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Crystal chemistry and physical properties of the ternary compounds $RE_5B_4C_5$ ($Re = Ce, Pr, Nd$)

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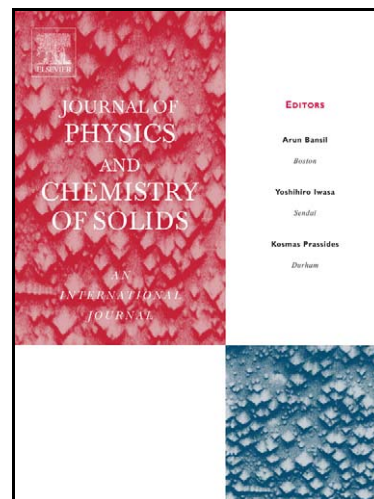
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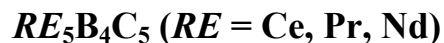
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Crystal chemistry and physical properties of the ternary compoundsVolodymyr Babizhetskyy^{a,*}, Kurt Hiebl^b, Hansjürgen Mattausch^a, and Arndt Simon^a

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Abstract

The ternary rare-earth metal boride carbides $RE_5B_4C_5$ ($RE = Ce, Pr, Nd$) were prepared by arc melting the mixtures of the pure elements and subsequent annealing at 1270 K. Their crystal structures were determined from single crystal X-ray diffraction data. They crystallize in the $Ce_5B_4C_5$ type of structure (space group $Pna2_1$, $Z=8$). Two new compounds were found, $Pr_5B_4C_5$: $a = 24.592(2)$ Å, $b = 8.4563(5)$ Å, $c = 8.4918(5)$ Å, $R1 = 0.043$ ($wR2 = 0.076$) for 2871 reflections with $I_0 \geq 2\sigma(I_0)$; for $Nd_5B_4C_5$: $a = 24.301(1)$ Å, $b = 8.3126(5)$ Å, $c = 8.3545(4)$ Å, $R1 = 0.035$ ($wR2 = 0.069$) for 3707 reflections with $I_0 \geq 2\sigma(I_0)$. Its structural arrangement consists of a three-dimensional framework of rare earth atoms resulting from the stacking of slightly corrugated two-dimensional square nets, leading to voids filled with B_4C_4 , B_3C_3 , BC_2 finite chains and isolated carbon atoms. $Ce_5B_4C_5$ is an antiferromagnet at 5 K followed by a metamagnetic transition in elevated external fields. $Pr_5B_4C_5$ and $Nd_5B_4C_5$ are ferromagnets below $T_C = 12$ K and 15 K, respectively.

Keywords: Rare-earth metal boride carbides; Crystal structure; Magnetism; Resistivity.

1. Introduction

Several ternary rare-earth (*RE*) metal boride carbides $RE_xB_yC_z$ have been characterized in recent years. The structures of the $RE_xB_yC_z$ display a variety of different arrangements with boron carbon substructures ranging from zero-dimensional units to one- and two-dimensional networks alternating with metal atom sublattices as well as interconnected boron icosahedra [1-4]. Several structural types have been reported for the most electron-rich compounds, so far, i.e., those containing finite quasi-molecular entities. These units embedded in the voids of the metal atom matrix can have different lengths ranging from 2 to 13 non-metal atoms, and also isolated C atoms may coexist. Such a broad diversity of unusual topologies, especially with respect to the bonding within the non-metal atom frameworks, has rendered these compounds of special interest for theoretical chemists who studied their electronic properties in detail. In contrast, little is known about the magnetic behaviour of this category of compounds. Magnetic measurements have been performed earlier for the $RE_5B_2C_5$ compounds ($RE = Y, Ce-Tm$). These prove that all $RE_5B_2C_5$ involving magnetic *RE* atoms undergo ferromagnetic transitions in the temperature region below 130 K. The heavy rare-earth metal (Tb-Tm) boride carbides exhibit a magnetic behaviour typical of narrow domain-wall ferromagnets [5]. The related series of compounds $RE_5B_2C_6$ ($RE = Pr-Tm$) also undergo ferromagnetic transitions, with the exception of $Gd_5B_2C_6$, which is a meta-magnet (Néel temperature $T_N \sim 27$ K) [6]. For $La_5B_2C_6$ the metallographic, analytical and structural investigations together with measurements of magnetic behaviour and specific heat clearly show that superconductivity is not an intrinsic property of this compound. Diamagnetic shielding observed below ~ 6 K must rather be ascribed to precipitations of a boron-containing

