $SmCo_5$ and Sm_2Co_{17} alloys.

EELS experiments have shown that Sm 4f electrons are localized and that the Co 3d electrons are fairly itinerant. The spectra were collected in the range 150–400 eV [45]. Schattchneider *et al.* [97, 98] have recorded and discussed the spectra from flash-evaporated films in the energy range 0–500 eV. The specimens were contaminated by carbon and Sm_2O_3. At low energy, two absorption edges at 5 eV (may be the surface plasmon) and 15 eV (volume plasmon) seem to characterize the $SmCo_5$ alloy.

2.3. Sm–Ti–Fe alloys

Recent studies of these alloys have been performed by Cadieu *et al.* [43, 44, 86, 89, 90, 99–102]. The early work indicated that a new metastable $SmFe_5$ phase (hexagonal) was stabilized by oxygen [86]. The experimental procedure was similar to that used to fabricate $SmCo_5$ films. In this way a Ti-stabilized $SmFe_5$ phase was directly synthetized in the crystalline state. In the case of a 1(Ti):9 (Fe) ratio, the intrinsic coercive force (at 300 K) was 500 kA m^{-1} with a static energy product of 44 T kA m^{-1}. The sample did not exhibit a rigid in-plane anisotropy. The Curie temperature could be above 873 K [99]. In the case of a 1:19 ratio, the in-plane coercive force was 800 kA m^{-1} with an energy product of 100 T kA m^{-1}. Curie temperatures were a function of the Ti content [89]. In the case of Co substitution for Fe[(Sm, Ti)(FeCo)$_5$ alloys] the as-deposited amorphous films were crystallized after heating at 1073 K. Intrinsic coercive force was 1920 kA m^{-1} with an energy product of 120 T kA m^{-1} and an easy axis rigidly in the film plane (1 0 0). For lower Fe contents, (Sm(Fe, Ti)$_2$ alloys, with a cubic structure), the films exhibited a large perpendicular to parallel remanent ratio of 3. The perpendicular anisotropy was estimated to be 4×10^{-7} J m^{-3}. Such films are textured [101]. Amorphous specimens exhibited low intrinsic force (0.5 kOe) and a large in-plane anisotropy [90].

For comparison, one can mention the results of Tsutsumi and Sugahara [103] in the case of r.f. sputtered partially crystallized $Nd_{34}Fe_{61}Ti_5$ films. The easy axis of magnetization was normal to the film plane and the anisotropy energy was 8.3×10^{-8} J m^{-3}.

2.4. Conclusion – applications

The three groups of materials, as thick films, were compared in great detail by Cadieu *et al.* [43] and Cadieu [44]. It has been demonstrated that the amorphous–crystalline transition produces high coercive forces and in-plane anisotropy. Both $SmCo_5$ and $Nd_2Fe_{14}B$ samples are uniaxial systems, while for Sm–Ti–Fe the high coercive force does not fully characterize its magnetic properties. The results were discussed in terms of preferential texturing of the crystal structures and of microcrystallite grain sizes.

$SmCo_5$ permanent magnets as thin films, are suitable materials for use in magnetic and optomagnetic storage [104–107]. Cadieu [44] has presented a method to build miniature periodic permanent magnet arrays useful as undulator structures to deflect alternately an electron beam. These powerful magnets will vibrate the positrons, causing them to emit beams of intense and highly focused X-ray, 10 000 times as powerful as any available today. The alternating layers were either $SmCo_5$ films with the (1 1 0) texture and $SmCo_5$ films with the (2 0 0) texture, or $SmCo_5$ films with the (1 1 0) texture and $Sm_2(Co, Fe, Zr)_{17}$ films. A small cladded magnet geometry was also discussed.

3. Superconducting materials

Since the recent discovery of the new superconducting ceramics (La, Sr)$_2$CuO$_4$, $RBa_2Cu_3O_7$, $BiCaSrCuO_x$, $PbSrYCaCuO_z$, etc.) with high transition temperature (T_c = 40–125 K), the importance of the other materials has, of course, fallen abruptly. However, it is worth remembering the numerous efforts which have been made since 1960 in order to try to obtain better superconducting performances with numerous alloys and compounds.

