Relationships Between Crystal Structure and Magnetic Properties in $Nd_2Fe_{14}B$

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Abstract

Determination of the crystal structure of $Nd_2Fe_{14}B$, a new ternary phase, is reported. It has recently been demonstrated that permanent magnets having large coercivities and energy products can be formed from this phase, underscoring its potential technological importance. We relate the crystal structure and intrinsic magnetic properties by considering analogies with previously known rare-earth-transition-metal materials.

Introduction

It has demonstrated[1,2] that melt-spun Nd-Fe-B alloys can exhibit intrinsic coercivities and energy products as large as 20 kOe and 14.1 MG Oe, respectively. Such properties approach those of $SmCo_5$ permanent magnets, and their realization in a light rare-earth-iron material is scientifically and technologically significant. X-ray diffraction studies[1-2,3] indicate that the alloys having the highest energy products are comprised of a new, tetragonal rare-earth-iron-boron phase.

Here we report the determination of its crystal structure and room-temperature moment arrangement, and we discuss relationships between the structural characteristics and observed magnetic properties via analogy with other rare-earth-transition-metal (*R*-TM) systems.

Since single crystals of the new phase are as yet unavailable, we conducted neutron-diffraction studies on powders obtained from a single-phase ingot and solved the structure using the Rietveld method.[4,5] To our knowledge this is the first determination of such a complex structure from powder information alone. Data were collected at 673 K (above the 627 K Curie temperature of the ingot) and at room temperature on the position-sensitive detector-diffractometer at the University of Missouri Research Reactor.

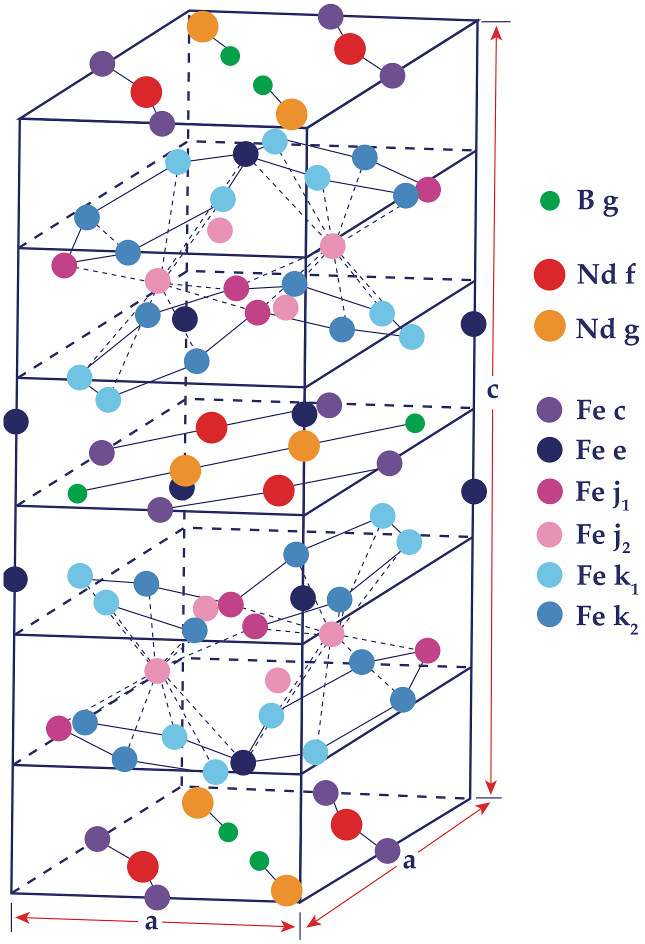

Figure 1 — Unit cell of $Nd_2Fe_{14}B$ ($P4_2/mnm$ space group). The c/a ratio in the figure is exaggerated to emphasize the puckering of the hexagonal iron nets.

