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Magnetic properties of $Ce_2Fe_{17-x}Al_x(N_y)$ compounds

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Abstract

We have studied the magnetic properties of the rhombohedral $Ce_2Fe_{17-x}Al_x(N_y)$ compounds. Aluminium substitution in Ce_2Fe_{17} leads to ferromagnetism for medium Al concentration and to cluster glasses for high Al concentration. The Curie temperature shows a maximum. Rare earth nitrides of composition $Ce_2Fe_{17-x}Al_xN_y$ can be prepared by the reaction of $Ce_2Fe_{17-x}Al_x$ with nitrogen gas at 500 °C. The crystal structure and lattice constants have been determined for all compounds. The Curie temperature becomes enhanced upon nitrogenation. The nitrogen absorption capacity decreases with composition x and vanishes for $x > 5$. The enhancement of the Curie temperature of the nitrides decreases along with the reduced absorption capacity.

1. Introduction

Many investigations on the magnetic properties of intermetallic rare earth (R) and 3d transition metal (T) compounds have been performed, since these compounds are of particular interest for application as permanent magnet materials. Iron-based compounds with the Th_2Zn_{17} structure have high saturation magnetization (see *e.g.* ref. 1). The relatively low magnetocrystalline anisotropy in R_2Fe_{17} compounds and the exceptionally low Curie temperature make them less attractive for application as permanent magnet materials. Considerable improvements with respect to the ordering temperature can be achieved upon partial substitution of the iron atoms by *e.g.* Ga or Al [2] or by interstitial solid solutions of *e.g.* C or N [3–5]. Cerium, the least expensive of all the rare earth elements, when present in a trivalent state, can give rise to rare earth anisotropies much larger than those of the other rare earth elements. However, cerium has a preference to be tetravalent when combined with 3d metals, which hampers the application of most cerium-based intermetallic compounds as permanent magnet materials. This investigation forms part of a series of crystal chemical studies in which we study the valence of Ce in ferromagnetic materials as a function of various types of substitutions and solutions of interstitial atoms.

2. Experimental details

The samples were prepared by arc melting from starting materials of at least 99.9% purity in an argon atmosphere. After arc melting, the samples were wrapped in tantalum foil and vacuum annealed in quartz tubes at 900 °C for 2 weeks. The annealed samples were pulverized and heated in an atmosphere of purified N_2 gas for about 4 h at 500 °C. After this treatment the samples were investigated by X-ray diffraction. The magnetic measurements were performed on a superconducting quantum interference device (SQUID) magnetometer and a home-built Faraday balance.

3. Results and discussion

X-Ray diffraction of $Ce_2Fe_{17-x}Al_x$ showed the samples to be approximately single phase for aluminium concentrations $x \leqslant 11$, with the rhombohedral Th_2Zn_{17} structure. The samples contained a few per cent of elemental iron as an impurity phase in some cases. For higher aluminium concentrations the samples were not single phase, containing a mixture of a 1:12 compound and α-Fe. The lattice constants for various aluminium compositions as shown in Fig. 1 were derived from the diffraction diagrams. Substitution of the iron atoms by aluminium clearly dilates the lattice.

A magnetic isotherm at 5.0 K has been measured for Ce_2Fe_{17} (Fig. 2). It shows a metamagnetic transition from a magnetic structure with zero net magnetization to a ferromagnetic structure at a field strength of 0.5 T. According to neutron diffraction experiments per-

