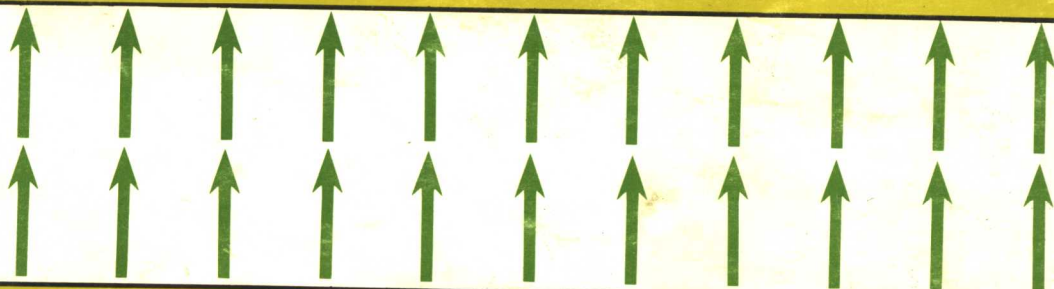


Handbook of Magnetic Materials

Edited by
K. H. J. Buschow

VOLUME
6



North-Holland

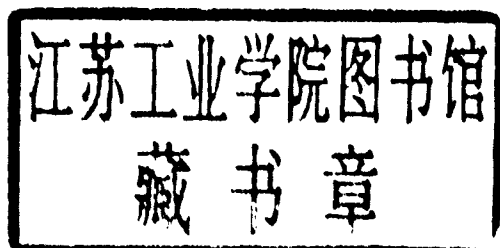
HANDBOOK of MAGNETIC MATERIALS

VOLUME 6

EDITED BY

K.H.J. BUSCHOW

Philips Research Laboratories
5600 JA Eindhoven
The Netherlands



1991

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PREFACE TO VOLUME 6

The Handbook of Magnetic Materials has a dual purpose. As a textbook it is intended to help those who wish to be introduced to a given topic in the field of magnetism without the need to read the vast amount of literature published. As a work of reference it is intended for scientists active in magnetism research. To this dual purpose, the volumes of the Handbook are composed of topical review articles written by leading authorities. In each of these articles an extensive description is given in graphical as well as in tabular form, much emphasis being placed on the discussion of the experimental material in the framework of physics, chemistry and materials science.

The original aim of Peter Wohlfarth when he started this Handbook series was to combine new developments in magnetism with the achievements of earlier compilations of monographs, to produce a worthy successor to Bozorth's classical and monumental book *Ferromagnetism*. It is mainly for this reason that *Ferromagnetic Materials* was initially chosen as title for the Handbook series, although the latter aims at giving a more complete cross-section of magnetism than Bozorth's book. Here one has to realize that many of the present specialized areas of magnetism were non-existent when Bozorth's book was first published. Furthermore, a comprehensible description of the properties of many magnetically ordered materials can hardly be given without considering, e.g., narrow-band phenomena, crystal-field effects or the results of band-structure calculations. For this reason, Peter Wohlfarth and I considered it desirable that the Handbook series be composed of articles that would allow the readers to orient themselves more broadly in the field of magnetism, taking the risk that the title of the Handbook series might be slightly misleading.

During the last few years magnetism has even more expanded into a variety of different areas of research, comprising the magnetism of several classes of novel materials which share with ferromagnetic materials only the presence of magnetic moments. Most of these areas can be regarded as research topics in their own right, requiring a different type of expertise than needed for ferromagnetic materials. Examples of such subfields of magnetism are quadrupolar interactions and magnetic superconductors. Chapters dealing with these materials were included in Volume 5 of this handbook series, which appeared in 1990. In the present Volume it is primarily

the Chapter on quasicrystals that has not much in common with ferromagnetism. Magnetic semiconductors, to be considered in Volume 7, is a further example of a class of materials with properties distinctly different from those of ferromagnetic materials, and the same can be said of substantial portions of the materials considered in the remaining Chapters of Volume 6. This is the reason why the Editor and the Publisher of this Handbook series have carefully reconsidered the title of the Handbook series and have come to the conclusion that the more general title **Magnetic Materials** is more appropriate than **Ferromagnetic Materials**. At the same time this change of title does more credit to the increasing importance of materials science in the scientific community.

