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Palstra, T. T. M.; Nieuwenhuys, G. J.; Mydosh, J. A.

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Magnetic properties of cubic La(Fe$_x$Al$_{1-x}$)$_{13}$ intermetallic compounds

T. T. M. Palstra, G. J. Nieuwenhuys, and J. A. Mydosh
Kamerlingh Onnes Laboratorium der Rijks-Universiteit Leiden, Leiden, The Netherlands
K. H. J. Buschow
Philips Research Laboratories, Eindhoven, The Netherlands

We report susceptibility and magnetization measurements for La(Fe$_x$Al$_{1-x}$)$_{13}$ which can be stabilized over the x range 0.46–0.92. At low x values a mictomagnetic regime occurs with distinct cusps in the ac susceptibility. Upon increasing the Fe concentration a soft ferromagnetic phase is found which at lower temperatures shows anisotropy effects related to mictomagnetic behavior. Finally for $x > 0.86$ antiferromagnetic order appears along with a very sharp metamagnetic transition in external fields of a few Teslas. The saturation moment increases linearly with x from $1.3\mu_B$ to $2.3\mu_B$ throughout the ferro- and metamagnetic regimes. These unusual properties are discussed in terms of local moment magnetism and the particular crystal structure which permits a large Fe-Fe coordination number at small distances.

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Recently, we have succeeded in fabricating several cubic NaZn$_{13}$-type pseudobinary compounds of the formula La(Fe$_x$Si$_{1-x}$)$_{13}$ and La(Fe$_x$Al$_{1-x}$)$_{13}$. The former compound which exists only with x between 0.8 and 0.9 exhibits unusual magnetic properties that were reported not long ago.[1] We now turn our attention to the La(Fe$_x$Al$_{1-x}$)$_{13}$ system which can be stabilized over a much wider x-range 0.46–0.92. In this paper we present susceptibility and magnetization measurements over the fully available x range. From these measurements we have determined a unique magnetic phase diagram which consists of a mictomagnetic, a ferromagnetic, and an antiferromagnetic regime. Surprisingly, there is a nearly linear increase in the Fe magnetic moment with increasing x throughout these three regimes.

The La(Fe$_x$Al$_{1-x}$)$_{13}$ samples were prepared by arc melting in an atmosphere of purified argon gas. The purities of the starting elements were better than 99.9%. After arc melting the samples were vacuum annealed for about 10 days at 900 °C. X-ray diffraction analysis showed that single-phase samples of the cubic NaZn$_{13}$-type of structure were obtained in the concentration region between $x = 0.46$ and 0.92. The low-field ac susceptibility was measured by means of a sensitive mutual inductance technique operating at a frequency of 118 Hz with a driving field less than 0.1 mT. The temperature was varied stepwise and determined to within 0.2% by means of calibrated carbon glass and platinum resistors. Magnetization 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. For all measurements perfect spheres were shaped by spark erosion.

The magnetic phase diagram of La(Fe$_x$Al$_{1-x}$)$_{13}$ can be divided into three regimes distinguished by the behavior of the magnetic susceptibility. A typical example of the susceptibility of each regime is shown in Fig. 1. All susceptibility measurements are plotted in units of the inverse demagnetizing factor, D^{-1} ($D = 4\pi/3$ for a sphere). Thus the full ferromagnetic state is indicated by a susceptibility of 1.00. In the first regime (I), $0.46 \leqslant x < 0.62$, the magnetic susceptibility has a distinct mictomagnetic cusp at about 50 K. The susceptibility of an $x = 0.58$ sample along with the inverse susceptibility is shown in Fig. 1(a). The large positive Curie–Weiss temperature intercept, $\theta = +110$ K, indicates the presence of predominantly ferromagnetic exchange interactions, i.e., mictomagnetism. The high-temperature slope of χ^{-1} yields an effective moment $p_{\text{eff}} = 5.3\mu_B$/Fe. Deviations from Curie–Weiss behavior start from $T = 230$ K which is five times the freezing temperature, $T_f = 44.5$ K. The susceptibility increases rapidly with increasing x reaching 0.25% of D^{-1} at T_f for $x = 0.46$, 1.1% for $x = 0.54$ and 14% for $x = 0.58$, respectively.

