

Nowotny Chimney Ladder Compounds in $\text{Nd}_{1+E}\text{Fe}_{4-x}\text{Co}_x\text{B}_4^{*,\dagger}$

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Structural investigations on $\text{Nd}_{1+E}\text{Fe}_{4-x}\text{Co}_x\text{B}_4$ show the presence of distinct new phases with multiplicative *c* axis extensions (ladder compounds) and limited homogeneous range. We also report on compounds $R_{1+E}\text{Fe}_4\text{B}_4$ (*R* = rare earth) for which several new representatives (e.g., with *R* = La and Lu) are described. The ladder compounds in both substitutional series appear related and a common sequence as a function of composition is suggested. As an example the first new ladder type $\text{Nd}_{1.06}\text{Fe}_{1.5}\text{Co}_{2.5}\text{B}_4$ to develop out of NdCo_4B_4 is similar to $\text{La}_{1.06}\text{Fe}_4\text{B}_4$ and the third namely $\text{Nd}_{1.09}\text{Fe}_3\text{CoB}_4$ resembles $\text{Pr}_{1.10}\text{Fe}_4\text{B}_4$. © 1987 Academic Press, Inc.

Introduction

Materials $R_2\text{Fe}_{14}\text{B}$ promise to become of great potential usefulness for a variety of purposes (e.g., magnetic recording, permanent magnets, magnetic cooling, hydrogen storage) (1). These properties, however, can critically depend on the properties of secondary phases such as $R_{1+E}\text{Fe}_4\text{B}_4$. It was pointed out (2) in the case of $\text{Nd}_{1+E}\text{Fe}_4\text{B}_4$ that the magnetically nonordered nature of this phase at room temperature plays a role in magnetic hardening of $\text{Nd}_2\text{Fe}_{14}\text{B}$ type materials. When this and Nd are secondary components, high values of coercive force can be achieved by fine particle sintering because no easy domain nucleation can occur from these magnetically nonordered secondary phases. On the other hand, samples which show Fe as secondary phase cannot be similarly hard-

ened. Here we expand on the behavior of $\text{Nd}_{1+E}\text{Fe}_{4-x}\text{Co}_x\text{B}_4$ materials as they are secondary phases of the technologically interesting $\text{Nd}_2\text{Fe}_{14-x}\text{Co}_x\text{B}$ type compounds and as they promised to show intriguing structural behavior.

The structure of NdCo_4B_4 was described (3) as tetragonal NdCo_4B_4 type. Compounds $R_{1+E}\text{Fe}_4\text{B}_4$ were described (4, 5) as complex variations of the NdCo_4B_4 type structure of ladder type with multiplicative *c* axis extensions. (The tetragonal phase referred to in Ref. (2) as NdFe_4B_4 , in fact, is identical with the phase given as $\text{Nd}_{1.1}\text{Fe}_4\text{B}_4$.) These phases can, in principle, be seen (4, 5) as resulting from two interpenetrating structures. A transition metal substructure corresponds in its X-ray diffraction reflections (e.g., 211*T*) to the unchanged NdCo_4B_4 type structure giving a lattice parameter *c* (*T*). A *R* substructure, however, is not any more contributing to reflections at identical locations compared with this transition metal substructure as it

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was in NdCo_4B_4 . Instead its c axis has dropped below the one containing T and produces new independent X-ray diffractions (e.g., $211R$) and a new lattice parameter c (R). An overall lattice parameter c_0 can then be found at multiples (4) of the respective substructures namely nc (T) and mc (R) although the question of commensurability is not always easy to answer. Similar adaptive structures with multiplicative c axis extensions have been referred to as Nowotny chimney ladder phases (5). Recently a paper on $\text{Nd}_5\text{Fe}_{18}\text{B}_{18}$ appeared (6) which treats this phase as a commensurate ladder type compound with a relatively short c axis (35.07 \AA) compared to the earlier work (144.57 \AA). In this study we proceed in the indexing of Refs. (4, 5). It was of interest to see whether ladder type structures would smoothly develop out of the parent structure (NdCo_4B_4) perhaps with infinitely adaptable c axis extension. Alternatively they would represent individual structure types and a certain ladder type would be given by a special radius ratio between R and T . In the following we shall show that the latter corresponds more closely to the facts.