Figure 1 illustrates the structure, and Table 1 summarizes information regarding it. The space group is $P4_2/mnm$ (structure No. 136 of Reference 6),[6] and there are four $Nd_2Fe_{14}B$ units (68 atoms) per unit cell. From Figure 1 it is evident that all the Nd and B atoms, but only four of the 56 iron atoms, reside in the $z = 0$ and $z = 0.5$ planes. Between these the other Fe atoms form puckered, yet fully connected, *hexagonal* nets. Although the z coordinate of the j_2 sites is not fixed by symmetry, it is very near $z = 0.25$; that is, the j_2 atoms are in planes almost precisely midway between the planes containing Nd and B.

Table 1 — Atomic Site Occupancies and Coordinates

Atom	Site	Occupancy	x	y	z
Nd	f	4	0.266	0.266	0.0
Nd	g	4	0.139	-0.14	0.0
Fe	k_1	16	0.224	0.568	0.128
Fe	k_2	16	0.039	0.359	0.176
Fe	j_1	8	0.097	0.097	0.205
Fe	j_2	8	0.318	0.318	0.247
Fe	e	4	0.5	0.5	0.113
Fe	c	4	0.0	0.5	0.0
B	g	4	0.368	-0.37	0.0

- Atomic sites, occupancies, and coordinates x, y, and z (in units of the lattice constants $a = 8.80$ Å, $c = 12.19$ Å) for $Nd_2Fe_{14}B$ obtained from analysis of room-temperature neutron diffraction data.
- The space group is $P4_2/mnm$. The quality-of-fit index for the nuclear structure is R (nuc) = 4.2%.
- These results imply a density of 7.60 g/cm^3 which agrees well with the measured value of 7.55 g/cm^3.

Near-neighbor Fe-Fe distances in the structure range between 2.4 and 2.8 Å, values characteristic of R-TM systems.

The boron coordination is simple and elegant. The B atoms occupy the centers of trigonal prisms (Figure 2) formed by the three nearest iron atoms above and the three below the basal (or $z = 0.5$) plane. As can be seen in Figure 1, the triangular prism faces participate in completing the hexagonal Fe nets over the square basal units. The prisms pucker the Fe nets since the Fe(e) and Fe(k_1) atoms in them are displaced significantly toward the B-containing planes as compared with the other Fe atoms in the nets. It is clear, therefore, that the prisms are strong structural units linking the Fe planes above and below those containing Nd and B. The prisms also coordinate all rare-earth and boron atoms; three R atoms are bonded to each boron through the rectangular prism faces. The prisms appear in pairs having a common Fe(e)-Fe(e) edge, and they share two rare-earth atoms. Gaskell has stressed[7] that such trigonal prisms are fundamental to the structure of many TM-metalloid systems, both crystalline (e.g., FeB and Fe_3C) and amorphous.

We have also determined the room-temperature magnetic structure by refinement of the neutron data. The moment arrangement is ferromagnetic, with all Nd and Fe moments parallel to the c axis of the tetragonal cell. This configuration is in accord with the general observation[8] that light rare-earth and TM moments align ferromagnetically in R-TM materials. The average iron moment is near saturation at 300 K, while the Nd moments are $\leq 1\mu_B$.[9]

We expect most of the intrinsic magnetocrystalline anisotropy of $Nd_2Fe_{14}B$ to originate in the crystal-field splitting of the rare-earth $4f$ levels. It is evident from Figure 1, however, that the Fe environments parallel and perpendicular to the easy c axis are quite distinct. This suggests that substantial magnetocrystalline anisotropy may be associated with the Fe sublattice itself. This supposition is supported by our observation[2] of ~2.5 kOe coercivity in the magnetically hardened Gd representative of this structure. The Gd^{3+} ion has no orbital moment and, hence, experiences no crystal-field splitting to first order.