The task to provide the readership with novel trends and achievements in magnetism would have been extremely difficult without the professionalism of the North-Holland Physics Division of Elsevier Science Publishers and I would like to thank A. de Waard and P. Hoogerbrugge for their great help and expertise.

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chapter 1

MAGNETIC PROPERTIES OF TERNARY RARE-EARTH TRANSITION-METAL COMPOUNDS

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1. Introduction

The magnetism of pure elements concerns the properties of about 20 metals, mostly from the 3d or 4f series. Binary intermetallic compounds are much more numerous. Magnetic binaries may involve one or both elements with magnetic moments (and even a few examples where both constituents are individually nonmagnetic, e.g., ZrZn_2). Composition adds a further dimension, with many binary diagrams exhibiting ranges of solid solubility and a number of intermetallic phases, each with its particular structure. Sometimes, the distinction is a matter of site preference, e.g., ordered substitution of one quarter of the sites of the fcc structure leads to a Cu_3Au -type structure (space group $\text{Pm}\bar{3}\text{m}$) compound, whereas complete disorder produces an $\text{A}_{75}\text{B}_{25}$ fcc solid solution. The magnetic properties of binary intermetallic compounds, usually involving a 3d or 4f element, and sometimes both, have been reviewed by many authors (Taylor 1971, Wallace 1973, 1986, Buschow 1977, 1979, 1980, Kirchmayr and Poldy 1979, Buzo et al. 1991).

Ternaries are at another level of complexity, with three elements and two composition variables. In magnetic ternaries, usually one or two of the constituent elements are magnetic. The structure is sometimes a specific *ternary* structure, unrelated to any known binary structure type (e.g., $\text{Nd}_2\text{Fe}_{14}\text{B}$). Otherwise, the ternary may be related to a binary by preferential occupation of one of the sites (e.g., CeCo_3B_2 is related to CaCu_5 by substituting B on the 2c sites of the latter structure). Degrees of preferential ordering of elements over the sites are possible; the extreme is a *pseudo-binary*, where two of the elements substitute at random over a set of sites, while the third has a unique site occupancy. Another way of generating a ternary structure from a binary is by introducing small interstitial atoms X, such as carbon or nitrogen in $\text{Y}_2\text{Fe}_{17}\text{X}_{3-\delta}$, which are *interstitial ternary* phases.

In the search for novel compounds, theories predicting the stability of intermetallic phases, like Miedema's 'macroscopic atom model' (de Boer et al. 1988c), Pettifor's structure maps (Pettifor 1988), and the structural stability diagrams of Villars (1985a,b) provide helpful guidelines. The parameter values which are assigned to the elements in these models give an impression of the chemical similarity of the elements. They are useful when trying substitutions in well-known compounds. Out of approximately 100 000 possible ternary systems, phase diagram information is available on fewer than 6000 of them. Often, this information is far from complete, relating to only a single isothermal section or a limited compositional field. Therefore, it is

reasonable to suppose that many novel ternary structure types are still awaiting discovery.

In the circumstances, it is inevitable that our knowledge of the magnetic properties of ternary compounds is far from complete. Some systems have been studied in great detail, others hardly at all. The systems of most interest magnetically involve a 3d element, and a 4f element, the other component being a metal or metalloid, particularly boron or carbon. Oxides and chalcogenides are generally nonmetallic, and they are treated elsewhere. Compounds with the $\text{Nd}_2\text{Fe}_{14}\text{B}$ structure are of particular importance, and they have already been discussed by Buschow (1988c).

Here, in sections 2–7, we present in order of decreasing transition-metal content the magnetic properties of ternaries with structures related to a binary structure type. The true ternary compounds are discussed in section 8. Work on the magnetism of these compounds has often been inspired by the search for new materials for high-performance permanent magnets. The iron-rich ThMn_{12} -structure compounds, the interstitial $\text{R}_2\text{T}_{17}\text{X}_{3-\delta}$ carbides and nitrides and the $\text{R}_2\text{T}_{14}\text{C}$ ternaries have all been studied with this in mind.