Experimental

Specimens were prepared by induction melting from the elements under inert atmosphere (annealing was attempted in selected cases but did not change results). The major part of this study is concerned with materials of stoichiometry $(1 - y) \text{Nd}_{1+y}\text{Fe}_4\text{B}_4 - \text{NdCo}_4\text{B}_4$. The parameter E in $\text{Nd}_{1+E}\text{Fe}_{4-x}\text{Co}_x$ is therefore smoothly varying over this series as illustrated in Fig. 1. As $1 + E$ is also reflected in the ratio $c(T)/c(R)$, the stoichiometry can therefore be directly correlated with the structural information. This holds even for multiple phase materials. A series of 13 specimens was also prepared in the as melted form from master samples of the ternaries. This

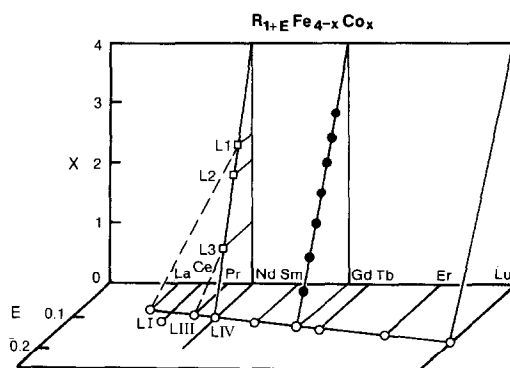


FIG. 1. Occurrence of ladder compounds in $R_{1+E}\text{Fe}_{4-x}\text{Co}_x$. Phases occurring in $\text{Nd}_{1+E}\text{Fe}_{4-x}\text{Co}_x$ are designated by Arabic symbols, phases occurring in $R_{1+E}\text{Fe}_4\text{B}_4$ are designated by Roman symbols. The dashed lines indicate the relationship between those phases (e.g., $\text{La}_{1.06}\text{Fe}_4\text{B}_4 = \text{L1}$ has similar n and m as $\text{Nd}_{1.5}\text{Fe}_{1.5}\text{Co}_{2.5}\text{B}_4 = \text{L1}$). The bold symbols indicate schematically our expectation of new ladder compounds in $\text{Gd}_{1+E}\text{Fe}_{4-x}\text{Co}_x$.

procedure required higher temperature for melting as the major part of the exothermic heat of formation was already lost in the master sample preparation. Independent preparations were also attempted for $\text{Nd}_{1+E}\text{Fe}_4\text{B}_4$ with different values of E .

Materials were subsequently investigated by powder X-ray diffraction, magnetometry, and concerning their hydriding behavior in a manner given in more detail elsewhere (2). Structural identification was focused on the observation of trends in the reflections stemming from R and T , respectively (Reflection $211R$ and $211T$), and the plane (310). These are prominent lines which are characteristic of all ladder compounds described.

Results

Data and indexing of a typical powder pattern for an as melted ladder compound $\text{Nd}_{1.1}\text{Fe}_4\text{B}_4$ are consistent with the one of Refs. (4, 5). A similar Debye Scherrer diagram compared to the one of the as melted specimen is obtained after the material has

TABLE I
SCHEMATIC REPRESENTATION OF COMPOUNDS
 $R_{1+E}T_4B_4$ AS A FUNCTION OF RADIUS RATIOS (r)
BETWEEN R AND T

Compound	r^a	Structure type ^b
LaCo ₄ B ₄	1.496	NdCo ₄ B ₄
La _{1+E} Fe ₄ B ₄	1.484	<i>L</i>
NdCo ₄ B ₄	1.456	NdCo ₄ B ₄
Nd _{1+E} Fe ₄ B ₄	1.444	<i>L</i>
NdRu ₄ B ₄	1.358	LuRu ₄ B ₄
NdOs ₄ B ₄	1.348	NdCo ₄ B ₄
ScCo ₄ B ₄	1.296	CeCo ₄ B ₄
ScRu ₄ B ₄	1.208	LuRu ₄ B ₄

^a Radius ratio between R and T . Examples for atomic radii are 1.82 Å for Nd and 1.26 Å for Fe.

