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Magnetic properties of $RFe_{12-x}Mo_x$ compounds with R=Y, Gd, Ho, Er versus the molybdenum content

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Abstract

Magnetic properties of the tetragonal $RFe_{12-x}Mo_x$ compounds with R=Y, Gd, Ho, Er and for x ranging from one to three have been analysed. For compounds with Curie temperatures larger than room temperature (RT), measurements were performed on oriented powders allowing an estimate both of the easy magnetisation direction and of the magnetocrystalline anisotropy. The Fe anisotropy always favours the c-axis whereas rare earth anisotropy depends on the sign of second order Stevens factor favouring the c-axis for Ho and the basal plane for Er. Then in the latter compound spin reorientations are observed at temperatures which increase with x. In these ferrimagnetic compounds the Fe sublattice magnetisation prevails over that of the rare earth sublattice except for R=Er and x=2.5 where a compensation temperature is observed. Analysis of the Curie temperatures allows an estimate of the R–Fe and Fe–Fe exchange interactions in the different compounds. They are comparable to those determined in other 1–12 compounds and tend to increase with the Fe amount as observed in a large number of rare earth-3d transition metal materials. © 1998 Elsevier Science S.A.

Keywords: R–Fe–Mo; Mo substitution; Permanent magnets

The intermetallic 3d-rich alloys of formula $RFe_{12-x}M_x$, where R is a rare earth element and M a non-magnetic element (M=Ti, V, Cr, Mo, W, Si) [1], form a series of compounds which have potential permanent magnet applications. These materials crystallise with the tetragonal $ThMn_{12}$ structure type. Substitution of a third M element, which is needed to stabilise the structure [2–4], also has a strong effect on the bulk magnetic properties, leading to a reduction of both Curie temperature (T_c) and magnetisation (M). In this paper we report on the dependence of the magnetic properties versus the molybdenum concentration of $RFe_{12-x}Mo_x$ compounds (R=Y, Gd, Ho and Er). Special emphasis is put on the compounds with Gd and Ho since a more detailed presentation of the parent comnpounds with Y and Er has been previously reported [5].

The compounds with x=1, 2, 2.5 and 3 were prepared by melting the constituents (purity better than 99.9%) in a cold crucible induction furnace under a purified-argon atmosphere. The quality of the samples was checked using a conventional X-ray powder diffraction technique. For compounds which order above room temperature, T_c was determined using the Faraday method. For those compounds with a low Mo content, T_c was deduced either from the x vs T curves in low field or derived from Arrott plots (M^2 versus H/M). For the compounds which order above room temperature, magnetisation measurements were performed on oriented powder samples. For those compounds with high molybdenum contents (x=2.5 and 3), measurements were performed on free powder samples.

Let us first quote that for the four series: (1) in a first order case, the c/a ratio does not depend on x, indicating an isotropic expansion of the lattice as the Mo content increases and (2) the unit cell volume increases almost linearly with x.

Magnetic characteristics of the studied compounds are gathered in Table 1 whereas in Fig. 1 the T_c values are plotted versus x. The low temperature magnetisation curves for the Gd and Ho compounds are shown in Figs. 2 and 3, respectively. Besides, for these two series of compounds the thermal dependencies of the spontaneous magnetisation are reported in Figs. 4 and 5, respectively. For the Y and Er compounds, the corresponding plots can be found in [5]. With the Y and Gd compounds it is evidenced that the Fe magnetocrystalline anisotropy favours the c-axis, the anisotropy field decreasing when x increases from one to two. In the Ho compounds, c is also

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Table 1
Magnetic characteristics of $RFe_{12-x}Mo_x$ alloys

R	T_c (K)	M_s (4K) μ_B/f.u.	M_s (300K) μ_B/f.u.	μ_0H_a (4K) T	μ_0H_a (300K) T
$x=1$					
Y	493	19.0	14.9	3.5	1.8
Er	430	12.3	3.7	>10	2
Gd	560	14.0	12.4	5.5	4
Ho	470	10.1	11.2	-	-
$x=1.5$[a]					
Y	410	15.2	13.2	3.8	2.1
Er	380	8.5	11.6	-	2.0
Gd	460	14.1	12.5	5.0	3.0
Ho	410	12.6	14.4	-	2.0
$x=2$					
Y	345	11.6	3.8	2.0	-
Er	325	3.7	2.4	4.0	1.0
Gd	440	11.2	8.6	4.0	1.8
Ho	340	6.9	4.7	7.0	-
$x=2.5$					
Y	275	7.3	0.0	-	-
Er	290	0.95	0.0	-	-
Gd	405	6.4	3.75	4.0	1.8
Ho	320	1.18	1.18	-	-
$x=3$					
Y	63	1.0	0.0	-	-
Er	-	0.0	0.0	-	-
Gd	290	2.8	0.0	-	-
Ho	50	1.0	0.0	-	-