Other ternary compounds of comparatively low transition-metal content are discussed by Szytuła, chapter 2 in this volume.

2. Compounds with structures related to NaZn_{13}

The cubic NaZn_{13} structure (space group $\text{Fm}\bar{3}\text{c}$) has Na on 8a, and Zn on 8b and 96i sites. The only rare-earth–transition-metal binary with this structure is LaCo_{13} , which is ferromagnetic with a cobalt moment of $1.58\mu_{\text{B}}$ and Curie temperature $T_{\text{C}} = 1290\text{ K}$ (Buschow and Velge 1977). Among the rare-earth–3d compounds it has the highest 3d-metal content and is of potential interest for application. The structure type can be stabilized for other 3d elements, including Fe and Ni, by substituting Si or Al.

The cubic $\text{La}(\text{Fe}_{1-x}\text{Si}_x)_{13}$ phase is found to be formed for $0.12 < x < 0.19$ (see table 2.1). Magnetic studies showed that T_{C} increases with x in this range (Palstra et al. 1983). For $\text{La}(\text{Fe}_{11}\text{Si}_2)$ ($x = 0.15$), T_{C} is 230 K and the average iron moment is $1.95\mu_{\text{B}}$. There is apparently no site preference of iron or silicon for the 8b site, so these alloys should be regarded as pseudo-binaries rather than ternaries. $\text{La}(\text{Ni}_{11}\text{Si}_2)$ is a Pauli paramagnet.

$\text{La}(\text{Fe}_{1-x}\text{Al}_x)_{13}$ compounds can be stabilized with x between 0.08 and 0.54 (Palstra et al. 1985). At high x values ($0.38 < x \leq 0.54$), a mictomagnetic regime occurs with distinct cusps in the AC susceptibility at about 50 K. The large positive Curie–Weiss temperature $\theta = +110\text{ K}$, indicates the presence of predominantly ferromagnetic exchange interactions. With the decrease of silicon concentration ($0.14 < x \leq 0.38$), a soft ferromagnetic phase was found which at lower temperatures shows anisotropy effects related to re-entrant mictomagnetic behaviour (fig. 2.1). The Curie temperature increases with decrease of x up to a maximum $T_{\text{C}} = 250\text{ K}$ and then decreases. When $0.08 < x \leq 0.14$, an antiferromagnetic order appears along with a sharp metamagnetic transition in external field of 4 T (Palstra et al. 1984).

Ido et al. (1990a) have reported the studies on $\text{La}(\text{Co}_{1-x}\text{Al}_x)_{13}$ with x up to 0.3,

TABLE 2.1

Structural and magnetic data for $\text{La}(\text{T}_{1-x}\text{Si}_x)_{13}$ compounds ($\text{T} = \text{Fe, Co or Ni}$), after Palstra et al. (1983).

Compounds $\text{La}(\text{T}_{1-x}\text{Si}_x)_{13}$	x	$T_c(\text{K})$	$\mu_{3d}(\mu_B)$ 4.2 K	Ref.*
$\text{LaFe}_{11.5}\text{Si}_{1.5}$	0.115	198	2.08	[1]
$\text{LaFe}_{11.2}\text{Si}_{1.8}$	0.139	211		[1]
$\text{LaFe}_{11.1}\text{Si}_{1.9}$	0.146	219		[1]
$\text{LaFe}_{11.0}\text{Si}_{2.0}$	0.154	230	1.95	[1]
$\text{LaFe}_{10.9}\text{Si}_{2.1}$	0.162	234		[1]
$\text{LaFe}_{10.8}\text{Si}_{2.2}$	0.169	245		[1]
$\text{LaFe}_{10.5}\text{Si}_{2.5}$	0.193	262	1.85	[1]
LaCo_{13}	0.000	1290	1.58	[1, 2]
$\text{LaCo}_{11.5}\text{Si}_{1.5}$	0.115		1.29	[1]
$\text{LaCo}_{11}\text{Si}_2$	0.154		1.14	[1]
$\text{LaCo}_{10.5}\text{Si}_{2.5}$	0.193		0.88	[1]
$\text{LaNi}_{10}\text{Si}_2$	0.154	$\chi = 2.5 \times 10^{-7} \text{ m}^3 \text{ kg}^{-1}$		[1]

* References:

- [1] Palstra et al. (1983).
- [2] Buschow and Velge (1977).

