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Dc and ac magnetic susceptibility measurements in $\text{LuFe}_{12-x}\text{Mo}_x$ ($2.3 < x < 0.5$) alloys

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Abstract

Magnetic phase transitions related to spin-glass-like behavior were detected by ac-susceptibility measurements in $\text{LuFe}_{12-x}\text{Mo}_x$ alloys with $x > 1.8$. Dc-magnetic measurements have been used to determine the saturation magnetization M_s and the ferromagnetic-like transition temperatures T_c as a function of Mo concentration. A linear variation of the lattice parameters a , c and unit cell volume V , with positive slope, has been found for increasing Mo concentration x from 0.5 to 2.3.

1. Introduction

Since 1992, when a variety of magnetic phase transitions (MPT) has been reported [1] in the permanent magnet intermetallic alloys $\text{RFe}_{10}\text{Mo}_2$ (R = rare-earth or yttrium), an extensive investigation of the members with $\text{R} = \text{Y}$ or Lu has been started because of their intricate spin-glass (SG)-like behavior. For the first time the SG-like properties of these alloys have been studied by Christides et al. [2,3] with ^{57}Fe Mössbauer spectroscopy and magnetic measurements. In their work the magnetic frustration, which is required for interpretation of the observed phenomena, has been attributed to a significant distribution of Fe–Fe and Fe–Mo interatomic distances around the critical value of 2.5 Å, by considering that the magnetic interactions follow the Slater–Néel curve for transition metal alloys [4]. The

preferential occupancy for half of the 8i Fe sites from Mo atoms, over the three crystallographically inequivalent sites with symmetry 8i, 8j and 8f, creates significant local disorder, that affect the sign of exchange integrals between 3d orbitals as well.

Neutron diffraction experiments for $\text{R} = \text{Y}$ [5] and Lu [6] indicate that there is ferromagnetic ordering of the Fe moments within the unit cell, whereas the induced magnetic moments in Y and Mo sites (with magnitude less than $0.7 \mu_B$) have been estimated to arrange in the opposite direction along the c -axis of the tetragonal structure [5]. This ferromagnetic arrangement of the Fe moments together with the absence of SG behavior in $\text{GdFe}_{10}\text{Mo}_2$, which has similar lattice parameters with $\text{YFe}_{10}\text{Mo}_2$ [7], has been used by Wang et al. [8] to debate the above described model in favour of the narrow Bloch-wall pinning mechanism [9], from a study of magnetohistory effects in $\text{YFe}_{12-x}\text{Mo}_x$ ($x = 1.5\text{--}3.0$). Recently Lorenz et al. [10] have reported a novel approach for

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calculation of the spin structure in $\text{YFe}_{12-x}\text{Mo}_x$ alloys, based on a method with local spin-quantization axes, which describes successfully the observed magnitude and distribution of magnetic moments. Their self-consistent band structure calculation leads to formation of non-collinear Fe spin configurations which arise from a competition of ferromagnetic and antiferromagnetic exchange interactions due to a variation of the Fe–Fe nearest neighbor distances between about 2.38 and 2.65 Å. This is in absolute agreement with the proposed model (two years ago) by Christides et al. [2] which unfortunately is not mentioned by Lorenz et al. However, for the first time a calculated spin structure describes so well the observed SG properties in $\text{YFe}_{12-x}\text{Mo}_x$ alloys suggesting that a cluster glass model rather than a narrow Bloch-wall mechanism can explain the magnetic behavior in this system. In addition Lu compounds were found [2,6] to present all the properties of a SG system for $x > 1.8$ in contrast to $\text{YFe}_{12-x}\text{Mo}_x$ compounds, where only some of the SG-properties have been observed at low temperatures.

