

Crystal structure and magnetic properties of $\text{CoR}(\text{BO}_2)_5$ ($\text{R} \equiv \text{Y}, \text{Gd}$) and $\text{NiR}(\text{BO}_2)_5$ ($\text{R} \equiv \text{Nd}, \text{Gd}$)

J.A. Campá^a, C. Cascales^b, E. Gutiérrez Puebla^{b,c}, J. Mira^d, M.A. Monge^{b,c},
I. Rasines^{b,*}, J. Rivas^d, C. Ruíz Valero^{b,c}

^a Facultad de Ciencias Geológicas, UCM, 28040 Madrid, Spain

^b Instituto de Ciencia de Materiales, CSIC, Serrano 113, 28006 Madrid, Spain

^c Laboratorio de Difracción de Rayos X y Cristalografía, Facultad de Ciencias Químicas, UCM, 28040 Madrid, Spain

^d Departamento de Física Aplicada, Facultad de Física, Universidad de Santiago de Compostela, 15706 Santiago de Compostela, Spain

Abstract

Single crystals of the title borates were grown from mixtures of R_2O_3 , NiO or Co_3O_4 and a large excess of B_2O_3 . Single-crystal X-ray diffraction showed them to be monoclinic, centrosymmetric space group $P2_1/n$ (No. 14), $Z=4$, with cell parameters (in ångströms) $a=8.494(2)$ and $8.560(4)$, $b=7.574(2)$ and $7.578(2)$, $c=9.364(6)$ and $9.370(2)$, and $\beta=94.03(3)^\circ$ and $93.35(3)^\circ$ for Co borates and $\text{R} \equiv \text{Y}$ and Gd respectively; the parameters were $a=8.617(2)$ and $8.514(6)$, $b=7.565(3)$ and $7.554(3)$, $c=9.472(2)$ and $9.4329(6)$, and $\beta=93.46(1)^\circ$ and $93.81(2)^\circ$ for Ni borates and $\text{R} \equiv \text{Nd}$ and Gd respectively. The crystals studied by X-ray diffraction were analyzed using energy-dispersive X-ray spectroscopy. Magnetic measurements were taken from 300 to 4 K for the four borates.

Keywords: Rare-earth borates; Nickel borates; Cobalt borates; Crystal structure; Magnetic susceptibility

1. Introduction

First-row transition metals T can combine with rare earths R ($\text{R} \equiv \text{Y}, \text{La}, \text{Ce-Lu}$), forming T–R intermetallics, borides, carbides, silicides, nitrides, phosphides, oxides, chalcogenides. At present all these T–R compounds are being studied extensively because some of them show very interesting transport, magnetic and optical properties, which can be related with the 3d and 4f band structure and interactions. A good number of the T–R compounds find applications, for example, as superconducting materials or permanent magnets, and as devices for magneto-optical recording or miniature lasers. The authors, who are interested in studying structure–property relationships in novel compounds, have just described [1] the properties of the stoichiometric $\text{BaNi}_{0.83}\text{O}_{2.5}$ oxide as a function its crystal structure, and have recently undertaken the task of reducing the lack of structural data established [2] on single crystals of T–R borates, with a view to studying their magneto-optical properties. Together with some

structural data determined for polycrystalline samples, only the crystal structure of six T–R borates of composition $\text{RCo}(\text{BO}_2)_5$ ($\text{R} \equiv \text{Y}, \text{La}, \text{Nd}, \text{Sm}, \text{Ho}, \text{Yb}$) is well established by single-crystal X-ray diffraction [2]. In this paper we present two crystal-structure refinements and the results of magnetic measurements for the four title borates.

2. Experimental details

2.1. Crystal growth

Analytical grade R_2O_3 , NiO or Co_3O_4 and a large excess of B_2O_3 were melted in open platinum crucibles, maintained in air at 1000°C during 3 h and cooled at 3°C h^{-1} . After being washed with dilute nitric acid, dried and filtered, the grown crystals were separated mechanically from the non-crystalline remaining borate.