The historic development, in the case of thin films, has been reviewed previously [108]. The first results were reported by Schwidtal [109, 110], in the case of lanthanum foils ($T_c = 4.9$ or 6 K depending on the structure, i.e. h c p or f c c) and of (La–Gd) dilute alloys ($T_c = 4$ K). Other work has concerned Pb–Gd [111], Pb–Ce [112], dilute systems such as $LaGe_2$ and YGe_2 [113] and $(Ti, Zr)_x$ Sm_y, $PbLa_x$ and Sm_xPb_y [114]. Transition temperatures near 6.5 K were measured for the latter two. One should also notice that in the case of $La_{1-x}Au_x$ samples, T_c decreases as the Au content increases [115]. To our knowledge, few additions were made to these experiments. Later (around 1980), various new compounds emerged. They have been classified according to four groups: RMo_6S_8 (Chevrel's phases), RRh_4B_4, $CeCu_2Si_2$ and La_3S_4. A special section will be devoted to multilayer systems.

3.1. RMo_6S_8 compounds

Chevrel's phase compounds are promising in high-field technology applications: these materials possess very high critical fields. Umbach [116] has shown that, in the case of rare-earth compounds, only $HoMo_6S_8$ exhibits the coexistence of the superconducting and ferromagnetic states. For some rare-earths (R = Gd, Tb, Dy, and Er) superconductivity and antiferromagnetism occur, whereas for the other rare elements (R = La, Pr, Nd, Sm, Tm, Yb and Lu) only superconductivity occurs. Przyslupski *et al.* [117] found that in the case of $LaMo_6S_8$ thin films, the critical current density reached values of 1.7×10^7 A m^{-2} (B = 0 and $T_c = 1.7$ K). Szmaszek *et al.* [118] measured a higher T_c value (7 K) for the same compound. The two papers showed that the pinning forces created in the films, followed a basic scaling law. The pinning mechanism was responsible of the magnitude of the critical current. Later, in the case of $Pb_{0.8-1.0}R_{0.1-0.2}Mo_{6-6.35}S_8$ compounds (R = La, Pr, Nd, Gd and Y), Przyslupski *et al.* [119] reported higher T_cs (10–13 K) and higher critical currents ($6–16 \times 10^7$ A m^{-2}). $Pb_{0.8}Gd_{0.2}Mo_{6.35}S_8$ and $Pb_{1.0}$ $Nd_{0.2}Mo_{6.35}S_8$ compounds exhibited the higher values. Critical currents were a function of external magnetic fields and heating treatments.

The characteristics of $Ho_xMo_6S_{8-y}$ thin films, prepared by d.c. getter sputtering, were studied by Przyslupski *et al.* [120]. To avoid oxygen contamination [1 2 1] the layers were annealed at 1473 K. X-ray diffraction analysis showed the presence of small amounts of Ho_2O_2S. RBS spectra revealed the composition $Ho_{1.15}Mo_6S_{7.7}$. The transition temperature was very low (between 1.88 and 2.54 K). The re-entrant transition temperature was studied as a function of different magnetic fields and estimated as 0.6 K (in the case of parallel magnetic fields). Maps *et al.* [122] studied this re-entrant behaviour in the case of $HoMo_6S_8$ films prepared by e-beam evaporation. The results are in agreement with those of Przyslupski *et al.* [120], except that the transition temperature is lower ($T_c = 1.5$ K). Webb *et al.* [123] showed that $HoMo_6S_8$ e-beam deposited films were contaminated by small amounts of Mo_2S_3 and Mo (Szymaszek *et al.* [118] noticed the presence of MoS_2 in the case of $LaMo_6S_8$ films). No re-entrant superconductivity was observed by Webb *et al.* [123]. Fujita *et al.* [124] for sputtered-films reported that the temperature dependence of the magnetization was a function of the film thickness. Such results are consistent with the magnetic phase diagram. Among these results, only Maps *et al.* [122] claimed that the $HoMo_6S_8$ compound was possibly antiferromagnetic rather than ferromagnetic at low temperature. Kotani *et al.* [125, 126], Tachiki *et al.* [127] and Takahashi *et al.* [128] have dealt theoretically with this problem as a coexistence of the ferromagnetic and superconducting states in thin films. The magnetic phase diagrams were described [127, 128].