$\text{La}_2\text{C}_{3-\delta}$ phase in the carbon-rich region and/or α - or β -La in the metal-rich region. For example, the complete coverage of boride carbide crystallites by La precipitates can lead to the observed total diamagnetic shielding of the samples [7]. Magnetic measurements have been performed recently also for the $RE_{10}\text{B}_9\text{C}_{12}$ ($RE = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$). $\text{La}_{10}\text{B}_9\text{C}_{12}$ is a temperature independent paramagnet down to 6 K. The remaining compounds show a tendency of ferromagnetic ordering at $T < 10$ K at elevated external fields (induced ferromagnets). The electrical resistivity for $\text{Ce}_{10}\text{B}_9\text{C}_{12}$ reveals a weak metal-like temperature dependence below room temperature. From heat capacity measurements it has been concluded that the magnetic order is rather a short range type ordering and field induced in case of $\text{Ce}_{10}\text{B}_9\text{C}_{12}$ and $\text{Pr}_{10}\text{B}_9\text{C}_{12}$ [8].

Recently we have reported about the crystal structure of $\text{La}_5\text{B}_4\text{C}_5$ [9]. This work reports on the synthesis, crystal structures of two new compounds $\text{Pr}_5\text{B}_4\text{C}_5$ and $\text{Nd}_5\text{B}_4\text{C}_5$ also physical properties of a series of ternary rare-earth metal boride carbides with composition $RE_5\text{B}_4\text{C}_5$ ($RE = \text{Ce}, \text{Pr}, \text{Nd}$) adopting the $\text{Ce}_5\text{B}_4\text{C}_5$ type of structure [10].

2. Experimental

2.1. Synthesis

The phases $RE_5\text{B}_4\text{C}_5$ ($RE = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$) were prepared from commercially available pure elements: rare earth metals with a purity of 99.99 at%, (Alfa – Aesar, Johnson Matthey Company, sublimed bulk pieces) crystalline boron powder, purity 99.99 at% (H.C. Starck, Germany) graphite powder, purity 99.98 at% (Aldrich). The graphite and boron powders were outgassed overnight at 950°C and $p < 10^{-5}$ mbar beforehand. All

handlings were carried out by Schlenk-technique or in a dry-box. The rare earth metals were filed to coarse powders with beryllium bronze files (Dönges GmbH, Germany). Stoichiometric mixtures of the constituents were compacted in stainless steel dies. The pellets were arc-melted under purified argon atmosphere [11] on a water-cooled copper hearth. The buttons of ~1g were turned over and remelted typically three times to improve homogeneity. The samples were then wrapped in molybdenum foil and annealed in silica tube under argon for 1 month at 1273 K. Our attempts to synthesize the phase of $\text{Sm}_5\text{B}_4\text{C}_5$ were not successful.

2.2. Microprobe analysis

For metallographic inspection and electron probe microanalysis (EPMA), the alloys were embedded in Woods metal (melting point of 75°C, Fluka Chemie, Switzerland). The embedded samples were polished on a nylon cloth using chromium oxide (Bühler Isomet) with grain sizes 1-5 μm . Quantitative and qualitative composition analyses of the polished samples were performed by energy dispersive X-ray spectroscopy (EDX) and wavelength dispersive X-ray spectroscopy (WDX) on a scanning electron microscope TESCAN 5130 MM with an Oxford Si-detector and with an Oxford INCA WAVE 700 detector. NdB_2C_2 was used as standard. From the WDX analysis the composition $\text{Nd}_{5.0(1)}\text{B}_{4.0(3)}\text{C}_{5.0(4)}$ was deduced. For the chemical microprobe, the polishing procedure had to be performed or repeated just before the measurements. The surface of the phase $\text{Nd}_5\text{B}_4\text{C}_5$ appears to be stable in air. Metallographic investigation, X-ray powder diffraction and EPMA analyses revealed the new compound $\text{Nd}_5\text{B}_4\text{C}_5$ to be in phase equilibria with Nd_2B_5 [12], NdBC [2], $\text{Nd}_{25}\text{B}_{12}\text{C}_{28}$ [13], $\text{Nd}_5\text{B}_2\text{C}_5$ [5] at 1270 K.