2.2. Data collection

The four crystals were mounted successively in a kappa Enraf-Nonius CAD4 diffractometer. The cell

* Corresponding author.

Table 1

Crystal and refinement data for $\text{NiR}(\text{BO}_2)_5$ ($\text{R} \equiv \text{Nd, Gd}$)

Formula	$\text{NiNd}(\text{BO}_2)_5$	$\text{NiGd}(\text{BO}_2)_5$
Formula weight	416.99	429.99
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Cell dimensions		
a (Å)	8.617(4)	8.514(6)
b (Å)	7.565(3)	7.554(3)
c (Å)	9.472(1)	9.4429(6)
α (deg)	90	90
β (deg)	93.46(1)	93.81(2)
γ (deg)	90	90
Z	4	4
V (Å ³)	616.3(3)	605.3(5)
ρ_{calc} (g cm ⁻³)	4.5	4.7
$F(000)$	772	788
Temp. (°C)	295	295
Radiation	Graphite-monochromated Mo $K\alpha$	Graphite-monochromated Mo $K\alpha$
λ (Å)	0.71069	0.71069
$\mu(\text{Mo } K\alpha)$ (cm ⁻¹)	114.9	141.0
Crystal dimensions (mm)	0.08 × 0.1 × 0.13	0.25 × 0.1 × 0.15
2θ range (deg)	2–52	2–50
Scan technique	$\omega/2\theta$	$\omega/2\theta$
Data collected	(0,0,11) to (10,9,11)	(0,0,11) to (10,9,11)
Unique data	1206	1057
Observed reflections	1168	1030
R_{int} (%)	4.0	8.0
Standard reflections	2/20	2/16
$R = \sum \Delta^2 F / \sum F_o $	3.4	4.6
$R_w = (\sum w \Delta^2 F / \sum w F_o ^2)^{1/2}$	3.7	5.8
Maximum shift/error	0.01	0.07
Absorption correction range	0.77–1.64	0.95–1.04

dimensions were refined by least-squares fitting the 2θ values of 25 reflections. The structure was refined for the Ni compounds. A summary of the fundamental data is given in Table 1. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Ni, Nd and Gd atoms were taken from Ref. [3].

2.3. Structure determination

In both structures the refinement was initiated with data from Ref. [4]. Empirical absorption corrections [5] were applied at the end of the isotropic refinements. Mixed full-matrix least-squares refinements minimizing $\sum w(|F_o| - |F_c|)^2$ with anisotropic temperature factors for all the atoms and weights [6] $w = 1/(a + b|F_o|)^2$ where $a = 2.47$, $b = -0.03$ if $|F_o| < 36$, and $a = 0.69$, $b = 0.02$ if $36 < |F_o| < 250$, for $\text{R} \equiv \text{Nd}$; $a = 1.37$, $b = 0.02$ if $0 < |F_o| < 300$ for $\text{R} \equiv \text{Gd}$. Most of the calculations were carried out with the X-RAY 80 system [7].

2.4. Magnetic measurements

SQUID (quantum design) and vibrating sample (DMS-1660) magnetometers, operating from 300 to 4

K under zero-field cooling conditions at various fields between 0 and 1000 Oe, were used for the magnetic measurements.

3. Results

Some crystals were up to 4 mm in size and all of them showed regular forms, more often prismatic. The Co compounds are purple ($\text{R} \equiv \text{Y}$) and garnet ($\text{R} \equiv \text{Gd}$); the Ni compounds are vermilion ($\text{R} \equiv \text{Nd}$) and transparent red ($\text{R} \equiv \text{Gd}$). Unit cell dimensions of all title compounds are given in Table 2. Atomic position coordinates and anisotropic thermal parameters as well as main interatomic distances and angles for both

Table 2

Unit cell dimensions of $\text{CoR}(\text{BO}_2)_5$ ($\text{R} \equiv \text{Y, Gd}$) and $\text{NiR}(\text{BO}_2)_5$ ($\text{R} \equiv \text{Nd, Gd}$), space group $P2_1/n$, $Z = 4$