In this work we present X-ray, dc and ac magnetic susceptibility measurements for the $\text{LuFe}_{12-x}\text{Mo}_x$ ($2.3 < x < 0.5$) alloys. The ac-susceptibility signals are evident for MPTs below 200 K which are related to some unidentified yet intrinsic magnetic structures. The enhanced SG-like properties for $R = \text{Lu}$ can be attributed to the smaller ionic radius relative to Y [2,3,11] which is responsible for the observed here reduction of the unit cell volume relative to $R = \text{Y}$ alloys. Our experimental results are discussed in terms of the calculated non-collinear Fe spin configuration proposed by Lorenz et al. [10] in $\text{YFe}_{12-x}\text{Mo}_x$ alloys.

2. Experimental details

$\text{LuFe}_{12-x}\text{Mo}_x$ samples with nominal composition $x = 0.5$ to 2.3 were prepared from 99.99% pure starting materials. After arc-melting, the samples were vacuum annealed at 1100°C for two days and quenched in water. From the X-ray powder diffraction (XRD) measurements (with a Siemens D500 diffractometer) the samples were found to contain less than 9% α -Fe in addition to the tetragonal

ThMn_{12} -type structure. The α -Fe content has been estimated from Rietveld refinement.

Dc magnetic measurements as a function of temperature were performed in the temperature range 150 to 310 K with a Quantum Design MPMSR2 SQUID magnetometer in a field of 5 mT for the samples with $x > 1.8$. Thermomagnetic measurements with a Perkin-Elmer TGA were used for the determination of Curie temperatures T_c in the temperature range 20 to 400°C for the samples with $x \leq 2$. The saturation magnetization M_s has been determined from isothermal SQUID measurements in a maximum field of 5 T. For the ac magnetic susceptibility measurements a field with an amplitude of 40 A/m (1 Oe) and frequency $f = 130$ Hz has been used.

The nominal stoichiometry of the samples has been checked with Energy Dispersive Analysis of

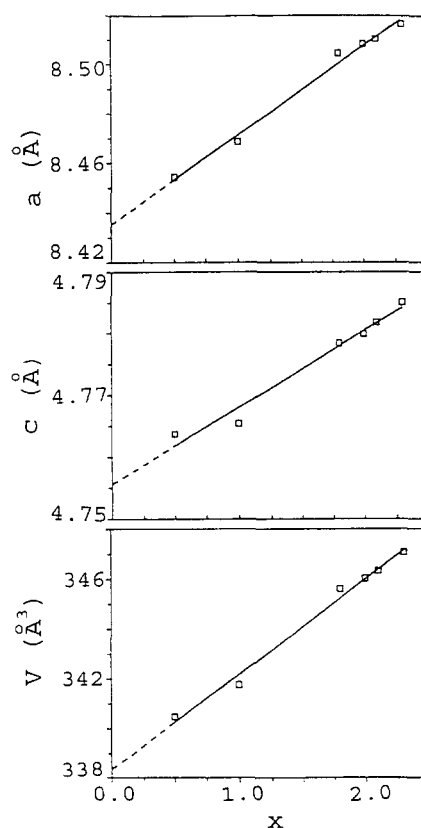


Fig. 1. Variation of lattice parameters a , c and unit cell volume V as a function of Mo concentration x at RT.

X-rays (EDAX) in a Philips SEM 515 microscope and has been found approximately correct within the experimental resolution.

3. Experimental results

3.1. XRD measurements

In Fig. 1 the estimated lattice parameters a , c and the unit cell volume V are plotted as a function of Mo concentration x . It is seen that for higher Mo concentration the expansion (0.7%) along the a -axis is larger than that along the c -axis (0.4%). A linear interpolation of the observed values may be used to estimate the lattice parameters for the hypothetical alloy LuFe_{12} : $a = 8.43(1) \text{ \AA}$, $c = 4.75(1) \text{ \AA}$ and $V = 338.3(1) \text{ \AA}^3$. A comparison of the unit cell volumes with those observed in $\text{YFe}_{12-x}\text{Mo}_x$ [11] shows that $V(\text{Y}) > V(\text{Lu})$, as expected from the larger atomic volume of Y.

