Journal of Alloys and Compounds, 207/208 (1994) 285–289
JALCOM 3050

Magnetic properties and ^{57}Fe Mössbauer effect in the substoichiometric Ln–Fe–(Re,Mo) systems with the $ThMn_{12}$ structure

D.A. Berezyuk and O.I. Bodak
Department of Inorganic Chemistry, Lvov State University, Lomonosova 6, 290005 Lvov (Ukraine)

F.G. Vagizov*, K. Wochowski, W. Suski** and H. Drulis
Polish Academy of Sciences, W. Trzebiatowski Institute of Low Temperature and Structure Research, P.O. Box 937, 50-950 Wrocław 2 (Poland)

Abstract

Magnetic properties and ^{57}Fe Mössbauer effect have been investigated in the following compounds: $Ce_{1.33}Fe_{8.8}Mo_{3.2}$, $Ce_{1.33}Fe_{10}Re_{2}$, $Pr_{1.64}Fe_{7.2}Re_{4.8}$ and $Sm_{1.8}Fe_{7.5}Re_{4.5}$ in the broad temperature range. All these compounds turned out to be ferromagnetic at low temperature; however, under an applied magnetic field of 5 T, saturation is not reached. The Curie points and saturation magnetic moments determined in both experiments are in fair agreement with previous results obtained on stoichiometric samples, except for the Pr compound. In all samples, an admixture of other phases was detected. The XRD patterns, however, do not give indication of their structure.

1. Introduction

The f-electron Fe compounds with $ThMn_{12}$-type tetragonal structure exist as ternaries with various additional elements that function only to stabilize the lattice. These compounds turned out to be promising magnetic materials (see *e.g.* [1]).

Magnetic investigations of the stoichiometric compounds of the $LnFe_{10}Mo_{2}$ [2] and $LnFe_{10}Re_{2}$ [3] type have shown them to be ferromagnetic below about 260 (Ce compound)–500 K(Gd compound) with a saturation magnetic moment of about 1.4–1.6 μ_B/Fe atom [3]. The value of the magnetic moment calculated per Fe atom is not quite realistic because the contribution of the lanthanide sublattice is not considered. The composition of the Pr and Gd compounds does not correspond exactly to the stoichiometry of $LnFe_{10}Re_{2}$ [3]; nevertheless, the total contribution of the Fe and Re atoms amounts to the index 12. The same was reported by Jurczyk for compounds of Tb, Ho and Y [4], but both the Curie points and saturation magnetization moments were reported to be higher than for the stoichiometric compounds.

A systematic study by the Lvov group has shown that the $ThMn_{12}$ phase in Ln–M–M′ systems exists in a broad composition range, with a serious deficiency of transition (Fe) and stabilizing (Re,Mo) elements (for review see [5,6]).

Preliminary investigations of the magnetic properties of the $Ce_{1.3}Fe_{12-x}Mo_{x}$ alloys performed at 78–800 K [7] have shown that this system is ferromagnetic below 250–325 K, depending on the stoichiometry. As mentioned above, T_c for the stoichiometric compound was determined to be 260 K [2], and the authors explain such a low value in relation to other $LnFe_{10}Mo_{2}$ compounds by the existence of the Ce ion with a valence above 3 [2]. The Curie points for $CeFe_{10}Re_{2}$, $PrFe_{10.52}Re_{1.48}$ and $SmFe_{10}Re_{2}$ are reported to be equal to 353, 397 and 475 K, respectively [3].

In the $ThMn_{12}$-type of structure, there are four inequivalent crystallographic positions available. The 2(a) position is occupied by the rare earth metal whereas the Fe and Re/Mo atoms are distributed in the remaining 8(f), 8(i) and 8(j) sites. For the Pr–Fe–Re system, Berezyuk [9] reported that the Pr atoms are partly located in positions other than 2(a) and the formula unit can be represented as $Pr(Pr_{0.025}Fe_{0.758-0.585}Re_{0.217-0.390})_{12}$, covering a broad composition range. In ref. 3, it is stated that in the Re-stabilized compounds, the last element enters mainly on the 8(i) site and in ref. 8, the authors claim that Mo occupies the same

---

*Permanent address: Physicotechnical Institute, Russian Academy of Sciences, 420029 Kazan, Sibirski Trakt 10/7, Russian Federation.