3d	R	a (Å)	b (Å)	c (Å)	β (deg)
Co	Y	8.494(2)	7.574(2)	9.364(6)	94.03(3)
Co	Gd	8.560(4)	7.578(2)	9.370(3)	93.35(3)
Ni	Nd	8.617(2)	7.565(3)	9.472(2)	93.46(1)
Ni	Gd	8.514(6)	7.554(3)	9.4329(6)	93.81(2)

$\text{NiR}(\text{BO}_2)_5$, $\text{R} \equiv \text{Nd, Gd}$, are included in Tables 3–5. The basic structure is composed of $[\text{B}_5\text{O}_{10}]^{5-}$ anionic layers that crosslink the Co or Ni octahedra and the RO_{10} polyhedra. Infinite sheets of $[\text{B}_5\text{O}_{10}]^{5-}$ are composed of three sets of BO_4 tetrahedra and two types of BO_3 planar triangles, joined by common corners. Although the triangles are not linked to one another, they play a bridging role for BO_4 tetrahedra. Fig. 1 shows the tetrahedra and triangular $[\text{B}_5\text{O}_{10}]^{5-}$ framework, and its mode of linkage. The R–O distances are markedly differentiated in value, typically between 2.3 and 2.9 Å. RO_{10} distorted polyhedra are linked via common edges forming chains along the *b*-axis. The CoO_6 or NiO_6 octahedra are also largely deformed, the Co–O and Ni–O distances ranging from 2.0 to 2.4 Å. These octahedra are joined two by two sharing one common edge, giving rise to isolated $[\text{Ni}_2\text{O}_{10}]$ units, so

Table 3

Atomic coordinates and thermal parameters for $\text{NiNd}(\text{BO}_2)_5$, esds in parentheses, $U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j 10^4$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Nd	0.18125(3)	0.18066(4)	0.23628(3)	40(1)
Ni	0.60261(9)	0.41130(9)	0.12737(8)	59(2)
O1	0.0322(5)	0.7117(6)	0.2355(5)	85(12)
O2	0.8123(5)	0.5357(6)	0.1299(5)	66(11)
O3	0.9852(5)	0.4116(5)	0.3059(5)	72(11)
O4	0.8158(5)	0.6538(6)	0.3654(5)	70(11)
O5	0.5847(5)	0.4722(6)	0.3515(4)	63(11)
O6	0.3267(5)	0.3916(5)	0.4180(4)	46(11)
O7	0.5426(5)	0.2251(6)	0.5134(4)	55(11)
O8	0.8162(5)	0.3749(6)	0.4908(4)	63(11)
O9	0.4969(5)	0.6514(6)	0.0695(4)	60(11)
O10	0.2381(5)	0.4514(6)	0.1195(5)	75(11)
B1	0.9131(8)	0.5785(8)	0.2599(6)	43(16)
B2	0.4820(8)	0.3239(8)	0.3924(7)	60(17)
B3	0.7202(7)	0.5355(8)	0.4447(6)	26(15)
B4	0.8414(8)	0.5987(9)	−0.0007(7)	61(16)
B5	0.9312(8)	0.3126(8)	0.4130(7)	55(17)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nd	40(2)	41(2)	39(2)	3(1)	3(1)	9(1)
Ni	56(4)	55(4)	68(4)	3(3)	2(3)	−5(3)
O1	93(21)	75(19)	85(20)	−9(17)	−5(16)	11(16)
O2	48(19)	80(20)	71(20)	−20(16)	−4(15)	16(16)
O3	87(19)	42(20)	90(20)	−4(16)	33(15)	8(15)
O4	81(20)	27(18)	103(20)	−30(16)	3(16)	−13(15)
O5	63(19)	72(20)	53(19)	−21(16)	9(15)	32(15)
O6	49(18)	49(19)	40(18)	5(15)	8(14)	−32(15)
O7	48(18)	51(18)	71(19)	3(16)	31(14)	−10(16)
O8	49(18)	73(20)	68(19)	35(16)	18(15)	−3(16)
O9	47(19)	61(19)	70(19)	0(16)	−21(15)	0(15)
O10	82(19)	49(19)	92(20)	−20(16)	−19(15)	−15(16)
B1	63(27)	57(28)	7(26)	21(23)	−16(21)	0(21)
B2	52(29)	44(29)	85(30)	−29(22)	19(23)	−16(23)
B3	45(27)	25(27)	9(26)	8(23)	8(21)	12(22)
B4	49(28)	61(29)	77(29)	−18(23)	32(22)	−34(23)
B5	60(29)	52(30)	52(28)	−7(21)	−9(23)	−4(21)