RMo_6S_8 compounds were tested as tunnelling junctions [120, 127]. Przyslupski and Poppe [129] have studied $LaMo_6S_8/Al_2O_3/Al$ diodes. After annealing, the transition temperature was 6.6 K. They reported the typical curves of differential conductance versus voltage at various temperatures.

3.2. RRh_4B_4 compounds

Crystallographic, magnetic and superconducting properties of these compounds were described by Umbach [116].

3.2.1. $ErRh_4B_4$

Only $ErRh_4B_4$ and $Er_{0.58}Ho_{0.42}Rh_4B_4$ are re-entrant superconductor materials [130, 131]. This was discovered by ultrasonic attenuation measurements in the bulk. The predicted type II-1 superconducting behaviour was confirmed [132]. However, this property does not exist at any composition other than the stoichiometric one. This implies great difficulties in preparing well-characterized sputtered thin films. The most important impurities result from the formation of RhB, $ErRhB_4$ and Er_2O_3 compounds [116, 133]. Grey *et al.* [134] have prepared high-quality d.c. sputtered films. They report the formation of two crystalline phases as primitive tetragonal and b c t. The first had a higher T_c (8.22 K) than the second (7–6.5 K). Some RhB was present as an impurity in both films. Numerous experiments allowed these authors to conclude that a type II–type I transition occurs in the primitive tetragonal re-entrant phase of $ErRh_4B_4$ as predicted by Tachiki *et al.* [135]. (The b c t crystal did not exhibit a re-entrant phase in zero field). This transition could explain the discrepancy observed between perpendicular and parallel critical fields. Gray *et al.* [134] did not agree with the ferromagnetic correlation proposed by Cantor *et al.* [136]. This was discussed theoretically by Gray [137] by analysis of the resulting intermediate state for the case of a type I-superconducting film in a perpendicular field at low temperature. In this case the effects of paramagnetism were analysed. Gray *et al.* [134] have tentatively determined the superconducting condensation energy in the primitive tetragonal phase. This energy was not Barden Cooper Schrieffer (BCS) type, but it was impossible to reach a definite conclusion. Cantor *et al.* [136] reported a T_c of about 7.5–8.5 K and a re-entrant temperature of about 0.6–1 K. They found that the perpendicular critical field was larger than the parallel. This unusual result was explained in terms of a substantial concentration of magnetic ion. Dharmadurai [138] studied the non-equilibrium phenomena in a photoexcited (induced by optical illumination) re-entrant film bridge, by investigation of the non-linear (voltage anomaly) I–V characteristics. This property was reported by Chashoo and Dharmadurai [139] in the case of the dissipative intermediate resistance state and it can be understood by a simple heating model [140].

Rowell *et al.* [141] have studied the effect of ion-damage (α-particles) on the superconducting and magnetic transition of $ErRh_4B_4$ films. Such damage reduced T_c and depressed the ferromagnetic transition. Comparison with A 15 and RMo_6S_8 compounds as a function of α-particles fluence were carried out. The results were discussed in terms of the band structure of cluster compounds. Its seems that the damage affected primarily the Rh clusters while leaving the Er lattice relatively unaffected. Resistivity measurements demonstrated a saturation effect, and showed that the re-entrant transition was strongly suppressed [142]. Rowell *et al.* [142] observed low critical currents (3.5×10^6 A m^{-2}) in the case of $ErRh_4B_4$ films; these currents decreased rapidly at the magnetic transition in the case of $Er_{0.43}Ho_{0.57}Rh_4B_4$ specimens.

These compounds were considered as very suitable for technological applications. In this way, Umbach [116], Umbach *et al.* [143–145] and Lin *et al.* [146, 147] studied tunnelling thin film properties. Various $ErRh_4B_4/R_xO_y$ (and $R(OH)_3$) (as artificial barriers with R = Er or Lu)/In), or Al, or Pb, or Sm, or Mg (as counter-electrode) thin film junctions were fabricated. Lin *et al.* [147] concluded that spontaneous magnetic moments were present above the transition temperature.