[a] From [6].

the easy magnetisation direction at any temperature showing that the crystalline electric field acting on Ho also favours the *c*-axis. As shown on the thermal dependence of the magnetic characteristics of the Er compounds (Fig. 6) intermediate directions of magnetisation observed at low temperature result from the competition between the Fe anisotropy and that of Er which favours the basal plane.

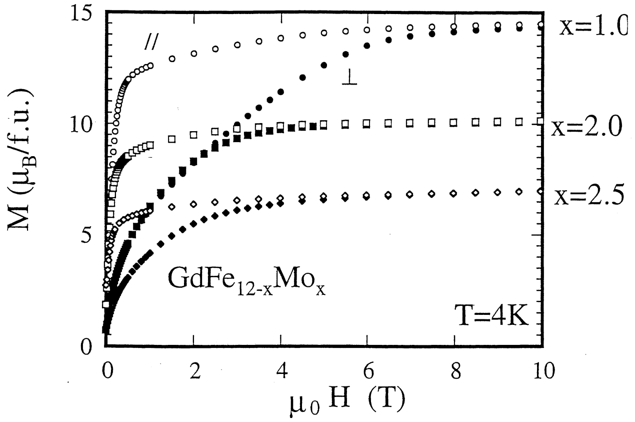

Fig. 2. Parallel and perpendicular to the *c*-axis field dependence of magnetisation measured at 4 K on the $GdFe_{12-x}Mo_x$ compounds.

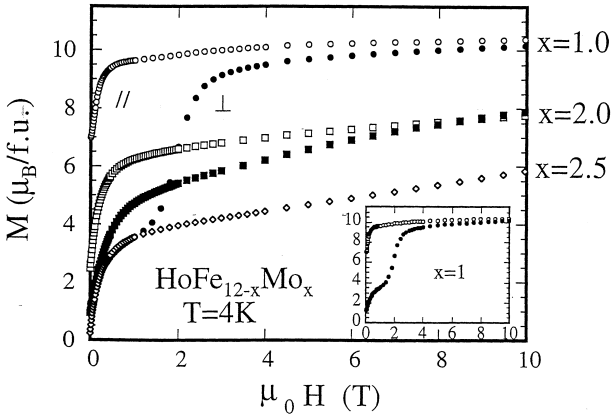

Fig. 3. Parallel and perpendicular to the *c*-axis field dependence of magnetisation measured at 4 K on the $HoFe_{12-x}Mo_x$ compounds. The inset shows more clearly the FOMP observed for $x=1$.

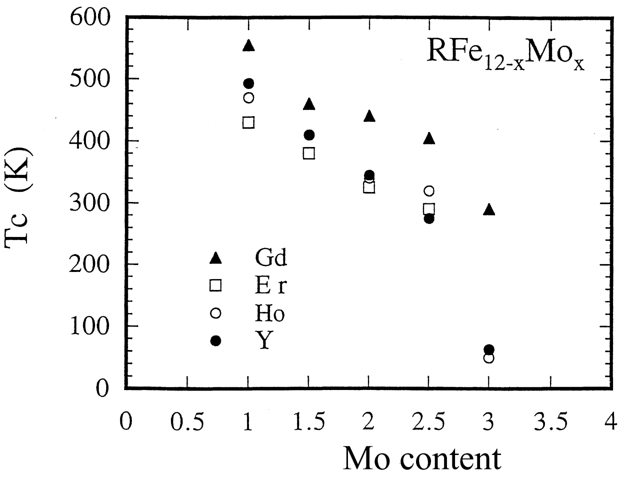

Fig. 1. Curie temperature variation versus the Mo content for $R=$Y, Gd, Ho and Er.

