parallel to (010), perpendicular to the Ca—H_2PO_4 chain. The cleavage planes parallel to (100) are consistent with the layer-type structures in this planar direction and the paucity of bonding between the layers.

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The Structure of a New Magnetic Phase Related to the Sigma Phase: Iron Neodymium Boride $Nd_2Fe_{14}B$

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Abstract. $M_r = 1081$, $P4_2/mnm$, $a = 8{\cdot}804\ (5)$, $c = 12{\cdot}205\ (5)$ Å, $V = 946{\cdot}0\ (9)$ Å^3, $Z = 4$, $F(000) = 1956$, $D_x = 7{\cdot}59\ (1)$ g cm^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu = 320$ cm^{-1}, $T = 293\ (2)$ K. Final $R = 0{\cdot}040$ (575 reflections $I > 2\sigma$). This is a new material of considerable current interest for making permanent magnets. The structure consists of layers of puckered sigma-phase-type nets (two main and one subsidiary layer) formed by Fe atoms, sandwiched between triangular nets in the mirror planes formed by Nd, Fe and B atoms. There are strings of alternating Nd and Fe (CN14) atoms parallel to the z axis corresponding to the rows of closely spaced CN14 atoms in the sigma phase. Our results agree with those of a recent neutron diffraction powder study [Herbst, Croat, Pinkerton & Yelon (1984). *Phys. Rev. B*, **29**, 4176–4178].

Introduction. The search for inexpensive materials for permanent magnets led Sagawa, Fujimura, Togawa, Yamamoto & Matsuura (1983) to the preparation of a material with the composition $Nd_{15}Fe_{77}B_8$, having high saturation magnetization and high magnetic anisotropy. The material was actually two-phase, with the main component a tetragonal phase of which they determined the cell dimensions. This tetragonal phase was subsequently prepared by one of us, RF (with Ph. l'Héritier), and a sample (of assumed composition $Nd_2Fe_{10}B$) was sent to CBS and DPS for structure determination since the powder pattern suggested a possible relationship to the σ phase (Bergman & Shoemaker, 1954). After completion of our crystal structure determination (which established that the composition actually was $Nd_2Fe_{14}B$) we learned that the crystal structure had been determined by powder neutron diffraction by Herbst, Croat, Pinkerton & Yelon (1984). The authors have kindly communicated to us their values of the atomic parameters, which are in essential agreement with ours, differing by 0·004 for Nd, at most 0·002 for Fe, and 0·009 for B (see Table 1).

Experimental. Crystal fragment, approximate dimensions $0{\cdot}12 \times 0{\cdot}06 \times 0{\cdot}04$ mm, Syntex $P\bar{1}$ diffractometer, graphite monochromator, Mo $K\alpha$ radiation, θ–2θ scan speed 1° min^{-1}, 2θ range 2·0° plus α_1,α_2

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angular separation. 15 reflections used for measuring lattice parameters. Ratio of background time to scan time 1:2, an octant of reciprocal space measured (h, $k = 0$–12, $l = 0$–16), $2\theta_{\max} = 60°$. Three standard reflections, intensity variation ±3·4%. 1458 reflections measured, 790 unique, 575 with $I > 2\sigma$ used in refinement. Reflections observed: $0kl$ only with $k + l = 2n$, highest-symmetry space group chosen and confirmed by refinement. Experimental absorption correction applied after isotropic refinement (Hope, undated), correction factors on F: 0·92–1·17. Structure solved by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) with 139 E values > 1·65 and 1029 phase relationships. E map with set of phases with highest combined figure of merit (RESID = 18·08) revealed all atoms except B, which was subsequently located on Fourier map. Full-matrix least-squares refinement, 49 parameters refined, Nd and Fe atoms with anisotropic thermal parameters, B isotropic (anisotropic temperature factor on B not positive-definite). Final $R = 0{\cdot}066$ (all 790 reflections), $R = 0{\cdot}040$ (575 reflections with $I > 2\sigma$), $R_w = 0{\cdot}042$, $S = 1{\cdot}34$. Computer programs: local versions of those of Zalkin (undated). Quantity minimized $\sum w(|F_o| - |F_c|)^2$ with $w^{-1} = C + Bt^2 + [0{\cdot}02(C - Bt)]^2$ [C is integrated count; B is total background count; t (= 2) is the ratio of scan time to background time]. $(\Delta/\sigma)_{\max} = 0{\cdot}055$ for x(B); $(\Delta/\sigma)_{\rm mean} = 0{\cdot}0035$. Final $\Delta\rho$ excursions $-2{\cdot}2$ to $+2{\cdot}2$ e Å^{-3} in the vicinity of Nd(2). Coefficients for analytical approximation to scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974).