Table 4

Atomic coordinates and thermal parameters for $\text{NiGd}(\text{BO}_2)_5$, esds in parentheses, $U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j 10^4$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Gd	0.18184(3)	0.17984(6)	0.23750(5)	106(2)
Ni	0.6004(1)	0.4098(2)	0.1282(1)	121(4)
O1	0.0358(9)	0.7100(11)	0.2320(9)	177(22)
O2	0.8112(9)	0.5358(9)	0.1246(8)	147(20)
O3	0.9873(8)	0.4067(10)	0.3004(8)	144(21)
O4	0.8175(9)	0.6529(10)	0.3633(7)	118(20)
O5	0.5851(8)	0.4713(9)	0.3498(7)	122(19)
O6	0.3234(8)	0.3903(9)	0.4190(7)	131(20)
O7	0.5446(8)	0.2264(10)	0.5181(7)	100(19)
O8	0.8190(8)	0.3745(10)	0.4896(7)	113(19)
O9	0.4937(9)	0.6514(9)	0.0715(8)	120(20)
O10	0.2427(8)	0.4443(10)	0.1244(8)	151(20)
B1	0.9157(13)	0.5730(15)	0.2564(11)	114(29)
B2	0.4827(14)	0.3231(14)	0.3945(13)	123(32)
B3	0.7214(13)	0.5348(15)	0.4438(13)	144(31)
B4	0.8373(13)	0.6017(16)	−0.0038(13)	146(32)
B5	0.9325(15)	0.3114(15)	0.4118(14)	147(33)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nd	106(4)	106(4)	107(4)	1(2)	10(2)	11(2)
Ni	120(7)	103(7)	140(7)	−2(4)	8(5)	−8(5)
O1	136(38)	185(35)	216(39)	−20(30)	49(30)	−4(32)
O2	174(37)	88(33)	179(35)	24(26)	6(29)	−17(28)
O3	114(33)	123(35)	205(38)	−21(27)	84(28)	32(28)
O4	146(35)	118(33)	96(33)	−27(28)	52(27)	3(27)
O5	161(35)	45(32)	152(33)	19(26)	−48(28)	34(26)
O6	126(35)	120(36)	145(35)	−17(27)	−1(27)	−9(27)
O7	106(32)	79(32)	122(33)	−24(26)	50(25)	5(28)
O8	89(32)	156(35)	97(32)	−4(27)	36(25)	43(27)
O9	170(37)	53(30)	130(36)	−11(26)	−36(29)	21(26)
O10	113(35)	190(37)	144(34)	−12(27)	−35(27)	30(29)
B1	147(51)	151(50)	52(46)	86(43)	63(38)	−6(39)
B2	140(56)	127(58)	113(52)	−33(39)	85(42)	−26(40)
B3	98(50)	132(54)	196(54)	−54(40)	−35(43)	77(44)
B4	85(50)	169(61)	193(55)	−28(42)	71(42)	−85(44)
B5	140(57)	120(58)	177(56)	−64(41)	−25(44)	−41(41)