2.3. X-ray diffraction and structure refinement

Small and irregularly shaped single crystals were selected from the crushed samples and sealed under argon atmosphere in glass capillaries. The single crystals of $RE_5B_4C_5$ are stable in air for several hours. These crystals were first examined by the Buerger precession technique in order to establish their suitability for the subsequent intensity collection. Single crystal intensity data of $RE_5B_4C_5$ crystals ($RE = Pr, Nd$) were collected at room temperature on a single crystal diffractometer. All relevant crystallographic data are listed in Table 1. The starting atomic parameters were derived from the $Ce_5B_4C_5$ structure type [10]. These were subsequently refined with the program SHELX-97 (full matrix least-squares on F^2) with anisotropic atomic displacements for rare earth atoms within the WinGX program package [14, 15]. The atomic coordinates and thermal parameters are listed in Table 2. Selected interatomic distances for $Nd_5B_4C_5$ are reported in Tables 3. The program DIAMOND was used to prepare the drawing of the crystal structure [16].

To check the homogeneity of the sample, X-ray powder diffraction patterns were obtained on a powder diffractometer STOE STADI P with monochromated $MoK_{\alpha 1}$ radiation ($7^\circ \leq 2\theta \leq 55^\circ$, step size 0.1° , measurement time per step: 100 s) using a linear position-sensitive detector in Debye-Scherrer geometry. The lattice parameters of the powder samples and the single crystals agree very well.

The density measurement of $\text{Ce}_5\text{B}_4\text{C}_5$ was performed under argon atmosphere in a pycnometer AccuPyc 1330 (Micrometrics GmbH, Germany) and was found to be $6.05(3) \text{ g/cm}^3$ in good agreement with the calculated X-ray density $\rho_{\text{calc}} = 5.99 \text{ g/cm}^3$.

2.4. Physical Properties.

The electrical resistance, ρ , was determined on pressed powder pellets of 3 mm diameter (thickness $h \approx 0.5 \text{ mm}$) by the four-point van der Pauw method [17] in a temperature range of 1.8-290 K. The temperature dependence of the electrical resistance of $\text{Ce}_5\text{B}_4\text{C}_5$ proves generally the metallic character of this rare earth boride carbide system.

Magnetizations M and the magnetic susceptibilities, $\chi = M/H$, in external fields $B \leq 7 \text{ T}$ were studied in the temperature interval 1.8 - 700 K using a MPMS XL-7 SQUID magnetometer (Quantum Design, Inc.). A dc Faraday pendulum magnetometer SUS-10 (A. Paar, Graz, Austria) was applied for measurements in external fields up to 1.3 T in the temperature range $80 \text{ K} < T < 900 \text{ K}$.

3. Results and Discussion

3.1 Structure

The new ternary compounds $\text{Pr}_5\text{B}_4\text{C}_5$ and $\text{Nd}_5\text{B}_4\text{C}_4$ (as well as $\text{La}_5\text{B}_4\text{C}_5$ [9]) crystallize with the $\text{Ce}_5\text{B}_4\text{C}_5$ -type structure type [10] (space group $Pna2_1$) which is closely related to the crystal structures of other ternary compounds containing isolated boron carbon chains of different lengths .

The structure consists of slightly corrugated two-dimensional metal atom square nets forming four types of polyhedra built from 6, 10, 14 and 18 rare earth metal atoms which are centered by single C atoms and also BC_2 , B_3C_3 and B_4C_4 units, respectively (Fig.1). These cages results from one, two and three distorted square antiprisms capped at both ends by single *RE* atoms (Fig.1 b, c, d). The single carbon atom is in octahedral voids of rare earth atoms. Nd-Nd distances in $Nd_5B_4C_5$ range from 3.350(1) Å (Nd6-Nd10) to 4.053(1) Å (Nd8-Nd9) (Table 3).

Interatomic distances in the nonlinear unit BC_2 are indicative of double bonds: $d(C4-B6)=1.42(2)$ Å and $d(C6-B6)=1.44(2)$ Å, angle $C6-B6-C4 = 164.6(2)^\circ$. Similar nonlinear BC_2 units were also found in ternary rare-earth boride carbides belonging to structure type of $Gd_5B_2C_5$ [5], where the B-C distances are 1.46 Å. Linear BC_2 units are known for Sc_2BC_2 [18], $Gd_4B_3C_4$ [19], and Lu_3BC_3 [20], where the B-C distances are 1.48 Å, 1.48, 1.44 Å respectively. For the Lu_3BC_3 the slabs of BC_2 units are separated by slabs of isolated carbon atoms and in $Gd_4B_3C_4$ linear BC_2 units are separated by slabs of infinite (BC) branched chains.

