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Metamagnetic transitions in cubic $La(Fe_xAl_{1-x})_{13}$ intermetallic compounds

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Abstract. Cubic $NaZn_{13}$-type compounds of the form $La(Fe_xAl_{1-x})_{13}$ were stabilised with compositions between $LaFe_6Al_7$ and $LaFe_{12}Al_1$. For compositions above $LaFe_{11.2}Al_{1.8}$ ($x=0.861$) a low-temperature antiferromagnetic state is present in small external fields. However, upon increasing the field to a few tesla, an exceedingly sharp spin-flip transition with remarkably large hysteresis occurs to the fully saturated ferromagnetic state. The origins of this unusual metamagnetic transition are discussed in terms of the special crystal structure.

Metamagnetism and spin-flip transitions, while rather common in insulating systems (Carlin and van Duyneveldt 1977), especially layered compounds, are more unusual in metallic systems. The few examples which are known to exist are generally described in terms of itinerant electron magnetism (Wohlfarth 1980, 1983) or localised moments in layered structures (Vinokurova *et al* 1979a, b, Herpin and Meriel 1961). Here the transitions are mainly sluggish, requiring large fields. Occasionally hysteresis is present and in some cases a first-order phase transition has been claimed (Adachi *et al* 1979, Buschow and Schinkel 1976, Vinokurova *et al* 1979a, b). In this paper we report on the exceptionally sharp metamagnetic transitions which occur in the cubic, mixed-magnetic intermetallic compounds $La(Fe_xAl_{1-x})_{13}$. These transitions are truly first order with temperature-dependent hysteresis and the saturated moment attains the full Fe value.

Recently we have succeeded in fabricating several cubic $NaZn_{13}$-type pseudobinary compounds with the formulae $La(Fe_xSi_{1-x})_{13}$ and $La(Fe_xAl_{1-x})_{13}$. The magnetic properties of the former compound were abnormal in so far as an increase of the Fe concentration was accompanied by an increasing Fe moment but a decreasing Curie temperature (Palstra *et al* 1983). Furthermore, zero-field susceptibility measurements showed that the critical exponent γ in the expression $\chi \propto (T-T_C)^{-\gamma}$ was equal to 1.38, characterising these materials as isotropic Heisenberg ferromagnets. The electrical resistivity exhibited anomalous critical behaviour which was explained in terms of lattice softening associated with the Invar effect (Palstra *et al* 1983). In order to obtain further insight into the origin of these peculiar phenomena we have extended our magnetic and transport investigations to the $La(Fe_xAl_{1-x})_{13}$ series. This latter system exhibits a most unusual phase diagram. At low x values ($x<0.62$) a mictomagnetic-like regime occurs with distinct cusps in the AC susceptibility. Upon increasing the Fe concentration a soft ferromagnetic phase is found

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which at lower temperatures shows re-entrant mictomagnetic behaviour. Finally, for $x > 0.86$ antiferromagnetic order appears together with a remarkable metamagnetic transition in external fields of a few tesla. We now focus upon the metamagnetic behaviour and reserve a complete description of the $La(Fe_xAl_{1-x})_{13}$ system for future publications (Palstra *et al* 1984).

The $La(Fe_xAl_{1-x})_{13}$ samples were prepared by arc melting in an atmosphere of purified argon gas. The purities of the elements were better than 99.9%. After arc melting the samples were vacuum annealed for about 10 d at 900 °C. X-ray diffraction analysis showed that single-phase samples of the cubic $NaZn_{13}$-type structure were obtained in the concentration region between $x = 0.46$ and 0.92. The concentration dependence of the lattice constant, a, is shown in figure 1 together with the crystal structure. Magnetisation was measured using a vibrating-sample magnetometer operating at a frequency of 21 Hz. Magnetic fields up to 5 T were produced by a superconducting solenoid and were varied in carefully controlled steps. The temperature was measured using a calibrated carbon glass resistor. The high-field (35 T) magnetisation measurements were performed at 4.2 K in the high-field magnet at Amsterdam (Gersdorf *et al* 1983). For all measurements perfect spheres were shaped by spark erosion.