The susceptibility in the second regime (II), $0.62 < x \leqslant 0.86$, exhibits soft ferromagnetic behavior. The Curie temperature T_C first increases with increasing x up to

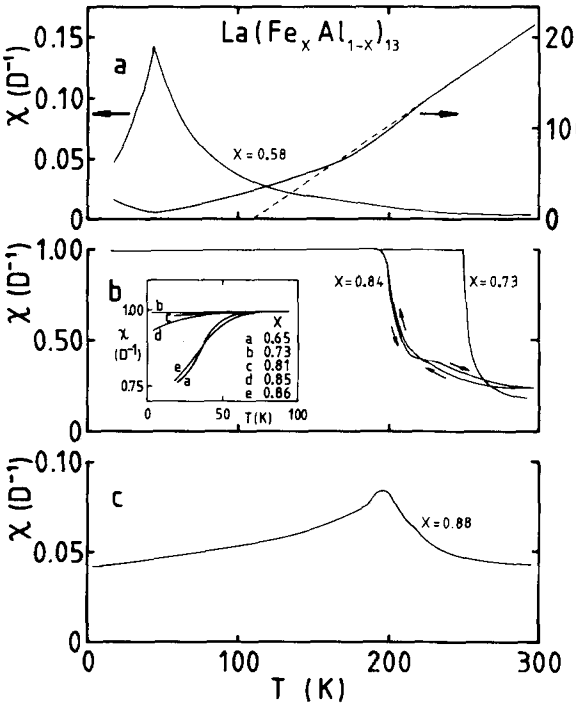

FIG. 1. Temperature dependence of the low field ac susceptibility for the three regimes of La(Fe$_x$Al$_{1-x}$)$_{13}$. In (a) we show a typical mictomagnetic behavior, in (b) a ferromagnetic transition, and in (c) an antiferromagnetic one. The insert in (b) shows the low temperature deviations from the ferromagnetic state. Note the different χ scales.

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a maximum $T_C = 250$ K for $x = 0.75$, and then decreases. At lower temperatures the susceptibility deviates from the inverse demagnetizing factor D^{-1} limit [see Fig. 1(b)]. The least deviation is for the samples with the highest T_C. This indicates that the soft ferromagnetic regime is being destroyed and a reentrant mictomagnetic state is appearing. In a small x interval, $0.84 < x < 0.86$, hysteresis has been observed where the susceptibility above T_C behaves differently when heating and cooling, but both curves yield the same T_C [see Fig. 1(b)].

In the third regime (III), $0.86 < x \leqslant 0.92$, the susceptibility has an antiferromagnetic character. In Fig. 1(c) we show a typical example for $x = 0.88$. The maximum susceptibility for all samples in this regime is about 10% of D^{-1}. Only at the concentration limit $x = 0.92$ does the susceptibility obtain a value about 80% of D^{-1}. This is probably due to a second phase that has been observed in the x-ray spectrum and is seen at the grain boundaries; however, its composition has not yet been determined. It is difficult to resolve accurate values of the Néel temperatures, defined as the maximum of $d(\chi T)/dT$, from the susceptibility measurements because the curves are very smooth. Therefore, we have evaluated these values from resistivity measurements where a sharp cusp in $d\rho/dT$ has been observed. These $\rho(T)$ measurements will be reported separately. In this regime (III) the Néel temperatures increase with increasing x. Also hysteresis above T_n has been observed in the limited concentration region $0.91 \leqslant x \leqslant 0.92$. From these results the magnetic phase diagram can be constructed (Fig. 2) for the three regimes.

In Fig. 3 the saturation magnetic moments in fields of 1.8 T are shown. The magnetic moment increases linearly with x having a slope of $(0.24\mu_B/\text{Fe})/\text{Fe}$ which results in $2.4\mu_B/\text{Fe}$ for the hypothetical compound LaFe_{13}. In the first regime $0.46 \leqslant x < 0.62$ there are deviations from this line. Here it was not possible to saturate the magnetization in fields up to 5 T and an S-shaped M-H curve was found, typical of the mictomagnetic state. In the second regime a soft ferromagnetic state is found with a remanent magnetization less than 1% of the saturation magnetization. The saturation moments of the third regime have been measured in high fields where metamagnetic transitions were found to the fully saturated $(2.2\mu_B/\text{Fe})$ moment.[2]