The shortest distance of $d(B3-B8) = 1.55(2)$ Å between boron atoms in the structure $Nd_5B_4C_5$ is observed in the unit B_3C_3 . Up to now no other crystal structures are known with such a type of boron carbon unit.

The B_4C_4 unit is already known from the crystal structures $RE_{10}B_9C_{12}$ [8] crystallizing in $Ce_{10}B_9C_{12}$ type of structure [21]. In the B_4C_4 units of $Pr_{10}B_9C_{12}$ and $Nd_{10}B_9C_{12}$ the sum of all interatomic distances is 10.27 Å, with B-B distances of 1.56 Å and 1.52 Å, respectively. In comparison, the corresponding sum for $RE_5B_4C_5$ ($R = Pr, Nd$) is slightly larger measuring 10.55(1) Å and 10.49(1) Å with B1-B4 distances 1.63(1)

Å and 1.61(1) Å (Table 3). For geometrical reasons, these chains cannot be linear inside the elongated voids formed by the metal atoms, see Fig. 1.

The isolated C10 atom in Nd₅B₄C₅ occupies the center of a slightly distorted metal octahedron where the C10-Nd distances range from 2.53(2) to 3.13(2) Å.

No interaction between carbon atoms was found in the structures RE₅B₄C₅ (R = La, Ce, Pr, Nd). A general observation for such a kind of compounds is that all B-C distances of external carbon atoms are slightly shorter than of internal ones. The distances Nd-B, Nd-C, B-C and B-B (Table 3) are similar to those commonly observed in such structure types.

3.2 Magnetism

In the paramagnetic regime (for $T > 50$ K) the reciprocal susceptibilities of Ce₅B₄C₅ deviate from a linear Curie-Weiss law, whereas both compounds, Pr₅B₄C₅ and Nd₅B₄C₅, do follow a linear Curie-Weiss behaviour as shown in the Figs. 2 - 4. The values of the effective magnetic moments and the paramagnetic Curie temperatures were nevertheless calculated by a least squares fit according to the general formula

$$\chi = \frac{C}{T - \theta_p} + \chi_0 \quad (1)$$

and are given in Table 4. The temperature independent term χ_0 ($\sim 10^{-8}$ m³/kg) accounts for core diamagnetism, van Vleck paramagnetism, Pauli paramagnetism of the conduction electrons and Landau diamagnetism etc. The values of the magnetic moments thereby agree with theoretical tripositive rare earths moment values except for Ce₅B₄C₅. It is inferred that moment reduction is the result of a weak hybridization of the 4f – 5d cerium states or 4f – p orbitals of the boron and/or carbon atoms.

In the low temperature regime ($T < 20$ K) all three compounds are characterized by the onset of magnetic order. In case of $\text{Ce}_5\text{B}_4\text{C}_5$ the following conclusion for the magnetic behaviour is drawn from magnetization versus temperature plots at various applied fields (B) (see Fig. 5): In low fields ($B < 1$ T) the $M(T)$ curves reversibly pass maxima at ~ 5 K. Hence the magnetic ground state of this compound is antiferromagnetic. In elevated fields no such maxima are revealed and the magnetization seems to saturize at the lowest temperatures. Furthermore the isothermal magnetization versus field at 2 K reveals the typical s-shaped plot of a metamagnetic transition ($B_{\text{crit}} \sim 1.5$ T). However from the reduced saturation moment, $\mu_S = 0.5 \mu_B$ at $B = 7$ T, it is inferred that the spin structure is not co-linear (canted ferromagnetism).

For both compounds, $\text{Pr}_5\text{B}_4\text{C}_5$ and $\text{Nd}_5\text{B}_4\text{C}_5$, it is conspicuous that the susceptibilities (M/H (T)) of the zero field cooled (zfc) samples rise in low external fields ($B < 0.1$ T) at increasing temperatures, see Figs. 6 and 7, passes a maximum and decreases rapidly to low values near the ordering temperatures. Upon cooling the sample in applied field (fc) a higher net magnetization below T_C is frozen in. Such a magnetic behaviour was earlier observed in the related compound *REBC* [22] and was attributed to the presence of narrow domain walls. From the literature it is known that the boron atoms act as pinning centers and hamper the domain wall movement, e. g. for $\text{Ho}_3\text{B}_x\text{C}_{4-x}$ [35]. The critical magnetic fields where wall movements set in are around $B \leq 0.1$ T at $T = 2$ K. From isothermal magnetization plots versus field at $T = 2$ K, see insets Figs. 3, 4, the values for the saturation moments were derived. The reduced moments $\mu_S < 2 \mu_B = 1/2gJ = 1.6 \mu_B$ for $\text{Pr}_5\text{B}_4\text{C}_5$ and $\text{Nd}_5\text{B}_4\text{C}_5$ are typical values for *bulk* samples of axial symmetry (in our case the lattice parameters are $b \sim c$) where the rare earth moments seem to reside