**Author to whom correspondence should be addressed.

SSDI 0925-8388(93)03050-S

TABLE 1. Magnetic parameters obtained from investigations of magnetometric and ^{57}Fe Mössbauer effects (T_C^M is the Curie point from magnetometric measurements, T_C^{ME} is the Curie point from ME, p_s is the saturation moment per Fe atom)

Compound	T_C^M (K)	T_C^{ME} (K)	M_s (μ_B/f.u.)	p_s (μ_B/Fe atom)	$\tilde{H}_{hf}$ (T)	p_{Fe} (μ_B)	Ref.
$Ce_{1.33}Fe_{8.8}Mo_{3.2}$	250	245	5.86[b]	0.67[b]	15.64[a]	1.07[a]	Present
	250			0.09[c]			7
$CeFe_{10}Mo_2$	260						2
$Ce_{1.33}Fe_{10}Re_2$	350	345	16.92[b]	1.69[b]	18.85[a]	1.3[a]	Present
$CeFe_{10}Re_2$	353		14.8[a]	1.48[b]			3
$Pr_{1.64}Fe_{7.2}Re_{4.8}$	50	50	3.98[b]	0.55[b]	7.0[a]	0.48[a]	Present
$PrFe_{10.52}Re_{1.48}$	397			1.6			3
$Sm_{1.2}Fe_{7.5}Re_{4.5}$	476	480	22.83[b]	3.04[b]	6.8[a]	0.46[a]	Present
$SmFe_{10}Re_2$	475			1.7[b]			3

[a] At 13 K. [b] At 4.2 K. [c] At 78 K; the coefficient 14.5 T/μ_B is used for the calculation of p_{Fe}.

position. The occupancy of this site by the atoms different from Fe strongly depresses the magnetism of the ternaries as shown by magnetometric and ^{57}Fe Mössbauer effect investigations of $UFe_{10}Si_{1.75}Mo_{0.25}$ [10].

At present, we report on the magnetic properties and ^{57}Fe Mössbauer effect of $Ce_{1.33}Fe_{8.8}Mo_{3.2}$, $Ce_{1.33}Fe_{10}Re_2$, $Pr_{1.64}Fe_{7.23}Re_{4.7}$ and $Sm_{1.8}Fe_{7.5}Re_{4.5}$, investigated to elucidate the influence of stoichiometry and occupation of the individual crystallographic positions on the magnetic properties of these alloys.

2. Experimental details

The alloys were prepared by melting the elements in stoichiometric quantities in an arc-furnace under a protective argon atmosphere. This procedure was followed by prolonged annealinq at about 1070 K during 800 h [7].

The magnetometric measurements were carried out using the Faraday method. The ^{57}Fe Mössbauer measurements (ME) were performed using a conventional, constant acceleration spectrometer with a ^{57}Co in a Cr matrix source from 13 to 565 K. The velocity scale was calibrated using an α-Fe absorber at room temperature.

3. Results and discussion

3.1. Magnetic measurements

Magnetic properties of the investigated compounds are given in Table 1 and Figs. 1 and 2. Figure 1 shows the magnetization of all compounds versus magnetic field at 4.2 K. One can see that $Ce_{1.33}Fe_{10}Re_2$ and $Sm_{1.8}Fe_{7.5}Re_{4.5}$ exhibit relatively high magnetization, but in spite of that they do not reach saturation like the other two compounds shown in Fig. 1 with apparently lower magnetization, even at a magnetic field of 5 T.