Rowell *et al.* [142] have prepared $ErRh_4B_4$/Al oxide/Pb junctions, without clear results (see also Section 3.5.3). All these experiments were done in order to measure the maximum d.c. Josephson current for these junctions. Brief discussions relating to the anomalous behaviour of the Josephson effect which occurs in these junctions allowed Tachiki *et al.* [127] to confirm the results of Umbach and Goldman [144].

3.2.2. $SmRh_4B_4$

In this compound one finds the coexistence of the antiferromagnetic and superconducting states [116]. Zasadzinski *et al.* [148] and Terris *et al.* [149] reported some properties of various films. In the case of the best sample, obtained by d.c. sputtering, a transition temperature of 2.36 K was measured. X-ray analysis [148] showed the presence of RhB, $SmRh_3B_2$, $SmRh_6B_4$ and $SmRhB_4$ compounds and also of RhAl which resulted from a reaction with the sapphire substrate. This was eliminated by use of a BN substrate. These impurity phases influenced the superconducting properties and tunnelling currents were reduced. However, the upper-critical-fields were similar to those of the bulk and were independent of T_c at low temperature. Lastly, it seemed that the anomalous dependence of T_c on the residual resistance ratio was significantly different from the universal behaviour of the A 15 and $ErRh_4B_4$ superconductors. This was explained by Terris *et al.* [149] by T_c, resistivity ratio and upper-critical-field measurements after film irradiation by α-particles and protons. The results allowed them to propose to an additional mechanism. The new model was discussed in terms of an enchancement of the spin–flip scattering due to the decrease of the long-range crystalline order.

3.3. $CeCu_2Si_2$ compounds

Bulk and single-crystal superconducting properties of these materials and of other similar compounds were reported by Spille *et al.* [150]. Such compounds, as heavy fermion systems, exhibit a very low T_c (0.67 K), which is strongly dependent on the copper concentration [151]. A few investigations have been made using thin films [152, 153]. The samples, prepared by d.c. magnetron sputtering, had varying composition (152). T_c was very low (0.6 K maximum), i.e. lower than for the bulk. As a function of the stoichiometry, various parameters were measured: magnetoresistivity, Hall coefficient, upper-critical-field, etc. It was concluded that lattice defects influence the sample properties and also the formation of heavy particles at low temperature. Adrian and Adrian [153] and Holter *et al.* [154] studied the influence of lattice disorder (defects) introduced at low-temperature by irradiation with fast ions (oxygen ions at 25 MeV) on the superconductivity and resistivity of the films. It was concluded that T_c was extremely sensitive to lattice defects, resulting in a complete suppression of T_c (6 mK) at an estimated concentration of displaced atoms of about 1%. A well-grounded explanation of this phenomenon appears to be very difficult to determine.

3.4. La_3S_4 compound

The bulk compound La_3S_4 (γ-phase) is characterized by a T_c of 8.25 K and a low density of carriers ($\sim 610^{27}$ m^{-3}). The cubic structure (fcc with $a = 0.875$ nm) exists in a continuous series of solid solutions between La_3S_4 (superconductor) and La_2S_3 (semiconductor). The formula unit is usually written as $La_{3-x}[\ \ ]_xS_4$, where [ ] corresponds to a vacancy and x ($0 < x < 1/3$) to the vacancy concentration ($x = 0$, corresponds to the superconductor state).

To our knowledge, the first preparation of thin films by thermal evaporation was carred out by Mironov *et al.* [155]. Later, Mel'nikova *et al.* [156] used this technique to prepare thin films deposited on to unheated and heated (800 K) quartz substrates. In the first case the samples were amorphous, whereas in the second they were crystalline (γ-phase). Films close to the stoichiometric composition exhibited a T_c below 6 K. Moreover, a negative temperature coefficient of resistance, was observed preceding the superconducting transition. Some optical investigations were also carried out, particularly the determination of the refractive indices and of the permittivity from absorption spectra.