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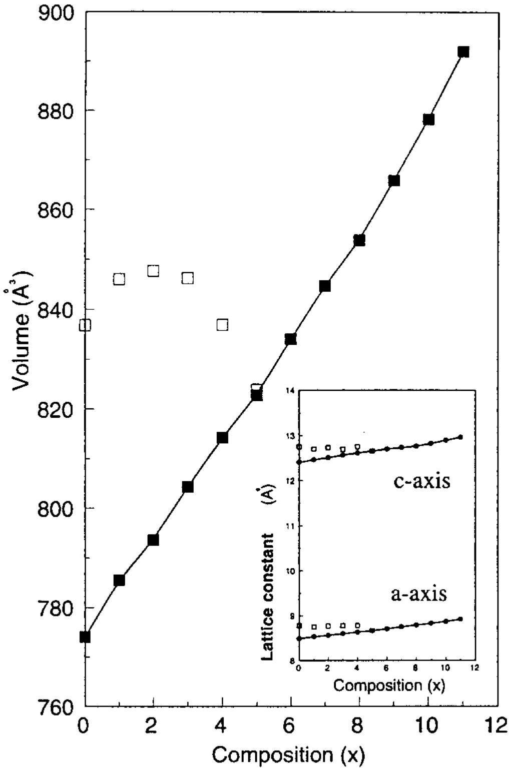

Fig. 1. Al concentration dependence of the unit cell volume for $Ce_2Fe_{17-x}Al_x$ (filled squares) and $Ce_2Fe_{17-x}Al_xN_y$ (open squares). The inset shows the *a* and *c* axes as a function of Al concentration. The line is a guide to the eye.

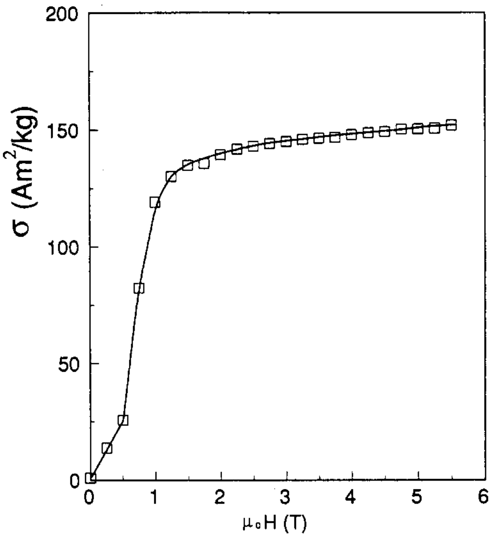

Fig. 2. Magnetic isotherm of Ce_2Fe_{17} at 5.0 K showing a metamagnetic transition at 0.5 T. The solid line is a guide to the eye.

formed by Givord and Lemaire [6], the Fe moments define a fan structure in zero field at 4.2 K. Our results show that magnetic fields larger than about 1 T are able to break this fan structure.

From isotherms of the $Ce_2Fe_{17-x}Al_x$ compounds at 5.0 K the saturation magnetization M_s was derived, which is shown in Fig. 3. Values for the saturation magnetization were obtained by extrapolating $M(1/B)$ curves to $1/B = 0$. From a comparison with the results of magnetization measurements on $Y_2Fe_{17-x}Al_x$ it can be concluded that Ce remains in the tetravalent state in $Ce_2Fe_{17-x}Al_x$. There is a stronger decrease in the Fe moments with x than one would expect from magnetic dilution (dotted line in Fig. 3). This indicates that Al not only dilutes the magnetic lattice but also leads to a decrease in the Fe moments themselves. The latter may be due to hybridization of the 3d band state of Fe with the valence electron states of Al, leading to lower 3d band splitting.

The temperature dependence of the magnetization $\sigma(T)$ for various Al compositions is shown in Fig. 4. Substitution of aluminium for iron leads to normal ferromagnetism for medium Al concentrations ($0 < x < 8$) (Fig. 4(b)). For higher Al concentrations the curves show sharp cusps suggesting the onset of antiferro-