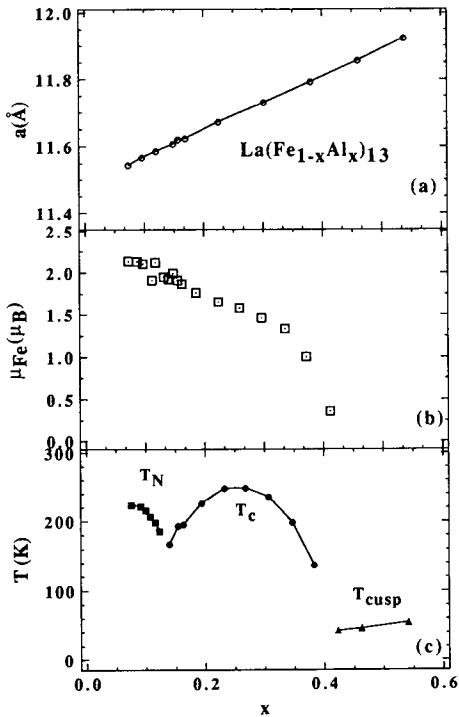


Fig. 2.1. Dependence on Al concentration in $\text{La}(\text{Fe}_{1-x}\text{Al}_x)_{13}$ of (a) lattice parameter, (b) iron saturation magnetic moment and (c) the cusp temperature (solid triangle), the Curie temperature (solid circle) and the Néel temperature (solid square).

$\text{La}(\text{Co}_{1-x-y}\text{Fe}_x\text{Al}_y)_{13}$ with $y = 0.15$ and x up to 0.3, $(\text{La}_{0.7}\text{Nd}_{0.3})(\text{Co}_{0.7}\text{Fe}_{0.3})_{13}$ and $\text{La}(\text{Co}_{1-x}\text{Fe}_x)_{13}$ with x up to 0.6. It is found that the Al-substitution decreases the Co moment as well as the Curie temperature and the Fe-substitution increases the magnetization significantly, but decreases the Curie temperature. The magnetization at 77 K increases by 20% in $\text{La}(\text{Co}_{0.85-x}\text{Fe}_x\text{Al}_{0.15})_{13}$ on Fe substitution of $x = 0.4$. These authors conclude that it is possible to produce a NaZn_{13} -type compound having a large magnetization, comparable to that of Fe-Co alloys.

3. Compounds with structures related to ThMn_{12}

3.1. Crystal structure

Examination of numerous ternary Fe-rich R-Fe-M alloys by means of X-ray or neutron diffraction has shown that the tetragonal ThMn_{12} structure forms quite generally for $\text{RFe}_{12-x}\text{M}_x$ when $\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Mo}, \text{W}, \text{Al}$ or Si and x is in the range $1.0 \leq x \leq 4.0$ (Yang et al. 1981, de Mooij and Buschow 1987, Ohashi et al. 1987, 1988b, Wang et al. 1988, Bigaeva et al. 1987, Müller 1988, Buschow and de Mooij 1989). However, the RFe_{12} end-member does not exist for any rare earth. The ThMn_{12} structure, illustrated in fig. 3.1, is tetragonal with space group I4/mmm and $Z = 2$. The rare-earth atoms occupy the single 2a thorium site which has a high point symmetry, $4/\text{mmm}$, while the transition elements are distributed over the three manganese sites, 8f, 8i and 8j. Iron atoms are found to occupy 8f and 8j site fully while the 8i site is populated by a mixture of Fe and M atoms. An exception occurs when $\text{M} = \text{Si}$. The Si atoms share the 8f and 8j positions with the Fe atoms in $\text{RFe}_{10}\text{Si}_2$ (Buschow 1988a).