Recently, Kent *et al.* [157, 158] have prepared La_3S_4 layers by reactive planar magnetron sputtering (H_2S and Ar atmosphere). The films (thickness 40–400 nm) are polycrystalline with very small grains (~ 20 nm). It was proved that various physical parameters (T_c, residual resistivity, specific heat) were very sensitive to stoichiometric changes inside the films. The authors concluded that the T_c of the films was the same as that of single crystals (~ 8 K) and that the mobility was a factor 2 to 300 lower than that found in the bulk. The upper-critical-field (H_{c2}) was understood within a percolation model. They observed a striking anisotropy in H_{c2} with different field orientations. They concluded that the qualitative behaviour of H_{c2} as a function of temperature and resistivity can be understood within a percolation model.

Lastly, Berkley *et al.* [159] have prepared their samples by multisource vapour deposition. They observed, in the case of a higher La concentration, the coexistence of the La_3S_4 and LaS compounds. For pure γ-La_3S_4 films the T_c is equal to 8 K and the carrier concentration is $6.5 \times 10^{27}\ m^{-3}$. According to these authors a possible application is in the fabrication of three-terminal field-effect-transistor (FET)-like devices, where superconduction is switched on and off by changing the voltage bias on a gate.

3.5. Multilayer systems

3.5.1. Nb/R as metallic systems

Green *et al.* [160, 161] have studied proximity effects between magnetic, non-magnetic and superconducting layers in the case of multilayer thin films. Three systems, Nb/Er, Nb/Tm and Nb/Lu were investigated. Various bilayer thicknesses (or superlattice periodicities) were used (2.5 to 250 nm). RBS and X-ray diffraction analysis were used to determine that rare-earth and Nb films did not interdiffuse and that they were textured. Superconducting properties were found to be a function of the bilayer thickness. In the case of the magnetic Nb/Er system, T_c decreased strongly (from 8 to 1.18 K) as the bilayer thickness decreased, whereas for the non-magnetic Nb/Lu system, T_c decreased more slowly (from 8 to 2.5 K).

3.5.2. Sm or Pb (Tl)/Gd or Y coaxial samples

Aoki and Katashiro [162] have investigated the magnetic interaction of superconducting fluxoids with magnetic (Gd for ferromagnetic and Y for paramagnetic) substances. The multilayer samples were prepared by alternate deposition of each metal by means of an e-beam evaporator. The authors observed that the critical current (with a perpendicular magnetic field) was enhanced more than ten times by the magnetic contact ($1.4 \times 10^5\ A\,m^{-2}$ at 4.2 K) in the case of a Pb (Tl) alloy. Little difference in the effect between Gd and Y was observed.

3.5.3. Rare-earth oxide barriers

Umbach [116] and Umbach *et al.* [163] have fabricated multilayers using various combinations of Nb, Nb_3Ge, V_3Si, Au, and $ErRh_4B_4$/R oxide (R = Er or Lu) Pb or In Josephson junctions with very low leakage. In this process the "natural oxide" barriers formed by the oxidation of the base electrode were substituted by "artificial" barriers formed on top of an unoxidized base electrode. The thickness of the rare-earth oxide film was about 0.3–0.6 nm. Compared to the other materials, very high quality junctions were formed on Nb films. Nb_3Ge, V_3Si and $ErRh_4B_4$ were of lower quality due to the presence of second phases and $ErRh_4B_4$ and Au did not form a resistive natural oxide. The Nb/Er(Lu) oxides/Pb Josephson junctions, undegraded after several thermal cycles, were the most stable materials.

Tedrow *et al.* [164] and Tkaczyk and Tedrow [165] have studied the spin-polarized electron tunnelling and the magnetic proximity effect in EuO–Al/Al_2O_3/Al or Fe and of EuO and R_2O_3 (R = Gd, Tb, Dy and Er)–Al/Al_2O_3/Fe junctions. An enhancement of an applied magnetic field in the superconducting Al film was observed (Gd_2O_3 was the better interface). It was also found that EuO–Al layered system behaves like a superconductor with an internal magnetic field.