In figure 2 we show the measured magnetisation curves for $x = 0.877$ as a typical example. The samples were cooled in zero field to helium temperature and then the magnetic field was increased. The spin-flip field at $x = 0.877$ and 4.2 K, measured with increasing field, is 3.88T, but only 0.61 T with decreasing field. The transition takes place within a field change of 1 mT, which is our measuring accuracy. Therefore it is most probably a first-order transition. Analogous behaviour was found for the other samples with $x > 0.877$. Also an instantaneous heating of the sample was observed at the spin-flip transition and, in addition, there are clear indications of large magnetostrictive effects. After the spin flip a saturation moment of about $2.2\,\mu_B$/Fe is found in the ferromagnetic state.

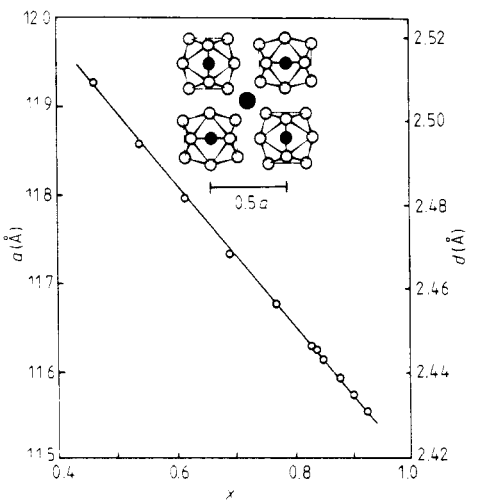

Figure 1. Dependence of the lattice constant, a, on Fe concentration in $La(Fe_xAl_{1-x})_{13}$. The right-hand scale refers to the distance, d, between the Fe^I and Fe^{II} atoms (see text). The inset shows a projection along the c axis for a part of the $NaZn_{13}$-type unit cell (●, Fe^I; ○, Fe^{II}; ●, La).

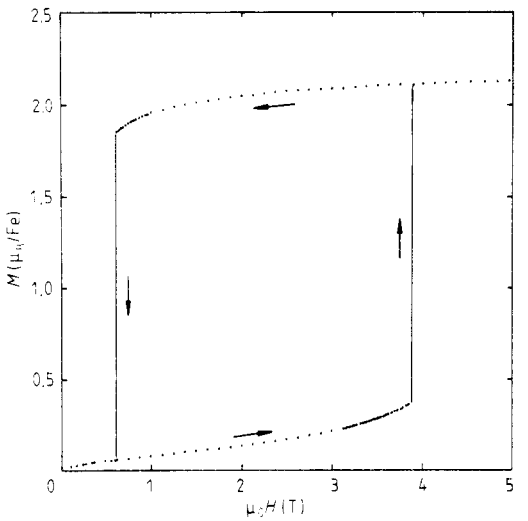

Figure 2. Magnetisation curve at 4.2 K for $LaFe_{11.4}Al_{1.6}$ ($x=0.877$). $\mu_0 H$ is the magnetic induction (in T) with μ_0 the MKS permeability constant.

When the temperature increases, the hysteresis loops become narrower and the centre field shifts to lower values. The resulting phase diagram is shown in figure 3, again for $x=0.877$ as a typical example. The Néel temperature $T_N=(190\pm2)$ K has been determined by AC susceptibility and DC resistivity measurements.

In figure 4 we show the concentration dependence of the transition fields. The spin-flip field is almost linear in x, and with increasing x the hysteresis loops become wider. For compounds with $x<0.86$ the AC susceptibility and DC resistivity exhibit ordinary ferromagnetic features. The Curie temperature increases with decreasing x up to 250 K for $x=0.75$ and then decreases. In the concentration range $0.46<x<0.62$ a mictomagnetic state is found which indicates that local moments and both ferro- and antiferromagnetic interactions are present. However, the antiferromagnetic interactions (Fe–Al–Fe

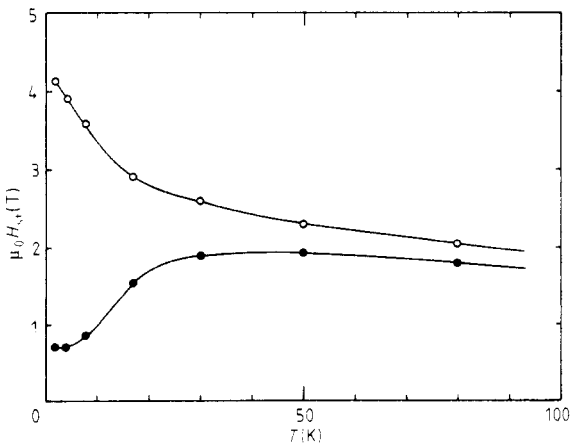

Figure 3. Temperature dependence of the spin-flip fields for increasing (open circles) and decreasing fields (full circles) for the compound $LaFe_{11.4}Al_{1.6}$ ($x=0.877$).