The site occupancies were studied in $\text{RFe}_{10}\text{V}_2$ compounds with $\text{R} = \text{Y}, \text{Tb}$ or Er by Helmholdt et al. (1988) and Helmholdt and Buschow (1989) using neutron diffraction; in YFe_{11}Ti by Moze et al. (1988a) and Yang et al. (1988c) using neutron diffraction and in $\text{NdFe}_{10}\text{Mo}_2$ by de Mooij and Buschow (1988a) from a detailed X-ray structure determination. It follows from these results that Ti, V and Mo atoms have a strong preference to occupy the 8i sites, but the distribution of Fe and M atoms within the 8i sites seems to be disordered. Formally, it is this M site preference

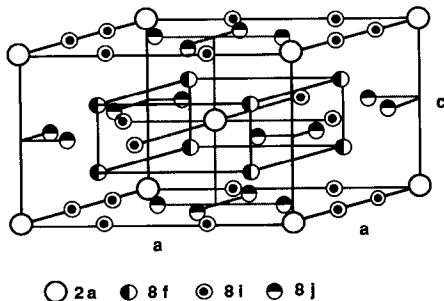


Fig. 3.1. Structure of ThMn_{12} .

that justifies considering these compounds as *ternaries* rather than *pseudo-binaries*. A number of binary structures, the ThMn_{12} structure included, can be derived from the hexagonal CaCu_5 structure (Yang et al. 1989a,b, Hu et al. 1990b). Replacement of Ca atoms by a dumbbell of Cu atoms leads to the different phases. When a third of the Ca atoms are thus replaced, one obtains the $\text{Th}_2\text{Zn}_{17}$ or $\text{Th}_2\text{Ni}_{17}$ structure, depending on the sequence of replacements. When half the Ca atoms are replaced, the ThMn_{12} structure results. Then, half of the transition-metal atoms on 2c sites in the CaCu_5 cell become equivalent to the substituting dumbbell atoms and together form the 8i site, one third of the atoms on 3g and the other half of the 2c atoms constitute the 8j site and the remaining atoms on 3g site form the 8f site. Figure 3.2 shows the structural relationship between $\text{Th}_2\text{Ni}_{17}$ or ThMn_{12} and CaCu_5 . There is also a considerable resemblance between the ThMn_{12} structure and the cubic $\text{Th}_6\text{Mn}_{23}$ structure (Johnson and David 1985, Solzi et al. 1989).

The Fe-Fe nearest-neighbour distances range from 2.40 Å for 8f-8f to 2.97 Å for 8i-8i in YFe_{11}Ti (Moze et al. 1988a). The number of nearest-neighbour sites for 2a are (0, 8, 4, 8), for 8f are (2, 2, 4, 4), for 8i are (1, 4, 5, 4) and for 8j are (2, 4, 4, 2), where the numbers in brackets refer to 2a, 8f, 8i and 8j site neighbours, respectively. The average Fe-Fe distances are 2.49, 2.69 and 2.57 Å for 8f, 8i and 8j sites, respectively (Hu et al. 1989a).

The structures observed for the various $\text{RFe}_{12-x}\text{M}_x$ compounds may be analysed in terms of metallic radii and enthalpy effects. The shortest R-T distances in the