Discussion. The final parameters are listed in Table 1 and the interatomic distances in Table 2.* The structure is related to the sigma phase (Bergman & Shoemaker, 1954) and may be described in terms of nets perpendicular to the z axis, as shown in Fig. 1. There are triangular nets formed by Nd(1), Nd(2), Fe(1) and B atoms in the mirror planes at $z = 0$ and $\frac{1}{2}$. The dotted lines indicate distances that are longer than 'bond distances' [B—Fe(1) = 3·49, B—Nd(2) = 3·25, B—B = 3·05 Å]. Between each pair of adjacent mirror planes are sandwiched two puckered sigma-phase main-layer-type nets ($z \simeq \frac{1}{8}$ and $\frac{3}{8}$), formed by Fe(2), Fe(3), Fe(5) and Fe(6) atoms, and one sigma-phase subsidiary-layer-type net ($z \simeq \frac{1}{4}$) formed by Fe(4) atoms. The coordinations and correspondences of the atoms with the sigma-phase atoms are given in Table 3.

Table 1. *Positional parameters and isotropic thermal parameters*

For Nd and Fe, $B_{\rm eq}$ is the arithmetic mean of the principal axes of the thermal ellipsoids. For each atom, the first line gives the present results, with positional parameters $\times 10^5$; the following line gives the results of Herbst *et al.* (1984) ($a = 8{\cdot}80$, $c = 12{\cdot}19$ Å), with positional parameters $\times 10^3$, derived by reversing the direction of their y axis and transforming to our part of the unit cell.

		x	y	z	$B_{\rm eq}/B$ (Å^2)
Nd(1)	4(f)	14278 (12)	14278	0	0·54 (3)
Nd(g)		139	139	0	
Nd(2)	4(g)	73016 (12)	26984	0	0·54 (3)
Nd(f)		734	266	0	
Fe(1)	4(c)	0	50000	0	0·56 (7)
Fe(c)		0	500	0	
Fe(2)	16(k)	72417 (22)	06755 (22)	37248 (14)	0·55 (4)
Fe(k_1)		724	068	372	
Fe(3)	16(k)	46273 (21)	14037 (22)	32374 (13)	0·56 (4)
Fe(k_2)		461	141	324	
Fe(4)	8(j)	18236 (23)	18236	25434 (20)	0·59 (5)
Fe(j_2)		182	182	253	
Fe(5)	8(j)	40210 (22)	40210	29551 (19)	0·54 (5)
Fe(j_1)		403	403	295	
Fe(6)	4(e)	0	0	38522 (26)	0·48 (7)
Fe(e)		0	0	387	
B	4(f)	37736 (305)	37736	0	1·40 (53)
B(g)		368	368	0	

Table 2. *Distances in* $Nd_2Fe_{14}B$ (Å)