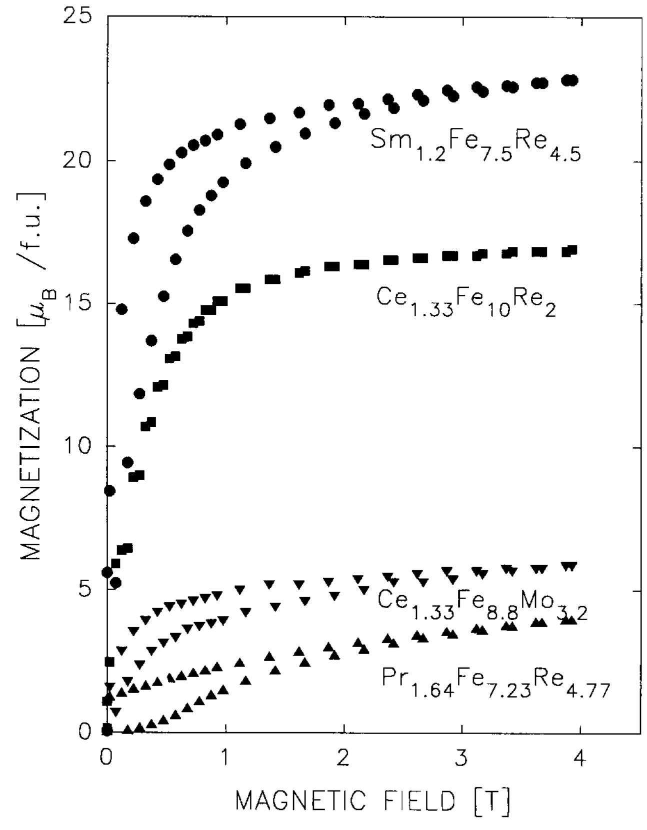

Fig. 1. Magnetization versus magnetic field at 4.2 K.

For this last compound (Sm), the high saturation moment (see Table 1) results apparently from the admixture of α-Fe which can also be detected in the ME spectrum. For all compounds except $Ce_{1.33}Fe_{10}Re_2$, considerable hysteresis is observed. An inspection of Table 1 shows that except for $Ce_{1.33}Fe_{8.8}Mo_{3.2}$, the magnetic moments determined in magnetic measurements are higher than those from ME investigations. For compounds other than Sm, the difference might result from the presence of a magnetic phase at LT without Fe contribution. The higher ME moment could

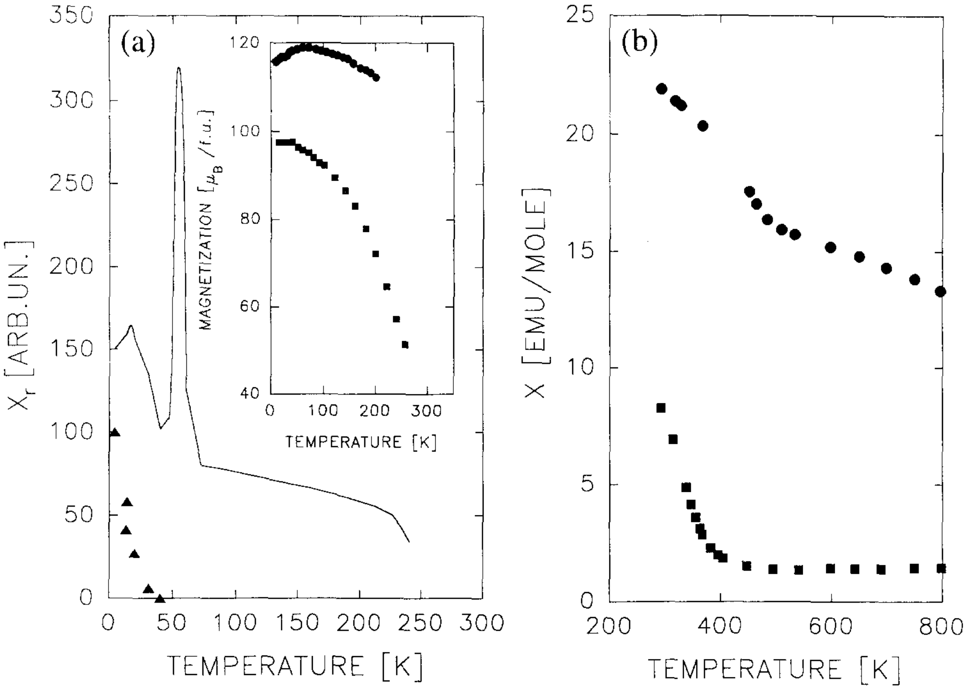

Fig. 2. (a) Remanence susceptibility versus temperature. Solid line, $Ce_{1.33}Fe_{8.8}Mo_{3.2}$; triangles, Pr compound. Inset shows magnetization versus temperature. Circles, Sm compound; squares, $Ce_{1.33}Fe_{10}Re_2$. (b) Magnetic susceptibility versus temperature above room temperature; symbols as in (a).