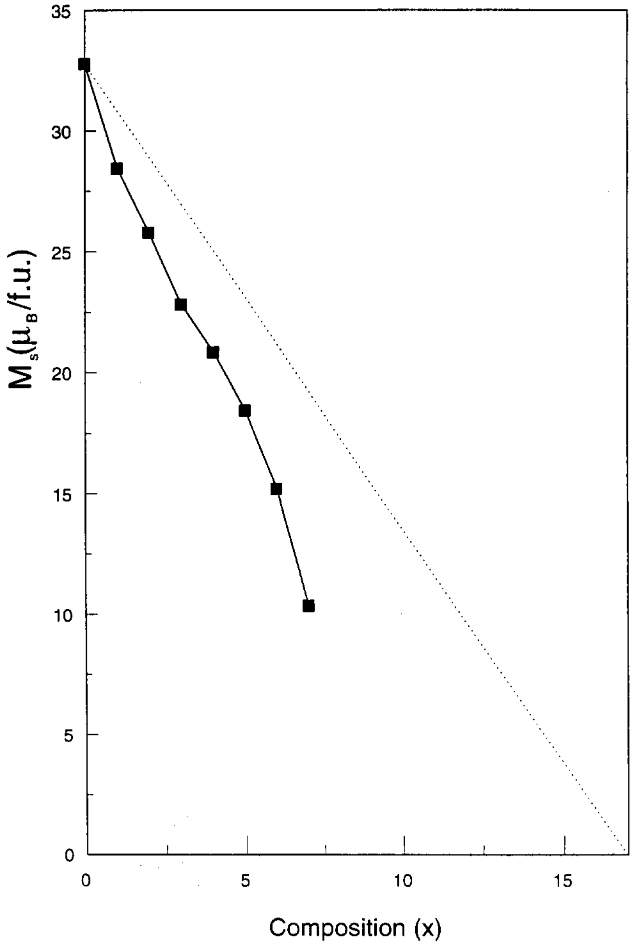

Fig. 3. Saturation magnetization M_S at 5.0 K as a function of Al concentration. The dotted line indicates the decrease in M_S due to magnetic dilution.

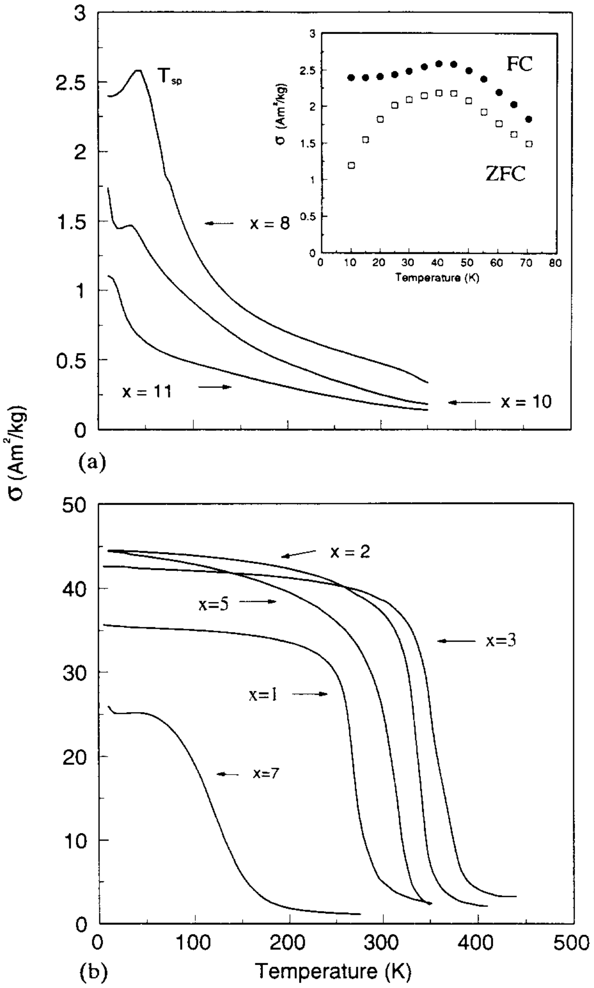

Fig. 4. Temperature dependence of the magnetization $\sigma(T)$ measured at 0.1 T for (a) high Al concentration and (b) medium Al concentration. The samples were cooled in a field of 2.0 T. The inset shows the ZFC and FC magnetization for $Ce_2Fe_9Al_8$ at 0.1 T.

magnetic ordering at about 48, 32 and 19 K. The divergence of the zero-field-cooled (ZFC) and field-cooled(FC) data as shown in the inset of Fig. 4(a), however, suggests that the low temperature phases for higher Al concentrations are not classical antiferromagnets. Such irreversibility indicates that we are dealing with spin glass systems. Magnetic Fe clusters can form as a result of Al concentration fluctuations in the compounds [7].