Nd(1)	B	2·921 (38)	Fe(3)	2 Fe(3)	2·552 (3)
	4 Fe(2)	3·072 (3)		Fe(3)	2·557 (4)
	2 Fe(4)	3·143 (3)			
	4 Fe(3)	3·284 (2)			
	4 Fe(5)	3·298 (2)	Fe(4)	2 Fe(3)	2·636 (3)
	2 Fe(1)	3·387 (2)		2 Fe(5)	2·648 (3)
	Nd(1)	3·555 (3)		2 Fe(3)	2·661 (2)
	2 Nd(2)	3·801 (2)		2 Fe(2)	2·716 (3)
				2 Fe(2)	2·756 (3)
Nd(2)	2 Fe(4)	3·057 (3)		Fe(5)	2·782 (4)
	4 Fe(3)	3·073 (2)	Fe(5)	2 Fe(3)	2·390 (3)
	4 Fe(2)	3·075 (2)		Fe(5)	2·438 (6)
	2 Fe(1)	3·122 (1)		2 Fe(2)	2·594 (3)
	2 Fe(6)	3·190 (2)	Fe(6)	2 B	2·072 (28)
	2 B	3·247 (18)		4 Fe(2)	2·505 (2)
	2 Fe(5)	3·288 (3)		2 Fe(5)	2·520 (4)
				2 Fe(4)	2·776 (3)
Fe(1)	4 Fe(3)	2·503 (2)		Fe(6)	2·802 (7)
	4 Fe(2)	2·583 (2)	B	4 Fe(2)	2·116 (11)
Fe(2)	Fe(3)	2·462 (3)		B	3·054 (76)
	Fe(3)	2·520 (3)			
	Fe(3)	2·532 (3)			
	Fe(2)	2·593 (4)			

Table 3. *Coordinations of the atoms in* $Nd_2Fe_{14}B$ *and correspondences with sigma-phase-type atoms*

	CN		Sigma type	Sigma CN
Nd(1)	20	Hexagonal prism + 8	*E*	14
Nd(2)	18 + (2B)	Same; 2 B are farther away	*E*	14
Fe(1)	12	Icosahedron	—	—
Fe(2)	12	Icosahedron	*D*	12
Fe(3)	12	Icosahedron	*C*	14
Fe(4)	14	σ-type CN14	*E*	14
Fe(5)	12	Icosahedron	*B*	15
Fe(6)	12 + 1 Fe(6)	Icosahedron + 1	*A*	12
B	7 + 2	Trigonal prism + 1 + 2	—	—

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39528 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