Like Lin *et al.* [147], in the case of $ErRh_4B_4$/$La(OH)_3$ or $Lu(OH)_4$/M (M = In or Sb) junctions, Stageberg *et al.* [166] have reported the tunnelling characteristics of so-called Pb/$R(OH)_3$/Pb junctions (R = Ho, Er and Lu). Here, an important problem must be discussed. The authors claimed that after oxidation in an oxygen plasma of a 1 μm thick rare-earth metal film, sufficient water vapour was present in the system to ensure the formation of the trihydroxide rather than the sesquioxide. This assertion was only supported by XPS and AES analyses [167] and not by X-ray or electron diffraction. It is well known that the formation of the sesquioxide occurs quickly, especially in the case of very thin films. Moreover the transformation $R_2O_3 \rightarrow R(HO)_3$ is not possible in the case of the heavy elements (from Gd to Lu) [26]. Lastly, the formation of $R(OH)_3$, for heavy elements (Dy to Lu) occurs only under special hydrothermal processes (high temperatures and pressures) [168–170]. The formation of $Lu(OH)_4$ [147] is absolutely impossible [26]. Under these conditions XPS and AES analyses have demonstrated only the insertion of water throughout the sesquioxide films [171]. Thus the results and the phenomena described by Stageberg *et al.* [166] are difficult to interpret. In this way, Kwo *et al.* [171] have studied Nb/Y_2O_3 (or Er_2O_3) $Pb_{0.9}Bi_{0.1}$ junctions. From XPS analyses they inferred the formation of a hydrated rare-earth sesquioxide of poorly-defined stoichiometry: the O (1s) absorption edge showed the presence of hydroxide (OH radicals). Yttrium was determined to be the better material for those junctions: Y_2O_3 strongly protects niobium against oxidation. One must also mention the work of Lemberger and Clarke [172] who have realized Al/AlO_x/AlEr and AlEr/AlO_x/Cu junctions. Erbium is taken as a pair-breaking magnetic impurity which induces elastic exchange charge relaxation. AlEr films possess a very low T_c (~ 1.51 K at best). The different electrical parameters vary widely as a function of the Er concentration.

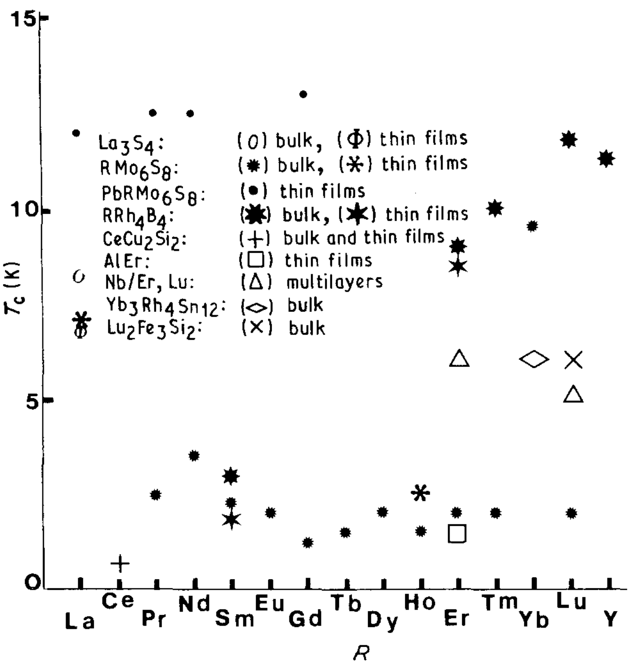

Figure 1 Maximum T_c for various compounds as thin films and bulk materials.

3.6. Conclusion

The fabrication of pure superconducting films and multilayers was evidently very difficult to achieve. The formation of additional phases and the presence of impurities were often an impediment in determining the exact characteristics of the specimens. The reported T_c did not exceed 13 K (Fig. 1). One may note that to our knowledge, no patent applications were filed.

Other recent papers indicate the fabrication of various new bulk compounds, e.g. Takano *et al.* [173] have fabricated YIr_2 and $LuIr_2$ alloys with $T_c = 3.5$ and 5 K, respectively, Werterveld *et al.* [174] have synthesized $Yb_3Rh_4Sm_{12}$ single crystals with $T_c \sim 7$ K and Xu and Shelton [175] have prepared $Lu_2Fe_3Si_5$ samples with $T_c \sim 6$ K. Finally, one must cite the very important paper of Subba Rao and Balakrishan [176], which details the more important properties of the bulk ternary systems known before 1984.

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