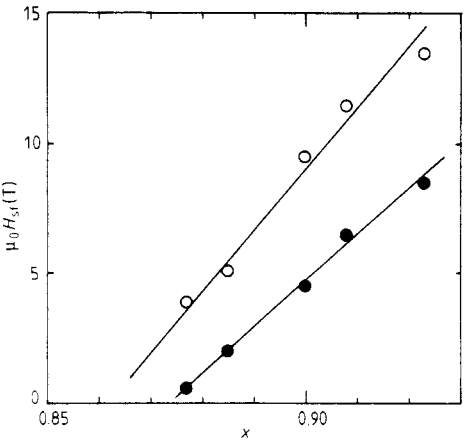

Figure 4. Concentration dependence of the spin-flip fields observed in $La(Fe_xAl_{1-x})_{13}$ at 4.2 K for increasing (open circles) and decreasing fields (full circles).

superexchange) are probably of a different nature to the antiferromagnetic interactions in the high-Fe concentration region where the spin-flip transitions were observed.

In metallic systems several kinds of metamagnetism have been found. Without being exhaustive, we recall several mechanisms and examples. First, there are layered structures like Au_2Mn (Herpin and Meriel 1961, Kazama *et al* 1968), Au_3Mn (Jacobs *et al* 1962), HoNi (Isikawa *et al* 1983), $ErGa_2$ (Doukouré and Gignoux 1982), etc, with ferromagnetic interactions within the layer and antiferromagnetic interactions between the layers. Second, we have temperature-induced phase transitions with metamagnetic features around the transition temperature like Y_2Ni_7 (Gignoux *et al* 1981), FeRh (Kouvel and Hartelius 1962) and MnAs (Ido *et al* 1983). Third, we have collective or itinerant electron metamagnetism with exchange-enhanced paramagnets like $TiBe_2$, YCo_2 and $Co(S_xSe_{1-x})_2$ (Wohlfarth 1980, 1983).

As a pseudobinary intermetallic compound, $La(Fe_xAl_{1-x})_{13}$ certainly belongs to another class with its metamagnetic transition from the antiferromagnetic ground state to the induced ferromagnetic state. In this case a layered structure can be excluded because of the perfect cubic arrangement of the Fe atoms with a coordination number up to 12. Therefore a comparison with Pt_3Fe (Vinokurova *et al* 1979a, b) is not warranted since here layered sheets of Fe atoms have also been observed.

Some striking metamagnetic properties of $La(Fe_xAl_{1-x})_{13}$, which distinguish it from other metamagnets, are as follows.

(1) The transition fields (<15 T) are much smaller than the magnetic ordering temperatures (≈ 200 K) converted to the same units.

(2) For a fixed composition the mean spin-flip field H_{sf} decreases slowly with increasing temperature.

(3) The hysteresis loops are sharp and can be as large as 5 T.

(4) The mean spin-flip field increases with increasing 3d moment.

(5) With increasing 3d concentration x, the metamagnetic region lies in the highest x range leading to the sequence spin glass or mictomagnetic → ferromagnetic → antiferromagnetic. In $Co(S_xSe_{1-x})_2$ the metamagnetic region lies in between a paramagnetic and a ferromagnetic region and in Pt_3Fe the metamagnetic region lies in between a ferromagnetic and an antiferromagnetic region.

The growing tendency towards antiferromagnetic order with increasing x in $La(Fe_xAl_{1-x})_{13}$ can be explained in two almost complementary ways. First, the decreasing lattice constant with increasing x (see figure 1) leads eventually to Fe–Fe nearest-neighbour (NN) distances even smaller than in ferromagnetic α-Fe. Such small Fe–Fe distances have often been observed to be associated with antiferromagnetic coupling between the Fe spins (see, e.g., Barbara *et al* 1973). Second, a particular iron coordination can arise at the Fe-rich end in $La(Fe_xAl_{1-x})_{13}$ where some of the Fe atoms have 12 NN Fe atoms. Such a situation does not occur in ferromagnetic α-Fe (BCC, 8 NN Fe atoms), but does appear in antiferromagnetic γ-Fe (FCC, 12 NN Fe atoms). Before considering these two possibilities a brief discussion of the crystal structure seems desirable.