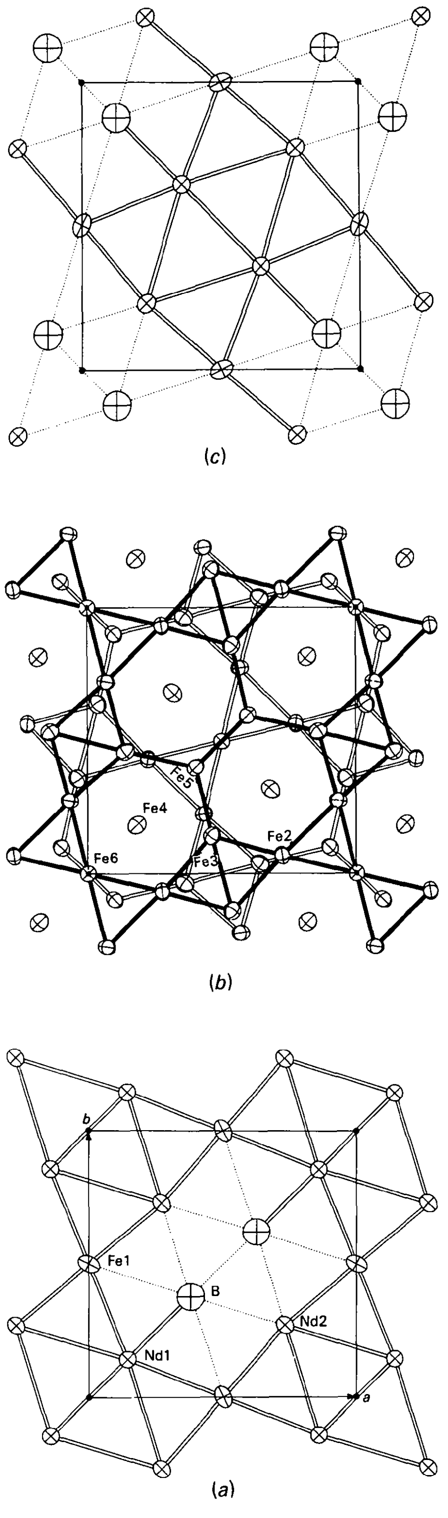

Fig. 1. *ORTEP*II projections (Johnson, 1976) of $Nd_2Fe_{14}B$ perpendicular to the z axis. Thermal ellipsoids at 99% probability. Boron isotropic. (a) Atoms in mirror plane at $z = 0$. (b) Atoms at $z \simeq \frac{1}{8}$ and $\frac{3}{8}$, and at $z \simeq \frac{1}{4}$ [Fe(4)]. The distances in Å of the marked atoms to the nearest mirror plane at $z = \frac{1}{2}$ are: Fe(2), 1·556; Fe(3), 2·151; Fe(4), 2·998; Fe(5), 2·496 and Fe(6), 1·401. (c) Atoms in mirror plane at $z = \frac{1}{2}$.

The coordination polyhedra of the Nd atoms are like those of the Ca atoms in $CaCu_5$ (*Strukturbericht* type $D2_d$), but for Nd(2) the two B atoms are at distances larger than 'bond distances'. The CN polyhedron of Fe(1) (which has no counterpart in the sigma phase) is an icosahedron, distorted to allow for larger distances to Nd. The Fe atoms corresponding with atoms A, B, C and D in the sigma phase (with CN respectively 12, 15, 14 and 12) all have distorted icosahedral environments in this structure. The icosahedron around the Fe(6) atom has one edge formed by two B atoms on the mirror plane above or below it. Another Fe(6), related to the first by the mirror plane, is close enough (2·80 Å) to be possibly considered a 'neighbor'. Fe(4) has a coordination very similar to that of the E atoms in the sigma phase. B is surrounded by six Fe atoms at the corners of a trigonal prism with one Nd(1) atom, and at somewhat larger distances two Nd(2) atoms, outside the quadrangular faces.

In the vertical direction there are infinite zigzag rows Nd(1)–Fe(4)–Nd(2)–Fe(4)–Nd(1)-. . ., with nearly linear Nd(1)–Fe(4)–Nd(2) segments. These rows correspond to the closely spaced straight vertical rows of E atoms in the sigma phase. [Similar straight rows of CN14 atoms occur in the directions of the cube axes in the Cr_3Si (β-W or $A15$) structure.] The hexagons of the sigma-phase-type nets perpendicular to these zigzag lines are almost planar, but are tilted in such a way that the nets are puckered. This results from the relative inclinations of the straight segments of the vertical zigzag rows, which lean inward toward the center in the lower half of the unit cell, and outward in the upper half (see Fig. 2).

The arrangement of triangular nets in this structure, and the sigma-phase nets above and below it, resembles the arrangement of layers in the $CaCu_5$ ($D2_d$) structure, which is the structure adopted by many compounds between rare earths and transition metals, among them the permanent-magnet material $SmCo_5$. In these compounds the rare-earth atom is surrounded by six

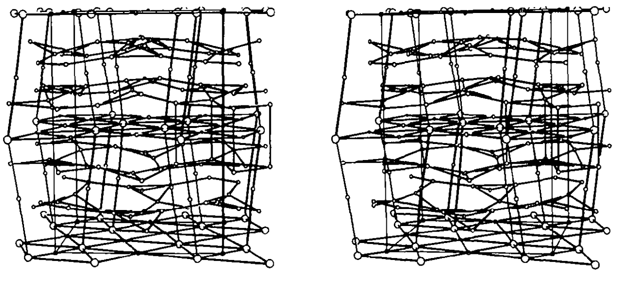

Fig. 2. *ORTEP*II stereoview (Johnson, 1976) of $Nd_2Fe_{14}B$. The z axis is vertical in the paper. Atoms are represented by spheres of arbitrary size, increasing in radius from B to Fe to Nd. Two trigonal prisms (sharing an edge) surrounding two B atoms are outlined in the middle right of the figure.