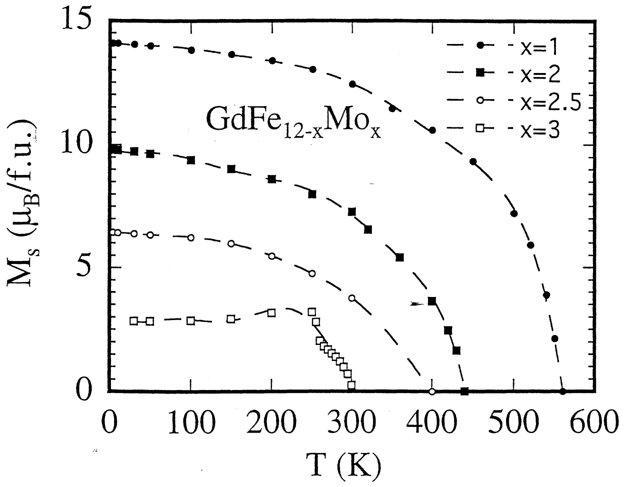

Fig. 4. Thermal variation of the spontaneous magnetisation of the $GdFe_{12-x}Mo_x$ compounds.

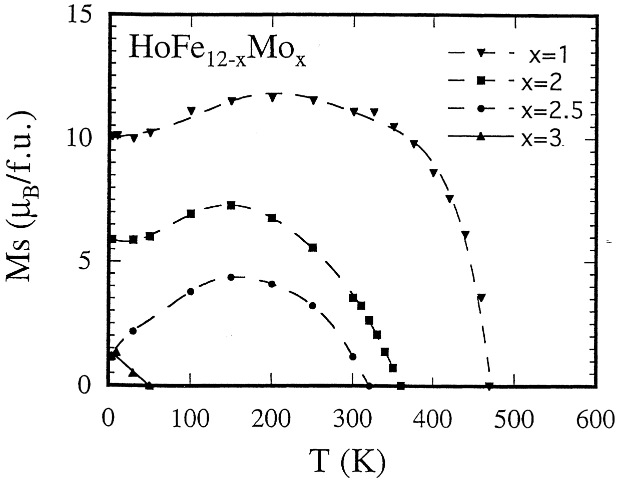

Fig. 5. Thermal variation of the spontaneous magnetisation of the $HoFe_{12-x}Mo_x$ compounds.

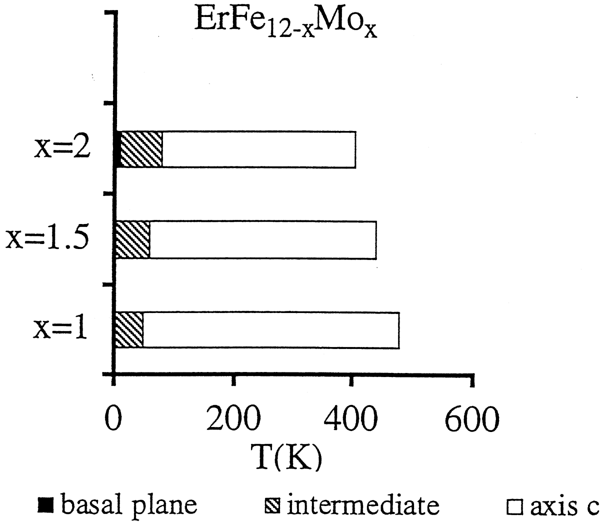

Fig. 6. Thermal variation of the easy axis direction of the $ErFe_{12-x}Mo_x$ compounds.

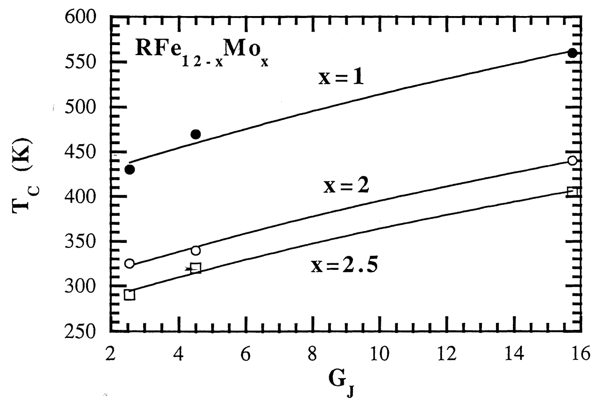

Fig. 7. Curie temperature variation versus the de Gennes' factor $G_J=(g_J-1)^2J(J+1)$ for different Mo contents.