3.2. Magnetic measurements

The estimated M_s values as a function of x at 5 K are plotted in Fig. 2. The presented M_s were extracted after subtraction of the magnetic contribution of α -Fe from the experimental values at 4.5 T. Dc-thermomagnetic measurements are plotted in Figs. 3 and 4, only in the temperature range where an ordering temperature T_c can be defined. Since it is

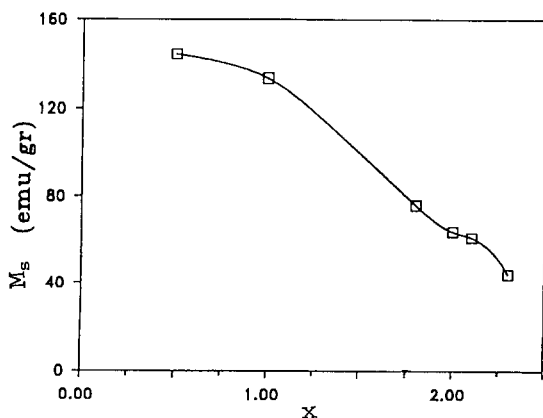


Fig. 2. Variation of M_s with Mo concentration x at 5 K. The solid line is a guide to the eye.

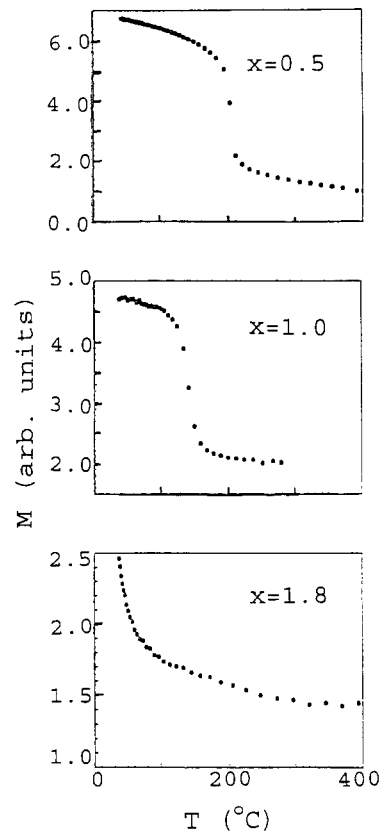


Fig. 3. TGA thermomagnetic measurements for determination of T_c .

known [2] that there are strong magnetohistory effects at lower temperatures, which are sensitive to the specific microstructure of the specimen in addition to the intrinsic SG-like state, we avoid to discuss them in the present paper. All the measurements were recorded by decreasing temperature.

The real part of the ac-susceptibility as a function of temperature, for Mo concentrations which present SG-properties, is given in Fig. 5. It is extremely interesting that for all the samples with $x > 1.8$ there are MPTs well below the T_c extracted from dc measurements. Specifically for $x = 1.8$ there are two peaks centered at 245 and 180 K below the $T_c = 333$ K, for $x = 2$ two peaks (or one peak with a shoulder) at 180 and 145 K below the $T_c = 270$ K, for $x = 2.1$ one broad peak at 160 K below the $T_c = 265$ K, and for $x = 2.3$ a very smooth peak which start to grow in intensity very close to the observed $T_c = 255$ K. It

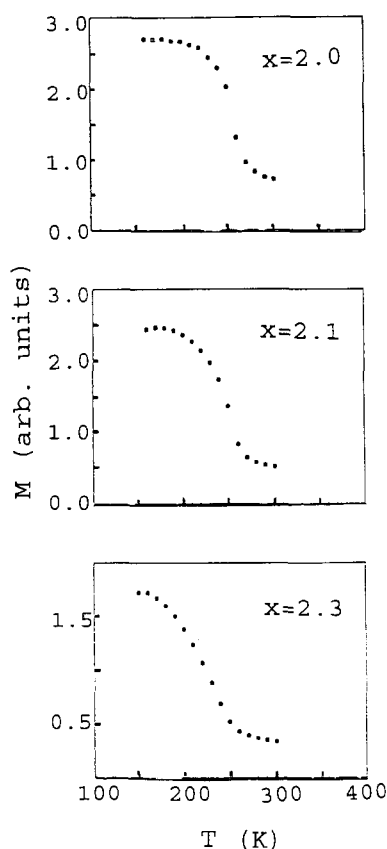


Fig. 4. SQUID thermomagnetic measurements in a field of 5 mT for detection of T_c .