Figure 1 also suggests that the j_2 atoms shared by the iron nets are cognates of the c ("dumbbell") atoms in hexagonal R-TM compounds such as R_2TM_{17} (cf. Figure 1 of Reference 10);[10] the Fe-Fe(j_2) bond lengths range from 2.6 to 2.8 Å, quite comparable with the Fe-Fe(c) distances in R_2Fe_{17}. Half of the hexagons in the R_2TM_{17} lattice do not have a c atom above or below to complete the net, and the Fe(h) atoms have only one Fe(c) neighbor. In contrast, all hexagons in $Nd_2Fe_{14}B$ are filled, and all atoms in the nets have two j_2 neighbors, making it likely that the average exchange interaction in the nets is stronger than in Nd_2Fe_{17}. This more complete coordination may be responsible for the significantly higher Curie temperature of $Nd_2Fe_{14}B$ (627 vs 330 K for Nd_2Fe_{17}).

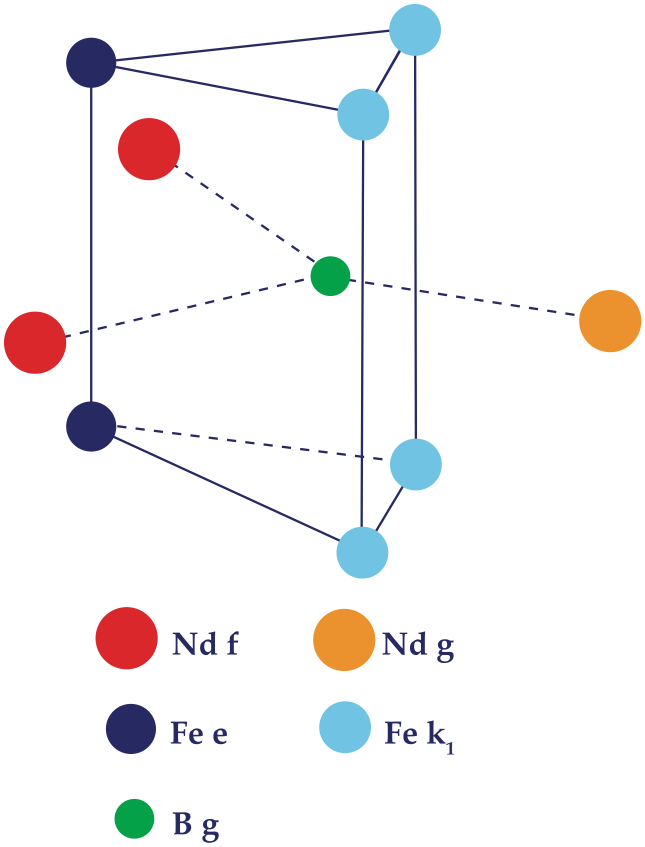

Figure 2 — Trigonal prism containing a boron atom in the $Nd_2Fe_{14}B$ structure. Distances between the B(*g*) atom and its nearest neighbors are B-Fe(k_1) = 2.09 Å, B-Fe(e) = 2.14 Å, B-Nd(*g*) = 2.86 Å, and B-Nd(*f*) = 3.34 Å. The vertical edge lengths are Fe(e) - Fe(e) = 2.75 Å, Fe(k_1) - Fe(k_1) = 3.12 Å. Distances in the triangular faces are Fe(e) - Fe(k_1) = 2.51 Å, Fe(k_1) - Fe(k_1) = 2.59 Å.

Finally, we emphasize two points. First, the $R_2Fe_{14}B$ phase forms with R = Ce, Pr, Sm, Gd, Tb, Dy, Ho, and Er in addition to Nd,[2] but large energy products have been achieved only with Pr and Nd.[1,2] Second, other investigators have prepared rare-earth-iron-boron materials either by powder metallurgy methods[11] or melt spinning;[12],[13],[14],[15] we believe that $R_2Fe_{14}B$ is the phase principally responsible for the high energy products observed, and that it is the compound whose stoichiometry has been tentatively identified as $R_3Fe_{16}B$ (Reference 16),[16] $R_3Fe_{21}B$ (Reference 17),[17] or $R_3Fe_{20}B$ (References 13 and 15).

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