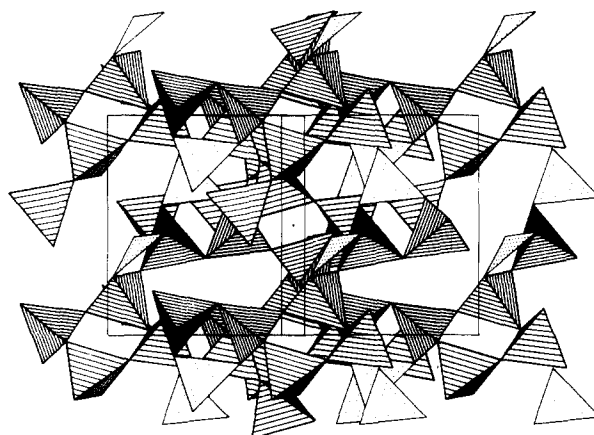


Fig. 1. STRUPLO [8] perspective along the $[101]$ direction of the borate framework in the $\text{RNi}(\text{BO}_2)_5$ structure, with BO_4 tetrahedra and BO_3 triangles.

Table 5
Main interatomic distances (ångströms) and angles (deg) in $\text{NiR}(\text{BO}_2)_5$

	R $\equiv$ Nd	R $\equiv$ Gd
R–O1 ¹	2.479(4)	2.413(8)
R–O3 ²	2.544(4)	2.482(7)
R–O5 ¹	2.864(4)	2.842(7)
R–O6	2.612(4)	2.577(7)
R–O6 ¹	2.629(4)	2.638(7)
R–O7 ³	2.468(4)	2.414(7)
R–O8 ³	2.695(4)	2.714(7)
R–O9 ¹	2.476(4)	2.426(7)
R–O10	2.393(4)	2.339(8)
R–O10 ¹	2.290(4)	2.272(7)
Ni–O1 ¹	2.345(4)	2.358(8)
Ni–O2	2.036(4)	2.034(7)
Ni–O4 ⁵	2.071(4)	2.063(8)
Ni–O5	2.187(4)	2.154(7)
Ni–O9	2.090(4)	2.092(7)
Ni–O9 ⁴	2.060(4)	2.051(7)
B1–O1 ⁶	1.466(8)	1.48(1)
B1–O2	1.500(7)	1.51(1)
B1–O3	1.462(8)	1.44(1)
B1–O4	1.458(8)	1.48(1)
B2–O1 ¹	1.478(8)	1.47(1)
B2–O5	1.495(8)	1.50(1)
B2–O6	1.467(8)	1.48(1)
B2–O7	1.439(8)	1.44(1)
B3–O4	1.455(8)	1.46(1)
B3–O5	1.499(7)	1.49(1)
B3–O6 ⁷	1.490(7)	1.48(1)
B3–O8	1.518(7)	1.51(1)
B4–O2	1.363(8)	1.34(1)
B4–O10 ⁴	1.337(8)	1.33(1)
B4–O7 ⁸	1.393(8)	1.39(1)
B5–O3	1.365(8)	1.38(1)
B5–O8	1.355(8)	1.34(1)
B5–O9 ⁵	1.373(7)	1.37(1)