is worth noting that by increasing x from 1.8 the two well separated MPTs progressively merge to a broader peak at lower temperatures. In the dc-ther-

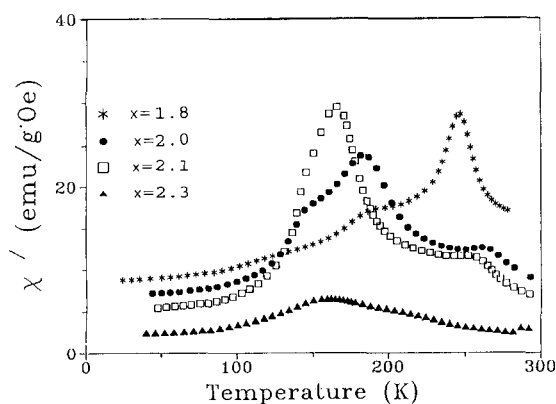


Fig. 5. The real part of the ac-magnetic susceptibility versus T in $\text{LuFe}_{12-x}\text{Mo}_x$ alloys with $x \geq 1.8$.

momagnetic measurements except the magnetohistory effects there is not detectable any other magnetic transition below the observed T_c .

4. Discussion and conclusions

It is clearly demonstrated that in addition to a ferromagnetic (FM)-like transition temperature T_c there are stronger MPTs at lower temperatures for all the $\text{LuFe}_{12-x}\text{Mo}_x$ alloys with $x > 1.8$. This effect does not occur in the SG-like $\text{YFe}_{12-x}\text{Mo}_x$ compounds with similar Mo concentrations where only magnetohistory effects appear at low temperatures. It has been shown earlier [2] that the Lu alloys exhibit a wider variety of magnetic properties than the Y compounds which are characteristic of an SG magnetic configuration below T_c . Particularly, only in $R = \text{Lu}$ alloys appear: (i) a shift of the hysteresis loop after zero field cooling (ZFC) and FC at 5 K; (ii) a difference between M_s and $\langle H_{\text{hf}} \rangle$, the average hyperfine field in the Fe nucleus, magnetic moments at 5 K; and (iii) a slope change of $\langle H_{\text{hf}} \rangle$ versus T curve by lowering T . In addition, neutron diffraction measurements [6] on $\text{LuFe}_{10}\text{Mo}_2$ powder shows an FM-like arrangement of the Fe magnetic moments from 5 to 325 K with a very broad transition temperature range between 200 and 270 K. Small-angle neutron-scattering [SANS] measurements on the same sample [6] reveal a significant deviation of the scattered intensity from the Lorentzian cross section form [12] below 250 K which is evidence for the existence of finite spin-correlation lengths below T_c . Experimentally, the low-temperature spin structure and its variation as a function of T can be derived by neutron scattering measurements on single crystals. On the other hand, after the considerable theoretical improvement of Lorenz et al. [10] to calculate the spin structure in $\text{YFe}_{12-x}\text{Mo}_x$ compounds, it is possible to extend these calculations to the $\text{LuFe}_{12-x}\text{Mo}_x$ alloys. It is very interesting to see from these calculations the effect of unit cell volume reduction between the $R = \text{Y}$ and Lu alloys as a function of the local disorder introduced by Mo atoms. The present work together with that published in Refs. [2,3,6], we believe, provides the necessary information from experimental results to support such calculations.

In summary, it is shown that a variety of MPTs occur well below the ill-defined FM-like T_c in $\text{LuFe}_{12-x}\text{Mo}_x$ alloys for $x > 1.8$. The observed intensity of the ac susceptibility signals suggests that the strength of those MPTs might be larger from that in T_c . The estimated M_s values and the linear variation of lattice parameters as a function of Mo concentration can be used for direct comparison with magnetic moments extracted from band structure calculations based on a method with local spin-quantization axes [10].

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