rather along the a axis (easy axis anisotropy). For both compounds a hysteresis is encountered and the remnant magnetization is approximately $10 \text{ Am}^2/\text{kg}$. The coercive forces were determined by reversing the direction of the magnetic fields and were found to be 0.06 and 0.15 Tesla, respectively.

4. Conclusion

The compounds of $RE_5B_4C_5$ ($RE = \text{Ce, Pr, Nd}$) were prepared by melting of mixtures of the elements and subsequent annealing at approximate 1270K. The $\text{Ce}_5\text{B}_4\text{C}_5$ - type crystal structure of the new compounds $RE_5\text{B}_4\text{C}_5$ ($RE = \text{Pr, Nd}$) has been determined and refined from single crystal X-ray diffraction data. The boron concentration in $\text{Nd}_5\text{B}_4\text{C}_5$ was confirmed by EPMA measurements. The specific stacking of slightly corrugated 2-D square nets of rare earth metal atoms gives rise to the formation of tubular voids in which finite C_3B_3 , C_4B_4 , B_2C units are encapsulated together with single C atoms in octahedral voids. $\text{Ce}_5\text{B}_4\text{C}_5$ is an antiferromagnet at 5 K, followed by a metamagnetic transition at a critical field $B_{\text{crit}} = 1.5 \text{ T}$. The magnetic properties of the Pr and Nd containing homologues are characterized by the onset of ferromagnetism below $T_C = 12 \text{ K}$ and 15 K , respectively.

Supplemental Information

Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (49)7247-808-666; E-mail: crystdata@fiz-karlsruhe.de) on quoting the depository numbers CSD- 418558 for $\text{Pr}_5\text{B}_4\text{C}_5$ and CSD- 419557 for $\text{Nd}_5\text{B}_4\text{C}_5$.

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Accepted manuscript

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Figure Captions

- Fig. 1. Structural arrangement of $RE_5B_4C_5$ along [001] (a) and rare-earth metal environments of B_3C_3 (b), B_4C_4 (c), BC_2 (d) and C (e).
- Fig. 2 Reciprocal susceptibility versus temperature for $Ce_5B_4C_5$ in applied field $B = 5$ T. Solid line fitted after Eq. (1). Inset: Isothermal magnetization versus applied field for $Ce_5B_4C_5$ at $T = 2$ K. Open symbols in rising fields, filled symbols in decreasing fields.
- Fig. 3 Reciprocal susceptibility versus temperature for $Pr_5B_4C_5$ in applied field $B = 5$ T. Solid line fitted after Eq. (1). Inset: Isothermal magnetization versus applied field for $Pr_5B_4C_5$ at $T = 2$ K. Open symbols in rising fields, filled symbols in decreasing fields.
- Fig. 4 Reciprocal susceptibility versus temperature for $Nd_5B_4C_5$ in applied field $B = 5$ T. Solid line fitted after Eq. (1). Inset: Isothermal magnetization versus applied field for $Nd_5B_4C_5$ at $T = 2$ K. Open symbols in rising fields, filled symbols in decreasing fields.
- Fig. 5 Magnetization versus temperature for $Ce_5B_4C_5$ at various magnetic fields. Open symbols in rising temperature, filled symbols in decreasing temperatures.
- Fig. 6 Susceptibility versus temperature for $Pr_5B_4C_5$ at various external fields. Open symbols in rising temperature, filled symbols in decreasing temperatures.
- Fig. 7 Susceptibility versus temperature for $Nd_5B_4C_5$ at various external fields. Open symbols in rising temperature, filled symbols in decreasing temperatures.