	R $\equiv$ Nd	R $\equiv$ Gd		R $\equiv$ Nd	R $\equiv$ Gd
O1 ¹ –Ni–O2 ²	139.4(2)	140.9(3)	O1 ¹ –B2–O5	103.8(5)	103.9(9)
O1 ¹ –Ni–O4 ⁵	63.5(2)	63.5(5)	O1 ¹ –B2–O6	107.8(8)	106.1(8)
O1 ¹ –Ni–O5	62.1(2)	62.1(3)	O1 ¹ –B2–O7	111.2(5)	112.0(8)
O1 ¹ –Ni–O9	118.8(2)	118.7(3)	O5–B2–O6	109.9(5)	110.1(8)
O1 ¹ –Ni–O9 ⁴	99.2(2)	101.1(3)	O5–B2–O7	113.8(5)	114.7(9)
O2–Ni–O4 ⁵	97.7(2)	98.3(3)	O6–B2–O7	109.9(5)	109.6(9)
O2–Ni–O5	90.3(2)	91.5(3)			
O2–Ni–O9	88.5(2)	87.5(3)	O4–B3–O5	109.7(4)	109.2(8)
O2–Ni–O9 ⁴	116.0(2)	112.4(3)	O4–B3–O6 ⁷	114.5(4)	114.0(8)
O4 ⁵ –Ni–O5	102.1(2)	102.0(3)	O4–B3–O8	109.0(4)	108.7(8)
O4 ⁵ –Ni–O9	165.4(2)	166.2(3)	O5–B3–O6 ⁷	112.9(4)	113.9(8)
O4 ⁵ –Ni–O9 ⁴	86.3(2)	86.2(3)	O5–B3–O8	107.8(4)	107.6(8)
O5–Ni–O9	90.9(2)	90.4(3)	O6 ⁷ –B3–O8	102.5(4)	102.9(8)
O5–Ni–O9 ⁴	151.3(2)	153.5(3)			
O9–Ni–O9 ⁴	79.1(2)	79.9(3)	O2–B4–O10 ⁴	123.5(5)	125(1)
			O2–B4–O7 ⁸	119.4(5)	120.2(9)
O1 ⁶ –B1–O2	113.2(5)	112.2(8)	O10 ⁵ –B4–O7 ⁸	117.1(5)	115(1)
O1 ⁶ –B1–O3	110.6(5)	111.6(8)			
O1 ⁶ –B1–O4	106.1(5)	104.3(8)	O3–B5–O8	120.4(5)	121.6(9)
O2–B1–O3	105.8(4)	106.8(8)	O3–B5–O9 ⁵	113.9(5)	112(1)
O2–B1–O4	108.6(5)	108.0(8)	O8–B5–O9 ⁵	125.6(6)	126(1)
O3–B1–O4	112.6(5)	113.9(8)			

Symmetry code: (1) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (2) $1-x, y, z$; (3) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (4) $1-x, 1-y, -z$; (5) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (6) $1+x, y, z$; (7) $1-x, 1-y, 1-z$; (8) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

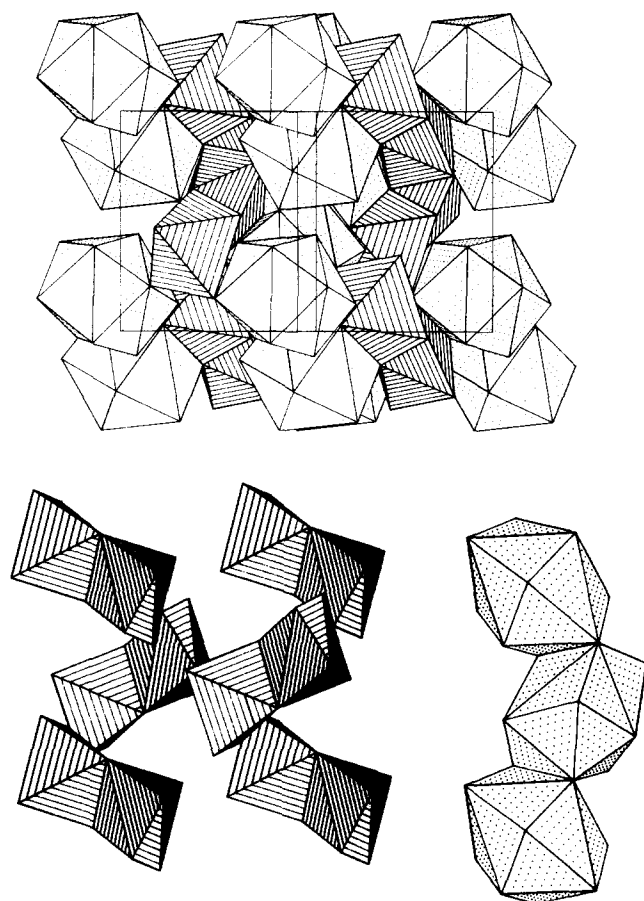


Fig. 2. STRUPLO [8] view along the [101] direction of the structure $\text{RNi}(\text{BO}_2)_5$ showing the assembly of edge-sharing R-coordination polyhedra and Ni octahedra. The borate groups have been removed for clarity. The inset shows various isolated $[\text{Ni}_2\text{O}_{10}]$ units (left), and the RO_{10} chains (right).