be due to the contribution of an additional phase ($Ce_{1-x}Fe_x$, see below) which is not yet saturated at 5 T. Figure 2(a) shows the low temperature dependence of the magnetization (inset) and remanent susceptibility whereas in Fig. 2(b), the high temperature dependence of the molar susceptibility for Sm and Ce–Mo compounds is presented. Appropriate Curie temperatures were estimated from the given plots and are collected in Table 1, together with Mössbauer data (ME). As one can see, the magnetic transitions are in line with the results obtained from ME. However, we have to note that results for the Sm compound are particularly complex. Also a sharp maximum in the $\chi_r(T)$ plot for the Ce–Mo alloy at about 50 K is peculiar and it might be related to the spin re-orientation transition. In the section devoted to the ME investigation, another explanation is considered. This anomaly was not observed in a previous report [7] because those measurements were performed above 77 K only.

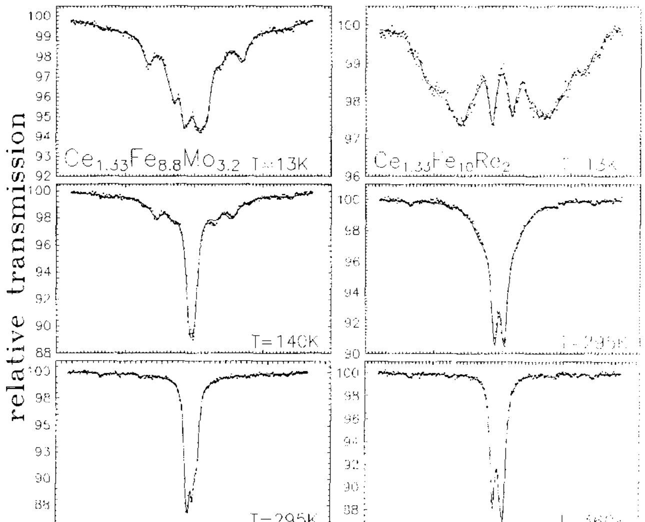

Fig. 3. ^{57}Fe Mössbauer spectra of $Ce_{1.33}Fe_{8.8}Mo_{3.2}$ (left) and $Ce_{1.33}Fe_{10}Re_2$ (right) at different temperatures.

3.2. ^{57}Fe Mössbauer effect studies

3.2.1. Ce-based alloys

The Mössbauer spectra for $Ce_{1.33}Fe_{8.8}Mo_{3.2}$ and $Ce_{1.33}Fe_{10}Re_2$ are displayed in Fig. 3. In the paramagnetic region, the Mössbauer spectra are composed of two doublets. These doublets are broadened markedly and transformed into spectra with a poorly resolved Zeeman structure at low temperatures. Such magnetic hyperfine structure in compounds with $ThMn_{12}$-type of structure usually results from the existence of three non-equivalent crystallographic sites of iron. However, an acceptable fit of the experimental spectra cannot be obtained considering only the distributions of the Fe atoms in these crystallographic sites. Therefore, the method of evaluation of hyperfine field distribution described in ref. 11 has been used. This procedure showed that in the distribution function $p(H_{hf})$, an additional peak appears in a low field range (~6 T) compared to the pattern expected for the ThMn$_{12}$-type structure around 16 T. In Fig. 4(a), the temperature dependence of the average hyperfine magnetic fields ($\bar{H}_{hf}$) for both Ce compounds is presented. One can see that this plot is in fair agreement with the $M(T)$ dependence presented in Fig. 2.

It follows from these results that in the investigated substoichiometric compounds, an additional phase (or phases) is present with Curie point $T_c = 50$–100 K. In the Mo compound, the concentration of an impurity phase reaches the value of about 43%, whereas for the Re compound, its concentration is 4–5 times smaller. Excess Ce promotes the formation of a compound (alloy) of the $Ce_{1-x}Fe_x$ type. On the other hand, the binary and ternary Ce–Fe compounds exhibit higher Curie points which exclude them from further discussion. At the same time, the XRD patterns do not reveal clearly other structures than the ThMn$_{12}$-type, although a strong background was indeed observed which could correspond to amorphous material. Therefore, we suggest that the impurity phase registered in our Mössbauer spectra is probably the amorphous phase of the $Ce_{1-x}Fe_x$ composition for which the Curie points are between 20 and 100 K for the concentration range $0.65 < x < 0.9$ [12]. One of the reasons for complicated phase relations in the Ce materials may be the possibility of the existence of the Ce ion in a form other than trivalent.