Table 1 Crystal data and structure refinement for $RE_5B_4C_5$ ($RE = Pr, Nd$), space group $Pna2_1, Z=8$

Empirical formula	$Pr_5B_4C_5$	$Nd_5B_4C_5$
Molar mass	1616	1643
Pearson symbol	oP112	oP112
Lattice parameters		
$a / \text{\AA}$	24.592(2)	24.301(1)
$b / \text{\AA}$	8.4563(5)	8.3126(5)
$c / \text{\AA}$	8.4918(5)	8.3545(4)
Unit cell volume / \AA^3	1765.9(2)	1687.6(2)
Calculated density / (g/cm^3)	6.077	6.466
Absorption coefficient / ($1/\text{cm}$)	26.993	16.001
Crystal size / mm^3	0.068 x 0.022 x 0.012	0.12 x 0.08 x 0.03
Radiation and wavelength / \AA	Mo $K\alpha$, 0.71069	Ag $K\alpha$, 0.56086
Diffractometer	STOE IPDS II	STOE IPDS I
Refined parameters	166	167
Refinement	F^2	F^2
$2\theta_{\max}$ and $(\sin\theta/\lambda)_{\max}$	54.2, 0.581	47.2, 0.646
h, k, l	-31 < h < 31 -10 < k < 10 -10 < l < 10	-34 < h < 34 -11 < k < 11 -11 < l < 11
Collected reflections	11362	21786
Independent reflections	3656 ($R_{\text{int}} = 0.076$)	4888 ($R_{\text{int}} = 0.074$)
Reflections with $I_0 \geq 2\sigma(I_0)$	2871 ($R_\sigma = 0.063$)	3707 ($R_\sigma = 0.051$)
Final R_1^{a} indices (R_1^{a} all data)	0.043 (0.063)	0.035 (0.053)
Weighted wR_2^{b} factor (wR_2^{b} all data)	^c 0.076 (0.082)	^d 0.069 (0.074)
Goodness-of-fit on F^2 :	1.01	1.02
Flack parameter	0.00(14)	0.00(15)
Largest diff. peak and hole / (\AA^{-3})	1.76/-2.25	3.34/-2.95

$$\text{a) } R_1(F) = [\Sigma(|F_o| - |F_c|)] / \Sigma|F_o|$$

$$\text{b) } wR_2(F^2) = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$$

$$\text{c) } [w^{-1} = \sigma^2(F_o)^2 + (0.033P)^2 + 0.000P], \text{ where } P = (F_o^2 + 2F_c^2) / 3$$

$$\text{d) } [w^{-1} = \sigma^2(F_o)^2 + (0.030P)^2 + 0.000P], \text{ where } P = (F_o^2 + 2F_c^2) / 3$$

Table 2 Atomic coordinates* and equivalent isotropic displacement parameters (in Å²) for RE₅B₄C₅ (RE = Pr, Nd)

Atom	Occ.	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
Pr₅B₄C₅					
Pr1	1	0.80397(4)	0.4335(1)	0.0040(1)	0.0068(2)
Pr2	1	0.80251(4)	0.0359(2)	0.7945(1)	0.0069(2)
Pr3	1	0.79833(4)	0.2348(2)	0.4061(1)	0.0081(2)
Pr4	1	0.82285(4)	0.8299(1)	0.2003(1)	0.0061(2)
Pr5	1	0.80339(4)	0.6362(2)	0.5975(1)	0.0112(2)
Pr6	1	0.56204(4)	0.4477(1)	0.4049(1)	0.0057(2)
Pr7	1	0.55802(4)	0.0473(2)	0.5939(1)	0.0057(2)
Pr8	1	0.57866(4)	0.8401(1)	0.1978(1)	0.0084(2)
Pr9	1	0.55081(5)	0.2464(1)	0.9879(1)	0.0090(2)
Pr10	1	0.56663(4)	0.6430(1)	0.7865(1)	0.0063(2)
C1	1	0.4057(8)	0.466(2)	0.592(2)	0.009(3)
C2	1	0.4100(8)	0.048(3)	0.385(2)	0.009(4)
C3	1	0.2020(8)	0.467(3)	0.800(2)	0.011(4)
C4	0.8(2)	0.304(1)	0.362(4)	0.108(3)	0.02(1)
C5	1	0.0849(7)	0.351(2)	0.302(2)	0.005(3)
C6	0.7(1)	0.407(1)	0.254(4)	0.987(3)	0.01(1)
C7	1	0.2030(7)	0.067(2)	0.996(2)	0.003(3)
C8	1	0.1947(7)	0.267(3)	0.399(2)	0.005(3)
C9	1	0.0746(7)	0.160(3)	0.693(3)	0.012(3)
C10	1	0.310(2)	0.166(8)	0.675(7)	0.02(1)
B1	1	0.5278(8)	0.936(3)	0.892(2)	0.005(4)
B2	1	0.1431(8)	0.039(3)	0.017(2)	0.009(4)
B3	1	0.9663(9)	0.049(3)	0.600(2)	0.012(4)
B4	1	0.0236(8)	0.371(3)	0.291(2)	0.010(4)
B5	1	0.1454(8)	0.492(3)	0.833(2)	0.007(4)
B6	1	0.3579(9)	0.336(3)	0.057(2)	0.009(4)
B7	1	0.1375(8)	0.305(3)	0.369(2)	0.005(4)
B8	1	0.5154(7)	0.367(2)	0.690(2)	0.004(3)
Nd₅B₄C₅					
Nd1	1	0.80355(3)	0.43376(9)	-0.0006(1)	0.0059(1)
Nd2	1	0.80227(3)	0.0385(1)	0.7932(1)	0.0060(2)
Nd3	1	0.79887(3)	0.23736(9)	0.4065(1)	0.0065(1)
Nd4	1	0.82152(3)	0.83156(9)	0.2000(1)	0.0076(1)
Nd5	1	0.80293(3)	0.6347(1)	0.5985(1)	0.0102(2)
Nd6	1	0.56197(3)	0.44800(8)	0.4049(1)	0.0055(1)
Nd7	1	0.55809(2)	0.0464(1)	0.5951(1)	0.0053(1)
Nd8	1	0.57996(3)	0.84010(9)	0.1987(1)	0.0082(1)
Nd9	1	0.55029(3)	0.2464(1)	0.9892(1)	0.0085(1)
Nd10	1	0.56612(3)	0.64282(9)	0.7874(1)	0.0062(1)
C1	1	0.4064(5)	0.464(2)	0.592(2)	0.012(2)
C2	1	0.4100(5)	0.052(2)	0.387(2)	0.005(4)