The cubic $NaZn_{13}$ structure (Zarechnyuk and Kripyakevich 1967) is characterised by two different Zn sites occurring in the ratio 1:12. In the hypothetical compound $LaFe_{13}$, the La and Fe^{I} form a CsCl structure. Each of the Fe^{II} atoms is surrounded by nine nearest Fe^{II} neighbours and one Fe^{I} neighbour, and each of the Fe^{I} atoms is surrounded by an icosahedron of twelve Fe^{II} atoms. The Fe^{II} icosahedra are packed in alternate directions so that the actual lattice constant is twice the Fe^{I}–Fe^{I} distance (see figure 1). The shortest Fe–Fe distance is between the Fe^{I} and the Fe^{II}, being 2% shorter than the Fe^{II}–Fe^{II} distance. There are no indications for preferential site occupancy of the Fe^{I} site by Al (Palstra *et al* 1983).

Returning to the cause of the antiferromagnetism, the first explanation can be based on the Fe–Fe distance dependence of the exchange interaction. The small Fe–Fe distances can be compared with those occurring in the compound $LaFe_{11}Si_2$. This compound has a lattice constant of 11.476 Å, which is significantly smaller than the lowest value found in $La(Fe_xAl_{1-x})_{13}$. Yet the former compound behaves like a 3d Heisenberg ferromagnet (Palstra *et al* 1983) until the crystal structure becomes unstable for $x > 0.88$. Therefore it may be concluded that the small Fe–Fe distance alone is not sufficient to give rise to antiferromagnetic order. Nevertheless, we should keep in mind that Al can cause antiferromagnetic superexchange along an Fe–Al–Fe exchange path (Shukla and Wortis 1980). This superexchange has never been observed in Fe–Si compounds. However, the tendency to antiferromagnetism increases with decreasing Al concentration. This means that the phenomena observed can only be resolved by a subtle combination of the decrease in lattice constant and the decrease in Al content.

A more likely explanation for the antiferromagnetism is the special local environment of the Fe^{I} sites at the Fe-rich end in $La(Fe_xAl_{1-x})_{13}$. The Fe^{I} atoms can be surrounded by up to 12 Fe^{II} atoms. This high coordination of 12 Fe atoms has only been found in γ-Fe and in FCC FeNi Invar alloys. γ-Fe is antiferromagnetic and in the high-Fe concentration region of FeNi, the Invar alloys, a negative Fe–Fe exchange interaction has been measured by neutron scattering experiments (Menshikov 1979). Here the antiferromagnetic state does not exist simply because of a $\gamma \rightarrow \alpha$ martensitic transformation. Combining this information with our data, we suggest that with increasing Fe concentration first a ferromagnetic coupling exists, then, beyond eight nearest Fe neighbours, an antiferromagnetic ground state can arise. In the system $La(Fe_xAl_{1-x})_{13}$, starting from a random site occupancy, a critical coordination number of 8.9 can be defined as the limit for antiferromagnetism. This collapse of long-range ferromagnetic order with increasing Fe concentration has been predicted from energy calculations of impurity states in the unrestricted HFA (Jo 1981, Gautier 1982). Here it was suggested that the ferromagnetic state with all magnetic moments parallel to the magnetisation can be unstable when a finite fraction of atomic moments appears antiparallel or canted to the magnetisation. In $La(Fe_xSi_{1-x})_{13}$ there is basically more ferromagnetic exchange present as exemplified by

its higher T_C values compared with $La(Fe_xAl_{1-x})_{13}$. So slightly larger x values should be required to induce a similar type of weak antiferromagnetism. Unfortunately, we have not succeeded in stabilising the $La(Fe_xSi_{1-x})_{13}$ compound with $x > 0.88$ to make a proper comparison.

In conclusion, we suggest that, due to the highly magnetic environment of the Fe^I sites, a weak antiferromagnetic coupling is present which can be overcome by applying rather small fields, thus causing the metamagnetic transition. Recently we have measured enormous magnetostrictive effects at the spin-flip transitions (Palstra *et al* 1984). The field-induced ferromagnetic state causes a huge magnetic expansion and generates a large amount of latent heat. This, we believe, is the reason why the hysteresis is so large. Mössbauer (van der Kraan *et al* 1983) and neutron scattering experiments are in progress to give more insight in this unique Fe system.

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