^b *L* stands for ladder type compounds.

been annealed for 200 hr at 800°C. Several preparations (as melted) with E varying between 0 and 0.2 show that the ladder type

compound of Table I is obtained the purest near $E = 0.11$. This also comports with the earlier work (4-6). On partial Co substitution for Fe according to Nd_{1+E}Fe_{4-x}Co_x, only the relative location and intensities of the lines change. Decreases in T substructure dimensions with increasing x are very small and could not be used for identification of extent of homogeneous regions. The R substructure, however, responds strongly and in a discontinuous manner to increasing x . As shown in Table II, we accordingly observe two new ladder modifications ($L1, L2$) around compositions with $x = 2$ and 2.5. Several preparations between these values show lines characteristic of both ladder types with unchanged lattice parameters. This indicates two phase materials in this region of composition and a very limited homogene-

TABLE II
STRUCTURAL DATA FOR COMPOUNDS $R_{1+E}T_4B_4$ (R = RARE EARTHS, T = TRANSITION METAL)
AND Nd_{1+E}Fe_{4-x}Co_xB₄

Compound	Type ^a	a_0 (Å)	$C(T)^b$ (Å)	$C(R)^b$ (Å)	$\frac{C(T)}{C(R)}$	C_0 (Å)	n, m^c	Ref.
La _{1.06} Fe ₄ B ₄	<i>L1</i>	7.221	3.873	3.640	1.06	127.81	33,35	PW
Ce _{1.12} Fe ₄ B ₄		7.090	3.910	3.4889	1.120	129.04	33,35	PW
Pr _{1.11} Fe ₄ B ₄	<i>LIII</i>	7.154	3.906	3.529	1.107	74.21	19,21	PW
Pr _{1.1} Fe ₄ B ₄		7.158	3.9042	3.5301	1.106	74.18	19,21	4
Nd _{1.10} Fe ₄ B ₄	<i>LIV</i>	7.141	3.9073	3.5241	1.1087	144.57	37,41	4
Sm _{1.13} Fe ₄ B ₄	<i>LVI</i>	7.098	3.9124	3.4574	1.1316	58.69	15,17	4
Gd _{1.14} Fe ₄ B ₄		7.073	3.921	3.442	1.139	113.73	29,33	4
Gd _{1.14} Fe ₄ B ₄		7.064	3.920	3.438	1.140	113.68	29,33	PW
Tb _{1.15} Fe ₄ B ₄		7.049	3.919	3.4109	1.149	105.81	27,31	4
Y _{1.15} Fe ₄ B ₄	<i>L</i>	7.013	3.916	3.399	1.152	58.74	15,13	PW
Er _{1.17} Fe ₄ B ₄	<i>L</i>	6.989	3.917	3.344	1.171	137.10	35,41	PW
Lu _{1.18} Fe ₄ B ₄	<i>L</i>	6.950	3.936	3.344	1.177	137.76	35,41	PW
Nd _{1.11} Fe ₄ B ₄	<i>LIV</i>	7.111	3.892	3.505	1.110	144.00	37,41	PW
Nd _{1+E} Fe ₃ CoB ₄	<i>L3</i>	7.095	3.852	3.527	1.092	80.89	21,23	PW
Nd _{1+E} Fe ₂ Co ₂ B ₄	<i>L2</i>	7.084	3.856	3.572	1.080	73.188	19,21	PW
Nd _{1+E} Fe _{1.5} Co _{2.5} B ₄	<i>L1</i>	7.074	3.833	3.617	1.060	134.155	35,37	PW
NdCo ₄ B ₄	tP18	7.060			1.000	3.795	1,1	PW
		7.07				3.82		3

^a *L* stands for ladder structure. Roman numerals identify sequence within R representatives, Arabic numerals indicate corresponding sequence within Nd_{1+E}Fe_{4-x}Co_xB₄.