The diminution of T_c and the value of the average hyperfine field $\bar{H}_{hf}$ for $Ce_{1.33}Fe_{8.8}Mo_{3.2}$ in comparison to the $Ce_{1.33}Fe_{10}Re_2$ compound is probably due to a high Mo concentration. As has been shown [10], Mo atoms prefer 8(i)-site occupation in the ThMn$_{12}$-type structure, which diminishes the number of ferromagnetically coupled Fe–Fe pairs in these positions and in turn, decreases T_c and H_{hf}.

3.2.2. Pr- and Sm-based alloys

In Fig. 5, the Mössbauer spectra for $Pr_{1.64}Fe_{7.23}Re_{4.7}$ and $Sm_{1.8}Fe_{7.5}Re_{4.5}$ are shown for various temperatures.

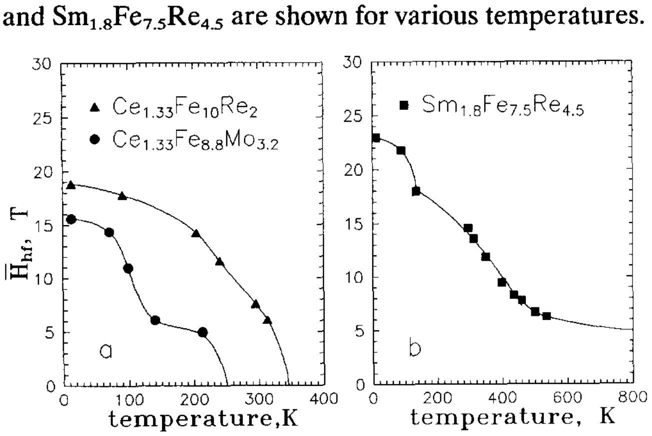

Fig. 4. Average hyperfine magnetic field, $\bar{H}_{hf}$ on the ^{57}Fe nucleus versus temperature: (a) $Ce_{1.33}Fe_{10}Re_2$ (triangles) and $Ce_{1.33}Fe_{8.8}Mo_{3.2}$ (circles) and (b) $Sm_{1.8}Fe_{7.5}Re_{4.5}$ (squares).

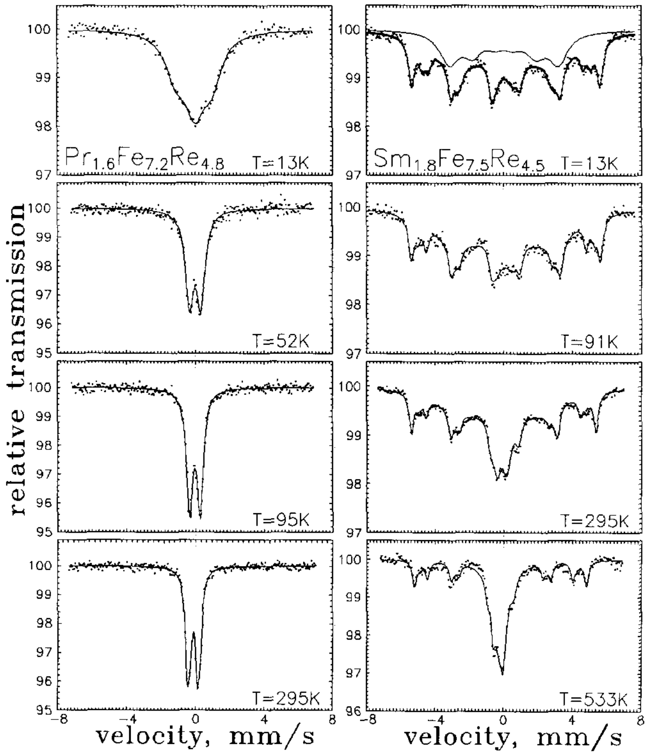

Fig. 5. ^{57}Fe Mössbauer spectra of $Pr_{1.6}Fe_{7.2}Re_{4.8}$ (left) and $Sm_{1.8}Fe_{7.5}Re_{4.5}$ (right) at different temperatures.