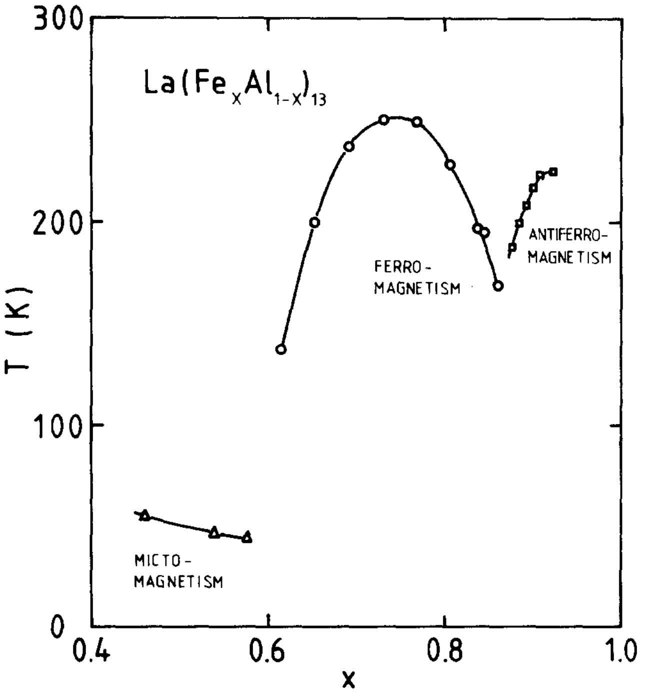

FIG. 2. Magnetic phase diagram of La(Fe$_x$Al$_{1-x}$)$_{13}$. The cusp temperature is indicated by △, the Curie temperature by O, and the Néel temperatures by □.

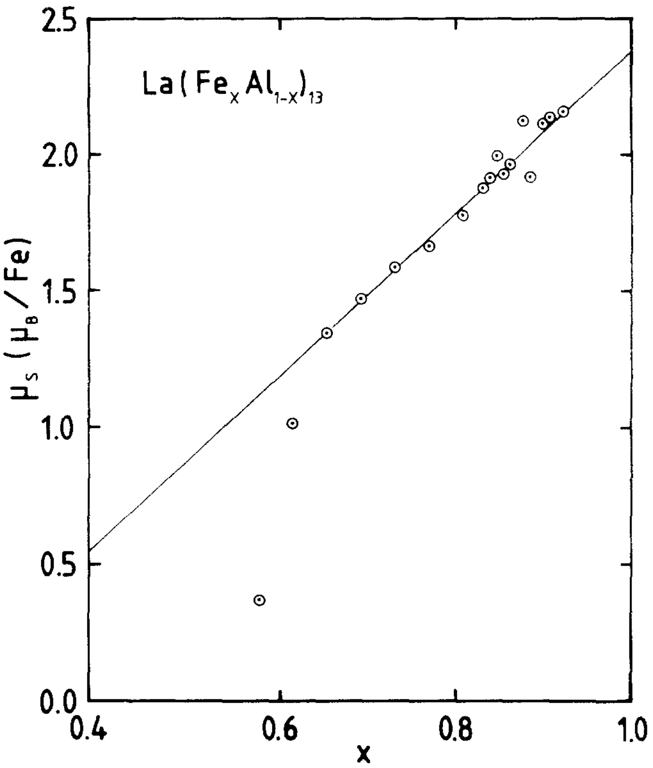

FIG. 3. Saturization moments of La(Fe$_x$Al$_{1-x}$)$_{13}$ as a function of x.

For the composition and stability of the La(Fe$_x$-Al$_{1-x}$)$_{13}$ compounds, the same arguments hold that have been discussed earlier for La(Fe$_x$Si$_{1-x}$)$_{13}$.[1] The magnetic properties will now be considered in terms of the local environment of the iron atoms. In the hypothetical compound LaFe_{13} the Fe atoms occupy two crystallographically different sites at a ratio of 1:12. The La and the Fe^{I} form a CsCl structure. The Fe^{I} atoms are surrounded by an icosahedron of 12 Fe^{II} atoms and the Fe^{II} atoms are surrounded by 9 nearest Fe^{II} neighbors and 1 Fe^{I} neighbor (see Fig. 4). The La atoms are surrounded by a regular polyhedron of 24 Fe^{II} atoms. The Fe^{II}-Fe^{II} distance is only 2% shorter than the Fe^{I}-Fe^{II} distance. This Fe^{I}-Fe^{II} distance, along with the lattice parameter, decreases linearly with x from 2.510 Å for $x = 0.46$ to 2.431 Å for $x = 0.92$.[2] There are no indications for preferential site occupancy of the Fe^{I} site by Al.

We believe that the mictomagnetic behavior arises by virtue of competition between a nearest neighbor Fe-Fe ferromagnetic exchange and a further-neighbor Fe-Al-Fe antiferromagnetic superexchange.[3,4] Short-range ferromagnetic order (clustering) causes the deviations from Curie-Weiss behavior up to 5 T_f.