^b Lattice parameters. Symbols $C(T)$ and $C(R)$ correspond to R and T metal substructures as described in the text.

^c n and m are multiples of the R and T metal substructures as described in the text.

ous range for the two ladder modifications involved. A similar situation also obtains for the case of the two phase region with the second ladder modification (*L2*). By contrast with the diffuse reflections stemming from the *R* sublattice in $\text{Nd}_{1.1}\text{Fe}_4\text{B}_4$ these reflections remain sharp with *L1* and *L2*. $\text{Nd}_{1+E}\text{Fe}_4\text{B}_4$ may have a homogeneous region to roughly $x = 1$ in $\text{Nd}_{1+E}\text{Fe}_{4-x}\text{Co}_x\text{B}_4$, although this composition more likely corresponds to a closely related ladder structure *L3*. Beyond $x = 3.0$ only the pattern characteristic of NdCo_4B_4 was observed.

Some experiments were also performed on related materials $R_{1+E}\text{Fe}_4\text{B}_4$ (Table II). Several new ladder structures were found including representatives with $R = \text{La}, \text{Er},$ and Lu . This suggests that all R^{3+} are capable of forming ladder type compounds. In the case of $R = \text{Er}$ and Lu the diffraction patterns show several new lines besides the ones typical of the ladder types described here. This could indicate the presence of secondary phases or a somewhat more complex structure. $\text{Y}_{1.2}\text{Fe}_4\text{B}_4$ showed all lines characteristic for the ladder type structure and also some extraneous lines characteristic of Fe_2B . Annealing for 200 hr at 800°C did not much influence the diffraction pattern.

Eight samples were prepared in $\text{Nd}_{1.1}\text{Fe}_4\text{B}_4\text{--Gd}_{1.2}\text{Fe}_4\text{B}_4$. They show more continuous ranges of ladder structures without clear indications for two phase regions. In the intermediary range of composition changes of the relative intensities of the respective reflections are observed. However, the *R* substructure reflections remain diffuse over the entire range in composition so that a definitive statement about extent of homogeneous range cannot be made.

Magnetic studies show ferromagnetic ordering of $\text{Nd}_{1.1}\text{Fe}_4\text{B}_4$ with $T_c = 15$ K and a moment of $2.6\mu_B$ per Nd. The situation for NdCo_4B_4 is less clear at present. There are

indications for weak antiferromagnetism at $T_N = 52$ K, but it has not established whether this is due to small impurities.

$\text{Nd}_{1.2}\text{Fe}_4\text{B}_4$ was exposed to 40 atm H_2 at room temperature. No noticeable H uptake was observed by pressure monitoring.

Discussion

The most interesting finding of this study pertains to the discontinuous structural changes with x in $\text{Nd}_{1+E}\text{Fe}_{4-x}\text{Co}_x\text{B}_4$ (Fig. 1). This is especially dramatic coming from NdCo_4B_4 . There exists a large single phase region (to $x = 3$) on partial substitution of Fe for Co followed by a two phase region with the first ladder modification (*L1*) and a two phase region with a second ladder type (*L2*). The ladder modifications develop with clarity and have no appreciable homogeneous range. The *c* axis is obviously not infinitely adaptable in this case. The accuracy of our measurements is however insufficient to be definitive on the question of simple commensurability of $c(R)$ and $c(T)$. The fact that a more ideal *R* substructure can be achieved by partial transition metal substitution compared to $R_{1+E}\text{Fe}_4\text{B}_4$ may have to do with partial ordering tendencies of Co and Fe on crystallographic sites leading to better spatial adaptations compared to the ternaries.

