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Metamagnetic behaviour of $La_{1-x}Gd_xFe_{12}B_6$ compounds

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Abstract

The magnetic properties of compounds of the type $La_{1-x}Gd_xFe_{12}B_6$ have been studied in high magnetic fields at 4.2 K. $LaFe_{12}B_6$ is a compound with Fe moments close to magnetic instability and values not larger than about 0.5 μ_B. Substitution of Gd for part of the La and application of high magnetic fields enhance the Fe moments to values in excess of 2 μ_B. The high-moment state in $LaFe_{12}B_6$ is reached via a metamagnetic transition. This first-order transition is associated with an extremely large hysteresis of nearly 7 T at 4.2 K.

Keywords: Rare-earth intermetallics; Itinerant electron magnetism; Metamagnetism; FE moment enhancement; High-field magnetism

1. Introduction

In a previous investigation, we have studied the magnetic properties of rare-earth compounds of the type $LaFe_{12-x}Co_xB_6$ [1,2]. These compounds crystallise in the hexagonal $SrNi_{12}B_6$ structure [3], characterised by a single Sr site and two different Ni sites. Compounds of the type $RCo_{12}B_6$ form for all common rare-earth elements R, whereas for Fe only the compound $LaFe_{12}B_6$ can be obtained by normal casting and annealing. From Fe-Mössbauer spectroscopy [1] and Co-NMR spectroscopy [2] it was derived that the moments at the two 3d sites in this crystal structure are strongly different. The compound $LaFe_{12}B_6$ orders antiferromagnetically at about 40 K but the Fe moments are fairly low and have been proposed to be close to magnetic instability [1]. This is the case for one of the two Fe sites in particular and has as a consequence that Co substitution initially leads to disappearance of magnetism because Co substitutes preferentially into the low-moment site [1].

In the present investigation, we have studied the magnetic properties of the compound $LaFe_{12}B_6$ in more detail. High-field measurements in particular are most suitable for studying magnetic materials close to magnetic instability. It will be shown that application of high magnetic fields leads to drastic changes in the magnetic behaviour of $LaFe_{12}B_6$.

Instead of external fields, one can also use internal fields in the form of molecular fields at the Fe sites to shift the compound away from the magnetic instability. For this reason we have included in the present study also compounds of the type $La_{1-x}Gd_xFe_{12}B_6$.

2. Experimental

The $La_{1-x}Gd_xFe_{12}B_6$ compounds were prepared by arc melting starting materials of at least 99.9% purity. A slight excess of La was used in order to suppress the presence of α-Fe as an impurity phase. The ingots were wrapped into Ta foil after arc melting, sealed into evacuated quartz tubes and annealed for four weeks at temperatures between 1000 and 1050°C. After this treatment the samples were investigated by X-ray diffraction and found to be approximately single phase for $x \leq 0.5$, the diffraction lines showing the hexagonal $SrNi_{12}B_6$ type as the basis structure. No single phase materials were obtained for concentrations higher than $x=0.5$, which is not surprising in view of the fact that the compound $GdFe_{12}B_6$ does not exist.

The magnetic isotherms of the $La_{1-x}Gd_xFe_{12}B_6$ compounds were studied at 4.2 K in the High-field Installation at the University of Amsterdam [4]. The measurements were performed on powder particles that were free to orient themselves in the applied magnetic field. For the $LaFe_{12}B_6$ compound we studied the magnetic isotherm

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also in comparatively low magnetic fields in a SQUID magnetometer.