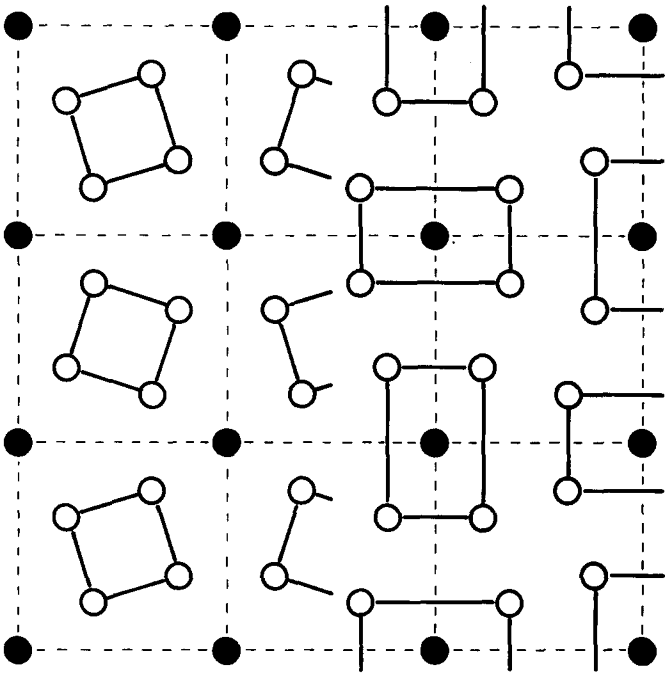

FIG. 4. The $z = 0$ plane of the hypothetical compound LaFe$_{13}$. Fe^{I} is denoted by ● and Fe^{II} by O. The complete iron sublattice can be obtained by cubic O_h^6 symmetry. The La atoms occupy the $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ sites plus their symmetry operations. The full lines in the left part of the figure connect the 24 nearest neighbors of La, and in the right part they connect the 12 nearest neighbors of Fe^{I}. One unit cell contains eight formula units.

The magnetic moment of Fe decreases when the number of nearest neighbor Fe atoms is less than five and the moment is zero when this number is less than four.[5] Thus, by decreasing the iron concentration, more and more iron atoms will loose their magnetic moment, thereby decreasing both the number of ferro- and antiferromagnetic interactions and eventually leading to Pauli paramagnetism.

Upon increasing the iron concentration above the limit $x_p = 0.6$, long-range ferromagnetic order is found. Here, the Curie temperature increases with increasing x because the number of ferromagnetic exchange pairs increases at the cost of the antiferromagnetic superexchange, and because the lattice parameter decreases.[6,7] However, upon increasing the iron concentration above $x = 0.75$ the Curie temperature decreases again and for $x > 0.86$ antiferromagnetic order appears. We believe that in this region where the coordination number of Fe can increase up to 12, a similar situation arises as in γ-Fe (fcc, 12 nearest neighbor Fe atoms) which is also antiferromagnetic.[8,9] In La(Fe$_x$Al$_{1-x}$)$_{13}$ a considerable number of Fe atoms will have this high coordination number, thereby causing an antiferromagnetic coupling. This coupling is rather weak and first order spin-flip transitions have been observed in external fields of only a few Teslas.[2]

The linear decrease of the magnetic moment with decreasing iron concentration down to $1.35\mu_B$/Fe remains rather peculiar. For low concentration of normal nonmagnetic elements dissolved in Fe, a linear decrease of the magnetic moment of Fe has been observed and can be explained satisfactorily with the rigid band model.[10] However, without detailed band structure calculations, we cannot say if the assumptions of this model are in agreement with the real band structure over such a large region of compounds. Thus, the La(Fe$_x$Si$_{1-x}$)$_{13}$ and La(Fe$_x$Al$_{1-x}$)$_{13}$ systems offer an unusual opportunity to study a variety of interesting magnetic properties.

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[1] T. T. M. Palstra, J. A. Mydosh, G. J. Nieuwenhuys, A. M. van der Kraan, and K. H. J. Buschow, J. Magn. Magn. Mater. **36**, 290 (1983).

[2] T. T. M. Palstra, H. G. C. Werij, G. J. Nieuwenhuys, J. A. Mydosh, F. R. de Boer, and K. H. J. Buschow (to be published).

[3] R. D. Shull, H. Okamoto, and P. A. Beck, Solid State Commun. **20**, 863 (1976).

[4] P. Shukla and M. Wortis, Phys. Rev. B **21**, 159 (1980).

[5] G. P. Huffman, J. Appl. Phys. **42**, 1606 (1971).

[6] M. B. Stearns, Physica B **91**, 37 (1977).

[7] L. Dobrzynski *et al.*, Solid State Commun. **46**, 217 (1983).

[8] R. J. Weiss, Proc. Phys. Soc. **82**, 281 (1963).

[9] D. M. Roy and D. G. Pettifor, J. Phys. F. **7**, L183 (1977).

[10] S. V. Vonsovskii, in *Magnetism* (Wiley, New York, 1979), Vol. 2, p. 754.