It is tempting to ascribe the presence of ladder type compounds to certain radius ratios between *R* and *T* metals, respectively. Such ratios are shown in Table I. Accordingly, ladder types should be observed at smaller radial ratios compared to the one of NdCo_4B_4 . It is then natural to assume a characteristic sequence of ladder types to be observed in systems both of the type $\text{Nd}_{1+E}\text{Fe}_{4-x}\text{Co}_x\text{B}$ and of the type $R_{1-x}R_x^I\text{Fe}_4\text{B}_4$. This is found to be indeed the case. In order to facilitate this comparison we denote ladder compounds in $\text{Nd}_{1+E}\text{Fe}_{4-x}\text{Co}_x\text{B}$ by Arabic and compounds in $R_{1-x}R_x^I\text{Fe}_4\text{B}_4$ by Roman numerals. We note

that $L1$ ($Nd_{1+E}Fe_2Co_2B_4$) is a limiting structural principle beyond which no ladder types should occur. It is gratifying to see that $La_{1+E}Fe_4B_4$ ($L1$) closely resembles $L1$. Accordingly, $Pr_{1+E}Fe_4B_4$ should correspond to a ladder type developing out of $Nd_{1+E}Fe_{4-x}Co_xB_4$ at small x . The material denoted as $L3$ is indeed rather similar in its structural characteristics such as $c(T)/c(R)$. Anticipating further analogy between ladder types of the two types of substitutional series we predict that in systems such as $Gd_{1+E}Fe_{4-x}Co_xB_4$ at least one additional characteristic ladder type corresponding to the one of $Sm_{1+E}Fe_4B_4$ will be found. Similar arguments also pertain to systems involving other T metals (Ni, Ru, etc). A strict correlation with radius ratios, r , however is not obeyed. This can be seen by inspecting the location of $Nd_{1+E}Co_4B_4$ in Table I. As it is surrounded by two ladder representatives it should itself have been a ladder compound.

It is interesting to note that while we have followed the procedure of Ref. (4) for giving n and m , simpler ratios involving integer numbers are also satisfactory. $L1$ can accordingly be approximated by a ratio of $m/n = 17/16$ and the second limit is reached with $Lu_{1+E}Fe_4B_4$ with $7/6$. Accordingly the c_0 parameter increases from $6xc(T)$ for $Lu_{1+E}Fe_4B_4$ to $16xc(T)$ for $L1$. Secondary phases related to $Nd_{1.1}Fe_4B_4$ with multiple c axis extensions are often observed in scanning electron microscopy in $Nd_2Fe_{14}B$ permanent magnet materials (7–9). It is possible that these materials correspond to different ladder modifications perhaps dependent on different heat treatments. So far, however, we have not found a pronounced influence of heat treatment on the formation of ladder type structures. We want, however, to indicate that the composition $Nd_2Fe_7B_6$ given (8) for one of these modifications will certainly be inaccurate, as it results in an unreasonably

large value of volume per atom (roughly similar to $Nd_2Fe_{14}B$).

The lack of H uptake of $Nd_{1+E}Fe_4B_4$ could be a detriment to the hydriding of $Nd_2Fe_{14}B$ type materials in case of strong phase boundary segregations of the former.

In summary we find that all trivalent R should be capable of forming ladder type structures at composition $R_{1+E}Fe_4B_4$ as the two extreme representatives La and Lu do so. All materials $R_{1+E}Fe_4B_4$ and $Nd_{1.1}Fe_4B_4$ – $Gd_{1.2}Fe_4B_4$ show diffuse peaks originating from the R sublattice. By contrast we find new ladder compounds with well-developed diffraction peaks and limited homogeneous ranges in $Nd_{1+E}Fe_{4-x}Co_xB_4$. A characteristic and common sequence of ladder types is suggested for these two types of substitutional compound series.

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