In Fig. 5 the Curie temperature T_C and the spin glass temperature T_{SP} are shown as a function of the Al concentration x. The Curie temperature shows a maximum at about $x=3$ in the ferromagnetic regime.

It is generally accepted that an increase in unit cell volume of the R_2Fe_{17} compounds results in an increase in the ordering temperature [1, 3]. Earlier investigations of these compounds had shown that the Curie temperatures decrease under applied pressure [8]. Combining results of dT_C/dP with results of compressibility measurements, the value of $\gamma = d(\ln T_C/d(\ln V)$ was calculated below the maximum in ordering temperature from the data in Fig. 5. The value is $\gamma = 15$, which makes it plausible to assume that the increase in Curie temperature is primarily a volume effect. The increase in Al concentration leads to a strong decrease in the Fe moments. Combined with the magnetic dilution effect, this leads to a decreasing influence on T_C, counteracting the volume effect.

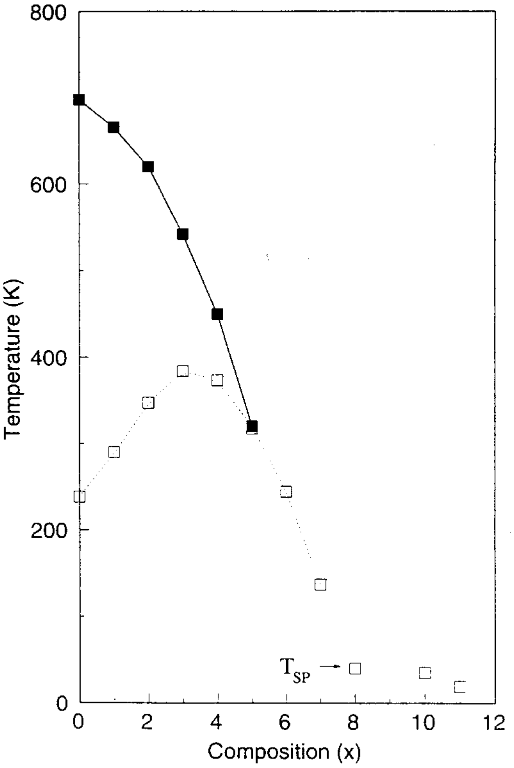

Fig. 5. Magnetic phase diagram of $Ce_2Fe_{17-x}Al_x$ (open squares) and $Ce_2Fe_{17-x}Al_xN_y$ (filled squares). T_C is the Curie temperature and T_{SP} the spin glass temperature. The dotted line and full line indicate the ferromagnetic regime.

Nitrogenation of $Ce_2Fe_{17-x}Al_x$ leads to an additional increase in lattice constants (Fig. 1). However, $\Delta V/V$ decreases owing to the decreasing absorption capacity of the lattice and vanishes for $x > 5$. From the relative increase $\Delta V/V$ in unit cell volume in conjunction with the data obtained by Isnard *et al.* [9], the value of the nitrogen concentration y was estimated to be 2.9, 2.6, 1.9 and 1.0 for aluminium concentrations $x=0$, 1, 2, 3 and 4 respectively. The investigations by Isnard *et al.* show that in the case of nitrogenation of R_2Fe_{17} compounds the interstitial holes of the type 9*e* will become occupied. Their results confirm Ce to be in the tetravalent state.

The uptake of nitrogen leads to an additional enhancement of the Curie temperature (Fig. 5). This enhancement (the difference between the full and dotted curves in Fig. 5 decreases with decreasing amount of nitrogen absorbed per $Ce_2Fe_{17-x}Al_x$ formula unit. In fact, there is a strong correlation between the additional Curie temperature enhancement and the volume increase in lattice constant upon nitrogenation as shown in Fig. 1. It is not clear why the nitrogen capacity is limited to the Al composition $x=5$. Further investigations are needed to clarify this point.

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