Table 2
Fe moment and J_{FeFe} and J_{RFe} coupling constants in the series $RFe_{12-x}Mo_x$ with $x=1$, 2 and 2.5

x	1	2			2.5		
m_{Fe} (μ_B)	1.8	1.4	1.2	1.0	1.2	0.9	0.6
J_{FeFe} (K)	66	73	90	116	82	120	201
J_{RFe} (K)	5.0	5.6	6.3	7	6.0	7.3	10

Increase of the spin reorientation temperature (SRT) when x increases, whereas T_c decreases, show that the relative strength of the Er anisotropy increases with x in comparison with that of Fe. In these compounds with heavy rare earth elements, the value of the spontaneous magnetisation and its thermal variation is characteristic of ferrimagnetic materials in which the R and Fe sublattice magnetisations are antiparallel (antiparallel coupling of the R and 3d spins observed in R-3d intermetallics). Moreover the Fe sublattice magnetisation prevails over that of the rare earth sublattice except in the compound with R=Er for $x=2.5$. In the latter, the R magnetisation, which is the largest at low temperature, decreases faster than the Fe magnetisation when temperature increases. This yields a compensation temperature close to 10 K.

Within the molecular field approximation and neglecting the R–R interaction, in such a type of intermetallics it is usual to write T_c as [7–9]:

$$T_c = 1/2(T_{Fe} + \sqrt{T^2_{Fe} + 4T^2_{RFe}}) \tag{1}$$

where $T_{Fe}=AJ_{FeFe}S(S+1)$ and $4T^2_{RFe}=BS(S+1)J^2_{RFe}G_J$ A and B are constant within a series of compounds; S and $G_J=(g_J-1)^2J(J+1)$ are the spin of Fe and the de Gennes factor, respectively. Assuming that the exchange constant J_{RFe} is almost independent of R (that has been shown to be rather correct for heavy rare earth alloys [9]) one expects that T_c depends only on G_J as:

$$T_c = 1/2(T_{Fe} + \sqrt{T^2_{Fe} + CG_J}) \tag{2}$$

With non-magnetic rare earth elements $T_c=T_{Fe}$ then T_{Fe} should be given by the Curie temperature of the Y compounds. However in the latter series T_c is higher than with the corresponding Er compounds which is in contradiction with Eq. (1), showing that J_{FeFe} is larger with Y than with 4f elements. This has been already observed but better estimates of T_{Fe} and $C+BS(S+1)J^2_{RFe}$ are found with R=La or Lu. Then for each series, T_c is plotted as a function of G_J as shown in Fig. 7 (the compounds with $x=3$, which are too close to the offset of 3d magnetism, are not accounted for). Then a fit of the experimental dots with the theoretical variations (full lines in Fig. 7) allows an estimate of T_{Fe} and C for each of the series. The values of T_c are 405, 289 and 262 K for $x=1$, 2 and 2.5, respectively, whereas the values of C are 12076, 11642 and 12521. Note that the continuous lines fit rather well to the experimental values which shows that the compound parameters follow the model rather well. From the values of T_{Fe} and C it should be possible to determine J_{FeFe} and $J_{R\mathrm{Fe}}$, but for different reasons a difficulty arises on the determination of S: (1) the Fe moment is measured only at low temperature and the resulting value is not very accurate because the thermal dependence of magnetisation can be rather large, particularly for compounds with a high Mo content, (2) in materials where 3d magnetism has an itinerant character the relationship between the magnetic moment and the spin is not easy to know. As other authors do, here S is taken as half the low temperature value of the Fe moment m_{Fe} (μB). In Table 2, are reported the estimated values of the exchange coupling constants. Due to a large uncertainty in the Fe moment, for $x=2$ and 2.5 only the extreme values are given. It appears that: (1) the values are similar to those determined in V-stabilised 1–12 compounds [10], here the relative strength of the R–Fe interaction being slightly smaller, (2) there is a clear trend for both the Fe–Fe and the R–Fe interactions to increase when the Fe amount decreases. This is not only observed with the 1–12 compounds [10] but also in a large number of rare earth-3d transition metal materials [11].

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