3. Experimental results

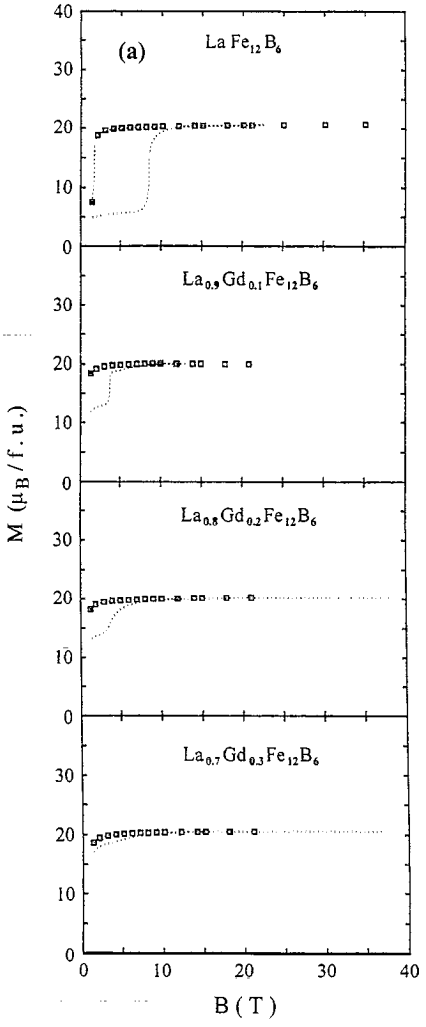
Results of high-field magnetic measurements on $LaFe_{12}B_6$ are shown in Fig. 1a. As is displayed in more detail in Fig. 1b, the magnetisation is virtually zero in zero applied field. With increasing field strength the magnetisation strongly increases initially and then reaches an almost field-independent level of about 6 μ_B per formula unit. At about 8.6 T there is a second jump-like increase of the magnetisation to a level of about 20 μ_B/fu. It can also be seen in Fig. 1a that this magnetisation jump is accompanied by a strong hysteresis, which is indicative of a first-order magnetic phase transition. The magnetic moments associated with the lower branch (M_l) and higher branch (M_h) of the hysteresis loop have been obtained by extrapolating the corresponding linear parts of the magnetic isotherm to zero field strength. These values are listed in Table 1.

The effect of Gd substitution on the magnetic behaviour of $LaFe_{12}B_6$ can be seen in the lower parts of Fig. 1. Increasing values of x in $La_{1-x}Gd_xFe_{12}B_6$ lead to an increase of the low-field jump of the magnetisation at the cost of the high-field jump. This has as a consequence that the values of M_l strongly increase with x initially. The values of M_h remain approximately the same. It can also be seen that the critical fields corresponding to the second magnetisation jump shift to lower values with increasing x. There is hardly any change in the magnetic behaviour for Gd concentrations higher than x=0.3. This can also be derived from Table 1 where values of M_l, and M_h have been listed for all concentrations studied.

4. Discussion

A shallow maximum observed in the temperature dependence of the magnetisation at about 40 K suggests that $LaFe_{12}B_6$ orders antiferromagnetically below this temperature. It was shown by Fe-Mössbauer spectroscopy [1] that the Fe moments associated with the two crystallographically unequivalent Fe sites in $LaFe_{12}B_6$ have fairly low values, corresponding to an average ordered Fe moment of about 0.35 μ_B/Fe or 4.2 μ_B/fu. A moment value of this magnitude is reached in the magnetic isotherm shown in Fig. 1 already in comparatively low fields. It can be assumed therefore that the lower level M_l of the magnetic isotherm of $LaFe_{12}B_6$ corresponds to a situation where the small Fe moments present in $LaFe_{12}B_6$ have become aligned parallel with the field direction. The small slope of M_l may be due to anisotropy effects or to a small field-induced increase of the Fe moments.

By far the most interesting feature of the magnetic



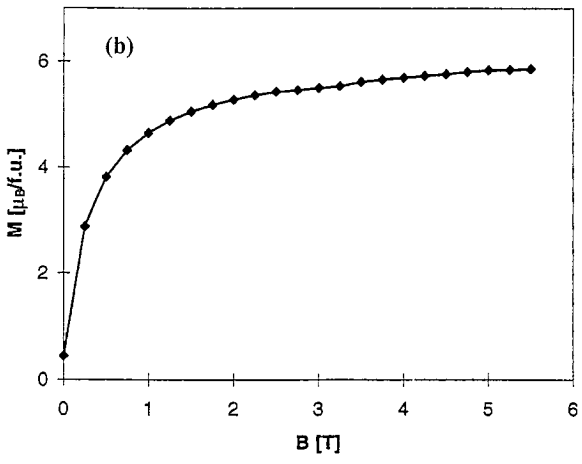


Fig. 1. (a) High-field magnetization of $La_{1-x}Gd_xFe_{12}B_6$ compounds measured at 4.2 K on free-powder samples. The dotted lines correspond to data taken in magnetic fields increasing and decreasing linearly with time. The open squares stand for the measurements done in fields that vary in a step-wise way. (b) Field dependence of the magnetisation of $LaFe_{12}B_6$ in comparatively low applied fields.