In spite of the very similar compositions, the Mössbauer spectra differ strongly. The Pr compound is paramagnetic above 50 K and at 13 K, the average hyperfine field $\bar{H}_{hf}$ is equal to 7 T, which corresponds to $p_{Fe} = 0.48\ \mu_B$. These very low T_c and H_{hf} values can be explained on the basis of the same arguments as we used for the Ce compound with Mo.

The isomer shifts (IS) and quadrupole splitting (QS) of the Mössbauer lines for the Pr compound are fairly close to those found for both Ce compounds.

The Mössbauer spectrum for $Sm_{1.8}Fe_{7.5}Re_{4.5}$ is very complex. Through the examined temperature range up to 560 K, several Zeeman sextets are observed together with a paramagnetic doublet, which transforms to sextets at about 90–100 K. In Fig. 4(b) the temperature dependence of the average hyperfine field $\bar{H}_{hf}$ is displayed. This plot exhibits two anomalies at about 100 and at 480 K. Both anomalies are confirmed by magnetometric measurements. The HT anomaly is related to the setup of magnetic ordering in the ThMn$_{12}$ phase and was also detected in an examination of the stoichiometric compound. The LT anomaly corresponds to another magnetic phase of unknown structure and composition. The persistence of the hyperfine field over the whole temperature range indicates an admixture of the third magnetic phase with the Curie point above 564 K. The concentration of both foreign phases is rather low and therefore we cannot detect them in the XRD pattern.

4. Conclusions

As one can see from Table 1, the investigated compounds are ferromagnetic. The present results are also in fair agreement with those obtained for stoichiometric materials except for the Pr compound. The ^{57}Fe ME examinations show that in spite of nearly single-phase XRD patterns, there exist other magnetic phases.

On the basis of our measurements, we are not able to tell more about those impurity phases. The excess of stabilizing elements (Mo or Re) generally suppresses magnetism, confirming the previous conclusion that in this type of structure, the 8(i)-position occupation by the Fe atoms is extremely important for producing materials with high T_c and saturation magnetization.

In the present research, the stoichiometry of samples turns out to be too far from the stability range of the ThMn$_{12}$ structure, resulting in additional phases. Nevertheless, on the basis of our experiments, we cannot produce a consistent picture of these materials. From the point of view of applications, the Sm compound seems to be most promising, but further experiments covering a broad composition range are still necessary to resolve the situation.

References

1 B.D. de Mooij and K.H.J. Buschow, *Philips J. Res., 42* (1987) 246.

2 A.S. Ermolenko, E.V. Shcherbakova, G.V. Ivanova and E.V. Belozerov, *Fiv. Metal. Metall.,* (1990) 59.

3 M. Gueremian, K. Yvon and F. Hullinger, *J. Less-Common Met., 175* (1991) 321.

4 M. Jurczyk, *J. Magn. Magn. Mater., 89* (1990) L5.

5 E.I. Gladyshevsky, O.I. Bodak and V.K. Pecharsky, in K.A. Gschneidner Jr. and L. Eyring (eds.), *Handbook on the Physics and Chemistry of Rare Earths,* Vol. 13, Elsevier, Amsterdam, 1990, p. 1.

6 A. Müller, *J. Appl. Phys., 64* (1988) 249.

7 D.A. Berezyuk, R.V. Skolozdra and O.I. Bodak, *Vest. Lvovsk. Univ., Ser. Khim., 27* (1986) 52.

8 D.B. de Mooij and K.H.J. Buschow, *J. Less-Common Met., 144* (1988) 65.

9 D.A. Berezyuk, *XII Ukrainskaya Respublikanskaya Konferenciya po Nieorganiczeskoj Khim.,* Simferopol, Tezisy Dokl., p. 156.

10 W. Suski, F.G. Vagizov, H. Drulis, J. Janczak and K. Wochowski, *J. Magn. Magn. Mater., 117* (1992) 203.

11 G. Le Caer and J.M. Dubois, *J. Phys. E: Sci. Instrum., 12* (1979) 9083; B. Window and A. Rübartsch, *J. Phys. E: Sci. Instrum., 7* (1974) 526.

12 K. Fukamichi, H. Komatsu, T. Goto and H. Wakabayashi, *Physica B, 149* (1988) 276.