Table 2 (continued)

Atom	Occ.	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}
C3	1	0.2018(4)	0.465(2)	0.803(2)	0.005(2)
C4	0.8(1)	0.3032(6)	0.369(2)	0.102(2)	0.010(6)
C5	1	0.0866(5)	0.352(2)	0.303(2)	0.009(3)
C6	0.8(1)	0.4067(8)	0.259(3)	0.992(3)	0.02(1)
C7	1	0.2022(5)	0.066(2)	0.994(2)	0.006(2)
C8	1	0.1970(5)	0.264(2)	0.397(2)	0.012(2)
C9	1	0.0758(4)	0.160(2)	0.695(2)	0.007(2)
C10	1	0.3073(7)	0.166(2)	0.693(3)	0.02(1)
B1	1	0.5279(6)	0.934(2)	0.893(2)	0.006(2)
B2	1	0.1445(5)	0.041(2)	0.013(2)	0.008(2)
B3	1	0.9680(5)	0.056(2)	0.598(2)	0.008(2)
B4	1	0.0249(5)	0.371(2)	0.295(2)	0.009(2)
B5	1	0.1447(5)	0.487(2)	0.826(2)	0.006(2)
B6	1	0.3580(6)	0.333(2)	0.057(2)	0.010(6)
B7	1	0.1398(6)	0.302(2)	0.372(2)	0.008(2)
B8	1	0.5150(5)	0.362(2)	0.692(2)	0.005(2)

* All atoms in Wyckoff position 4*a*.