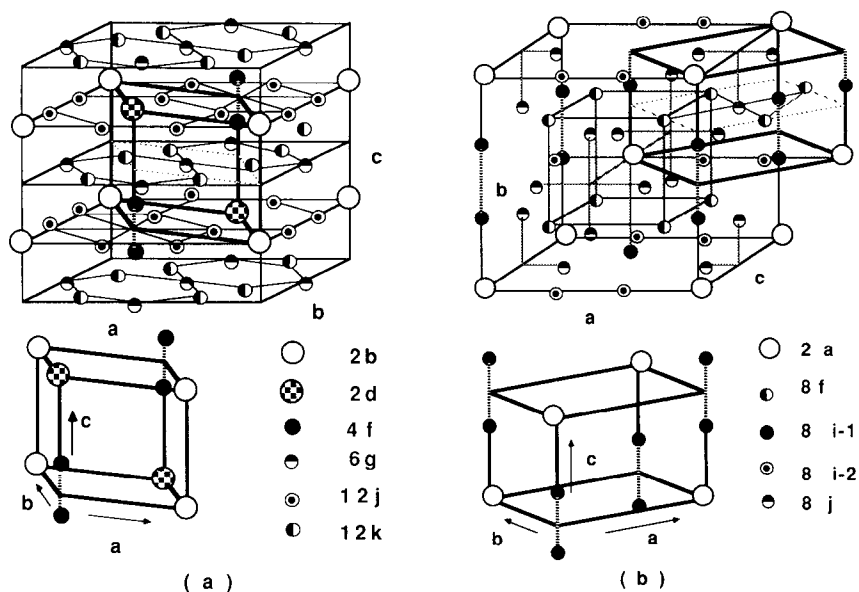


Fig. 3.2. Schematic representation of the relationship between (a) the $\text{Th}_2\text{Ni}_{17}$ -type and (b) the ThMn_{12} -type structures and the CaCu_5 structure.

structure of $RFe_{12-x}M_x$ occur between R atoms and the T atoms at the 8i sites. Progressively larger R–T distances are involved for the 8f and 8j sites, respectively. Since the metallic radii of all of the M elements, except for Si, are substantially larger than that of Fe, one might have expected the M atoms to preferentially occupy 8j sites rather than 8i sites (Buschow 1988a). However, on the basis of average T–T distances, the 8i site is expected to be preferred over the 8f or 8j sites for T atoms larger than Fe. This latter argument seems to be in accord with the observed preferential occupancies in these systems, so it can be concluded that the distances between the transition-metal atoms play a critical role. It follows that Si, which is smaller than Fe, should prefer 8f and 8j sites rather than the 8i site. This is in fact observed in $LuFe_{10}Si_2$ (Buschow 1988a). Enthalpy also plays a part in reinforcing the site preference. The difference in structure between $RFe_{10}Si_2$ on the one hand and $RFe_{10}T_2$ (T = Ti, V, Mo) on the other may be related to the fact that the heat of mixing between R and Si is negative and the heat of mixing between R and Ti, V or Mo is positive (Niessen et al. 1983). Since an R atom has only four nearest 8i-site neighbours compared with eight nearest 8f- and 8j-sites neighbours, it follows that the 8i sites have by far the smallest area of contact with the R sites. In view of the positive enthalpy contribution associated with R and Ti, V or Mo contents, one may expect therefore that the 8i site will be preferred by those three elements. The comparatively large negative heat of mixing between R and Si leads to an equally large stabilizing effect if the contact between the R and Si atoms is as large as possible. Hence, from enthalpy considerations, one would again expect the Si atoms to occupy the 8f and 8j sites (Buschow and de Mooij 1989).

3.2. Alloys rich in Fe or Co

3.2.1. Magnetic properties

Lattice parameters and magnetic data for all the $RFe_{12-x}M_x$, $RCo_{12-x}M_x$ and $RFe_{12-x}(M'_1-yM''_y)_x$ compounds are listed in table 3.1. Some general features emerge from the mass of data on the iron series:

(a) The average iron magnetic moment is observed to be $1.35\mu_B$ – $1.93\mu_B$ depending on the specific M element. The iron compounds appear to be weak ferromagnets (Coey 1989).

(b) Curie temperatures are in the range 400–650 K (except for the Mo series where they vary from 260–500 K), with the highest values for the Gd compound in each series.

(c) The anisotropy due to the iron sublattice is uniaxial. The magnitude of K_1 (Fe) is a monotonic function of temperature, decreasing from 1.93 MJ m^{-3} at 4.2 K to 0.89 MJ m^{-3} at room temperature for $YFe_{11}Ti$ (Li and Hu 1988).

(d) The second-order crystal field coefficient A_{20} at the 2a, rare-earth site is negative and considerably smaller in magnitude than that found for either RCo_5 or $R_2Fe_{14}B$ (Li et al. 1988a, Buschow et al. 1988a). This implies that the contribution to the uniaxial anisotropy is relatively small for those rare-earth ions, $R = Sm^{3+}$, Er^{3+} , Tm^{3+} and Yb^{3+} , having a positive second-order Stevens coefficient α_J . The room-temperature anisotropy field observed in all these $RFe_{12-x}M_x$ compounds is