transition metal atoms in the plane and six above and below it in planar kagomé nets (*i.e.* nets with only 3636 tessellations). In the present structure there are in the mirror planes rhombs formed by Nd atoms which are surrounded by B and Fe atoms. The sigma-phase nets (which contain 3636, 6^3, and 3^26^2 tessellations) above and below the mirror plane are severely puckered in such a way that Fe(6) (which is above and below a B—B connected line) is 1·1 Å closer to that plane than the pair of Fe(5) atoms (which lies above and below the Nd rhomb).

The structure of $Nd_2Fe_{14}B$ also resembles that of Mn_5SiC (Spinat, Fruchart, Kabbani & Herpin, 1970), which consists of two layers and one subsidiary layer of Laves-type structure ($MgZn_2$, C14), sandwiched between mirror planes which are less densely populated by Mn and C atoms. In this case the puckered sigma-phase nets in $Nd_2Fe_{14}B$ consisting of *hexagons* and triangles are replaced by less puckered nets of *pentagons* and triangles which occur in $MgZn_2$ perpendicular to [110] (Shoemaker & Shoemaker, 1967). In both cases the 'interstitial' atoms (B in $Nd_2Fe_{14}B$ and C in Mn_5SiC) are in trigonal prisms connecting pairs of double layers together.

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A New Ordered Structure of the *C*15-Type Laves Phase, $Mg_{28.4}Cu_{57.9}Si_{13.7}$

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Abstract. $M_r/100 = 47·54$, cubic, space group $P4_132$ (or $P4_332$), $a = 6·9598\,(4)$ Å, $V = 337·12$ Å^3, $D_m = 5·66\,(2)$, $D_x = 5·62$ Mg m^{-3}, 24 atoms per unit cell, $\lambda(\text{Mo } K\alpha) = 0·7107$ Å, $\mu(\text{Mo } K\alpha) = 22·8$ mm^{-1}, $F(000) = 530·7$, $R(F) = 0·046$ for 82 independent reflections, room temperature. A new ordered structure of the Laves phase was found at the off-stoichiometric composition Mg_2Cu_3Si. The structure is characterized by ordered fourfold screw arrangements of Cu and Si atoms located on four tetrahedra in the unit cell leaving Mg atoms on 8(*c*) sites. The order parameter $S = \alpha_1 - \alpha_2$ is estimated from the refinement of the structure to be 0·74 in this specimen; α_1 and α_2 are the occupancy factors of Cu on sites 12(*d*) and 4(*a*) of $P4_132$, respectively.

Introduction. Laves phases are classified into the three fundamental structures *C*14, *C*15 and *C*36 which are typified by $MgZn_2$, $MgCu_2$ and $MgNi_2$, respectively. These structures were analyzed by Friauf (1927*a,b*) and Laves & Witte (1935). The pseudo-binary system $MgCu_2$–$MgSi_2$ has been studied thoroughly by Witte (1939). In this system the terminal solid solution of the cubic *C*15 type ($MgCu_2$ structure) extends from $MgCu_2$ to 20% $MgSi_2$; the hexagonal *C*14 type ($MgZn_2$ structure) then follows in the range 25–35% $MgSi_2$. The structure of the latter phase whose ideal composition is Mg_2Cu_3Si has shown an ordered arrangement of Cu and Si in the 6(*h*) and 2(*a*) sites, respectively, in $P6_3/mmc$. Moreover, a disordered *C*36-type structure was found as a high-temperature phase of the Mg_2Cu_3Si compounds. Witte (1939) also found a compound ($Mg_6Cu_{16}Si_7$) having the $D8_a$-type structure away from the pseudo-binary section of MgX_2. Ellner & Predel (1979) have carried out X-ray and neutron

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