Table 1
Magnetic moments and average Fe moment at 4.2 K in $La_{1-x}Gd_xFe_{12}B_6$ before the metamagnetic transition (l) and after the metamagnetic transition (h)

$La_{1-x}Gd_xFe_{12}B_6$	M_l [μ_B/fu]	$\mu_{l,Fe}$ [μ_B/Fe]	M_h[μ_B/fu]	$\mu_{h,Fe}$ [μ_B/Fe]
x=0.0	4.6	0.38	20.0	1.67
x=0.1	11.6	1.00	20.0	1.72
x=0.2	12.6	1.16	20.0	1.78
x=0.3	17.2	1.61	20.0	1.84
x=0.4	16.6	1.62	20.5	1.94
x=0.5	16.2	1.64	21.0	2.04

isotherm is, however, the second magnetisation jump at about 8.6 T. As can be seen in Fig. 1, the magnetisation increases by about a factor of four at this jump. Similar types of metamagnetic transitions from a low-moment state in low or zero applied field to a high-moment state in comparatively high fields have been reported earlier only for relatively few compounds including YCo_2, $ThCo_5$, and $LaFe_{13-x}Al_x$ [5–7]. An explanation of such metamagnetic transitions in terms of the itinerant-electron model has been offered by Wohlfarth and Rhodes already many years ago [8]. Electronic-band-structure calculations dealing with such transitions have been discussed by Brooks and Johansson [9]. The total energy of a metamagnet as a function of the magnetic field can schematically be represented in the Wohlfarth-Rhodes model as in Fig. 2. Curve 1 applies to YCo_2, which compound has no moment in zero field.

Curve 2 applies to $ThCo_5$ and $LaFe_{13-x}Al_x$ where a 3d moment is already present in zero field. We propose that the latter situation applies also to $LaFe_{12}B_6$. The similarity in behaviour between $LaFe_{12}B_6$ and $ThCo_5$ offers the possibility to interpret the shallow maximum in the temperature dependence of the magnetisation [1] not as a Néel type transition but arising through thermal remagnetisation, a feature inherent in the collective electron magnetism [8,10].

All the metamagnetic transitions are accompanied by hysteresis effects. In Fe-based materials, the hysteresis effects can become extremely large because they are due to large magnetovolume effects [11]. Very likely this is also the reason for the very large hysteresis observed for $LaFe_{12}B_6$ (see Fig. 1).

In order to be able to assess the effect of Gd on the first-order metamagnetic transition we have plotted in Fig. 3 the concentration dependence of the Fe moments derived from the values of M_l and M_h listed in Table 1. Here, we have assumed that the Gd-sublattice magnetisation is oriented antiparallel to the Fe-sublattice magnetisation, as is invariably observed in compounds of rare earths and 3d transition metals. The corresponding curves are denoted in Fig. 3 by L and H, respectively. Curve L can be regarded as representing the Fe moment before the first-order transition, whereas curve H represents the Fe moment after the transition. The difference between the two curves can be taken as representing the moment increase associated with the transition. It is seen in Fig. 3 that the effect of the Gd-Fe exchange interaction is to increase the Fe moment before the transition. For low x values, this moment increase depends strongly on the Gd concentration but becomes somewhat saturated for concentrations higher than x=0.3. From the upper curve (H) in Fig. 3 it can be derived that the Gd-Fe exchange interaction also affects the Fe moment size after the transition, albeit the moment increase is less spectacular here.