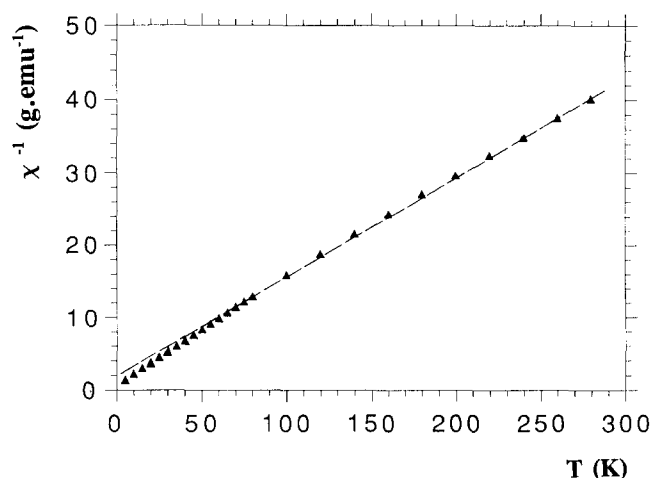


Fig. 3. Reciprocal magnetic susceptibility χ^{-1} vs. temperature, at 1000 Oe, for $\text{NiNd}(\text{BO}_2)_5$.

that the NiO_6 octahedra chains along the b axis are, in fact, interrupted every two links (see the inset to Fig. 2). The Ni–Ni distances in the $[\text{Ni}_2\text{O}_{10}]$ units are 3.199(1) and 3.175(2) Å in the Nd and Gd compounds,

and the shortest Ni–R distances are 3.491(1) and 3.456(2) Å, for R≡Nd and Gd respectively.

The d.c. magnetic susceptibilities of the four borates follow a Curie–Weiss law almost above 75 K, with Weiss constants $\theta=7.5$ and 2.9 for the Co compounds with R=Y, Gd, respectively, and $\theta=-7.5$ and -2.2 K for the Ni compounds and R=Nd, Gd. The deviation from the linearity observed at low temperature in the inverse susceptibility vs. T plot (Fig. 3) for NiNd(BO₂)₅ could be due to a magnetic coupling between Ni and Nd moments, although more frequently it is attributed [9] to the splitting of the free-ion ground state under the influence of the crystal field. The Weiss constant could then be entirely due to the crystal field. For the remaining compounds, magnetic measurements in the same temperature range show no appreciable deviations from paramagnetic behavior: the crystal field appears not to have an important influence on the ground states of the rare earths present in those borate compounds.

References

- [1] J.A. Campá, E. Gutiérrez Puebla, M.A. Monge, I. Rasines and C. Ruíz Valero, *J. Solid State Chem.*, 108 (1994) 230.
- [2] G. Heller, in F.L. Boschke (ed.), *Topics in Current Chemistry*, Vol. 131, Springer, Berlin, 1986, p. 39.
- [3] D.T. Cromer and J.T. Waber, in J.A. Ibers and W.C. Hamilton (eds.), *International Tables for X-Ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, 1974, pp. 99, 149.
- [4] G.G. Dzhaferov, G.K. Abdullaev and Kh.S. Mamedov, *Azerb. Khim. Zh.*, (1985) 110.
- [5] N. Walker and D. Stuart, *Acta Crystallogr. A*, 39 (1983) 158.
- [6] M. Martínez-Ripoll and F.H. Cano, *PESOS Program*, Instituto Rocasolano, CSIC, Madrid, 1975.
- [7] J.M. Stewart, F.A. Kundell and J.C. Baldwin, *The X-Ray 80 System*, Computer Science Center, University of Maryland, College Park, MD, 1980.
- [8] R.X. Fischer, *J. Appl. Crystallogr.*, 18 (1985) 258.
- [9] E. Antic-Fidancev, J. Aride, J.P. Chaminade, M. Lemaitre-Blaise and P. Porcher, *J. Solid State Chem.*, 97 (1992) 74.