Inspection of the isotherms displayed in Fig. 1 shows that sharp hysteresis loops are observed only for the

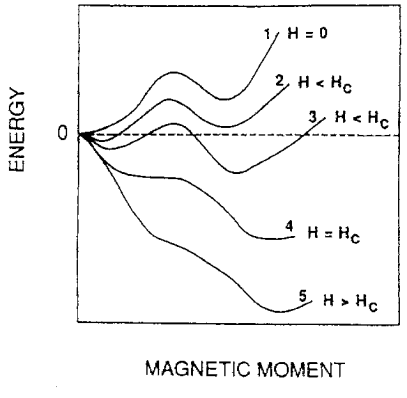


Fig. 2. Schematic representation of the moment behavior according to the Wohlfarth–Rhodes model, showing the total energy of metamagnets as a function of magnetic moment for several values of the applied field.

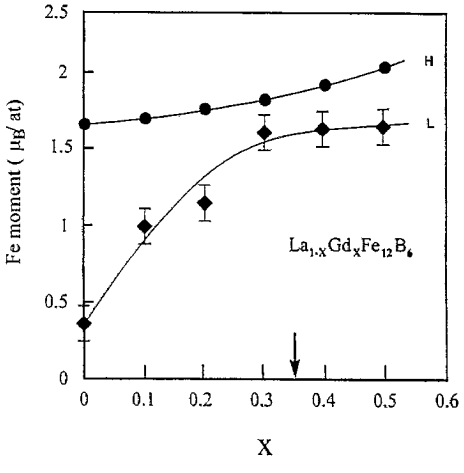


Fig. 3. Concentration dependence of the average Fe moment in $La_{1-x}Gd_xFe_{12}B_6$ before the metamagnetic transition (curve L) and after the metamagnetic transition (curve H).

compounds with $x \leq 0.2$. For larger Gd concentrations, the first-order transition becomes somewhat smeared out, presumably due to concentration fluctuations. Nevertheless, it can be inferred from the results shown in Fig. 1 that there is a strong correlation between the width of the hysteresis and the associated moment increase. This is in concord with the suggestion made above that the hysteresis accompanying the transition originates mainly from magnetovolume effects.

We mentioned already that stable compounds of the type $RFe_{12}B_6$ do not exist for rare earth elements heavier than lanthanum. However, it has been reported that it is possible to synthesise a metastable compound $NdFe_{12}B_6$ by first preparing an amorphous alloy of this composition followed by controlled crystallisation and quenching [12]. In contradistinction to $LaFe_{12}B_6$ this compound is ferromagnetic with a Curie temperature of 230 K and has a saturation moment at 4.2 K of 19.7 μ_B/fu (measured in a field of 1.1 T). Using the free-ion value for the Nd moment, one can calculate a value of 1.4 μ_B for the Fe moment in this compound, but this should be regarded as a lower limit.

It is interesting to compare these results with the data displayed in Fig. 3. Before doing this we have to bear in mind that the exchange field experienced by the Fe moments is proportional to $(g-1)J$ of the rare-earth component. The exchange field experienced by the Fe moments in $NdFe_{12}B_6$ then corresponds to a situation indicated by the arrow in Fig. 3. In this situation, the exchange field due to the rare-earth is expected to have broken the antiferromagnetic structure of the Fe sublattice and to have induced Fe moments of considerable magnitude compared to $LaFe_{12}B_6$. In fact, the magnetic properties predicted for $NdFe_{12}B_6$ on the basis of Fig. 3 are very close to those observed, taking into account that the results reported for $NdFe_{12}B_6$ were reached in fairly low fields and that the Nd moment used in the calculation of the Fe moments may be lower than the free-ion value due to crystal field effects.

Concluding, the results of high-field measurements have shown that $LaFe_{12}B_6$ is a compound with Fe moments close to magnetic instability. In zero field the Fe moments adopt small values not larger than about 0.5 μ_B. Substitution of Gd for part of the La and application of high magnetic fields can enhance the Fe moments to values in excess of 2 μ_B, values that are close to those found in pure iron. The high-moment state in $LaFe_{12}B_6$ is reached via a metamagnetic transition. This first-order transition is characterised by an extremely large hysteresis of nearly 7 T at 4.2 K.

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