Table 3 Selected interatomic distances / Å and bond angles / deg for Nd₅B₄C₅

Nd1 - C7	2.46(1)	Nd3 - Nd4	3.828(1)	Nd7 - C9	2.61(1)
B6	2.63(2)	Nd4	3.897(1)	C5	2.68(2)
C8	2.65(2)	Nd8	3.919(1)	C2	2.69(1)
C4	2.66(2)			B1	2.69(1)
C3	2.67(1)	Nd4 - C9	2.49(1)	B4	2.72(2)
C10	2.69(2)	C4	2.66(2)	B1	2.76(2)
B7	2.80(1)	C7	2.66(1)	C6	2.81(3)
C6	2.98(2)	C3	2.67(1)	B5	2.87(1)
B5	3.07(1)	C8	2.69(2)	B8	2.93(1)
Nd7	3.581(1)	B2	2.94(2)	B4	3.00(1)
Nd3	3.629(1)	B5	2.96(1)	B7	3.00(2)
Nd2	3.660(1)	B7	3.10(2)	Nd8	3.591(1)
Nd5	3.682(1)	Nd5	3.737(1)	2Nd9	3.693(1)
Nd2	3.710(1)	Nd10	3.832(1)	Nd10	3.725(1)
Nd4	3.733(1)	Nd7	3.866(1)	Nd8	3.767(1)
Nd5	3.743(1)	Nd6	3.877(1)		
Nd3	3.774(1)	Nd9	4.005(1)	Nd8 - C6	2.61(3)
Nd8	3.864(1)	Nd5	4.028(1)	C1	2.71(1)
Nd4	4.027(1)			C5	2.71(1)
		Nd5 - C4	2.58(1)	C10	2.74(2)
Nd2 - C3	2.44(1)	C3	2.61(1)	B3	2.76(1)
C10	2.60(2)	C10	2.62(2)	C2	2.76(1)
C7	2.65(1)	C8	2.63(2)	B8	2.85(1)
C8	2.66(2)	C7	2.64(1)	B4	2.87(1)
C4	2.69(2)	B7	2.73(2)	B1	2.95(2)
B2	2.76(2)	B5	2.80(1)	Nd10	3.823(1)
B6	2.80(2)	B2	3.06(1)	Nd9	3.872(1)
C1	3.04(1)	Nd9	3.797(1)	Nd9	4.053(1)
Nd6	3.510(1)	Nd8	3.847(1)		
Nd3	3.630(1)			Nd9 - C9	2.65(2)
Nd3	3.634(1)	Nd6 - C9	2.61(2)	C1	2.76(1)
Nd5	3.699(1)	C6	2.65(3)	B3	2.77(2)
Nd5	3.729(1)	C5	2.70(1)	B1	2.77(1)
Nd4	3.838(1)	B8	2.75(2)	C2	2.79(1)
Nd8	3.886(1)	B3	2.79(1)	B8	2.80(2)
Nd4	3.948(1)	B3	2.81(2)	B4	2.80(2)
		C1	2.82(2)	C5	2.88(2)
Nd3 - C8	2.48(1)	B7	2.82(1)	B2	2.89(1)
C10	2.53(2)	B4	2.94(2)	Nd10	3.721(1)
C3	2.62(1)	B6	2.95(2)	Nd10	3.880(1)
C7	2.624(1)	B8	3.028(1)		
C4	2.70(2)	Nd10	3.350(1)	Nd10 - C9	2.643(14)
B5	2.76(1)	Nd10	3.584(1)	B6	2.67(2)
B2	2.83(1)	Nd7	3.698(1)	C6	2.68(3)
Nd10	3.517(1)	Nd8	3.712(1)	C2	2.73(1)
Nd5	3.669(1)	Nd9	3.793(1)	B1	2.74(1)
Nd5	3.674(1)	Nd9	3.866(1)	B8	2.77(1)

Table 3 (continued) Selected interatomic distances / Å and bond angles / deg for $\text{Nd}_5\text{B}_4\text{C}_5$

Nd10 - C1 2.78(2)	C6 - B6 1.44(3)	C5 - B4 - B1 143.5(1)
B3 2.82(2)	C7 - B2 1.43(2)	C1 - B3 - B8 143.4(1)
B4 2.91(1)	C8 - B7 1.44(2)	C7 - B2 - C1 154.1(1)
B2 3.08(1)	C9 - B8 1.49(2)	C2 - B1 - B4 143.3(1)
B3 3.30(1)	B1 - B4 1.61(1)	B7 - C5 - B4 156.3(1)
C1 - B3 1.51(2)	B3 - B8 1.55(1)	B3 - C1 - B2 149.6(1)
B2 1.54(2)	C8 - B7 - C5 164.5(1)	B1 - C2 - B5 155.1(1)
C2 - B1 1.51(2)	C4 - B6 - C6 164.6(2)	C9 - B8 - B3 142.8(1)
B5 1.53(2)	C3 - B5 - C2 161.3(1)	
C3 - B5 1.41(2)		
C4 - B6 1.42(2)		
C5 - B7 1.48(2)		
B4 1.51(2)		

Table 4. Magnetic data for boride carbides $RE_5\text{B}_4\text{C}_5$.

Compound	T_C (K)	T_N (K)	θ_p (K)	μ_{eff} (μ_B)	$\mu(RE^{3+})$ (μ_B)	μ_s (μ_B)
$\text{Ce}_5\text{B}_4\text{C}_5$		5	-8.5	2.17	2.54	0.5
$\text{Pr}_5\text{B}_4\text{C}_5$	12		5.5	3.73	3.58	1.3
$\text{Nd}_5\text{B}_4\text{C}_5$	15		14.5	3.67	3.62	1.7

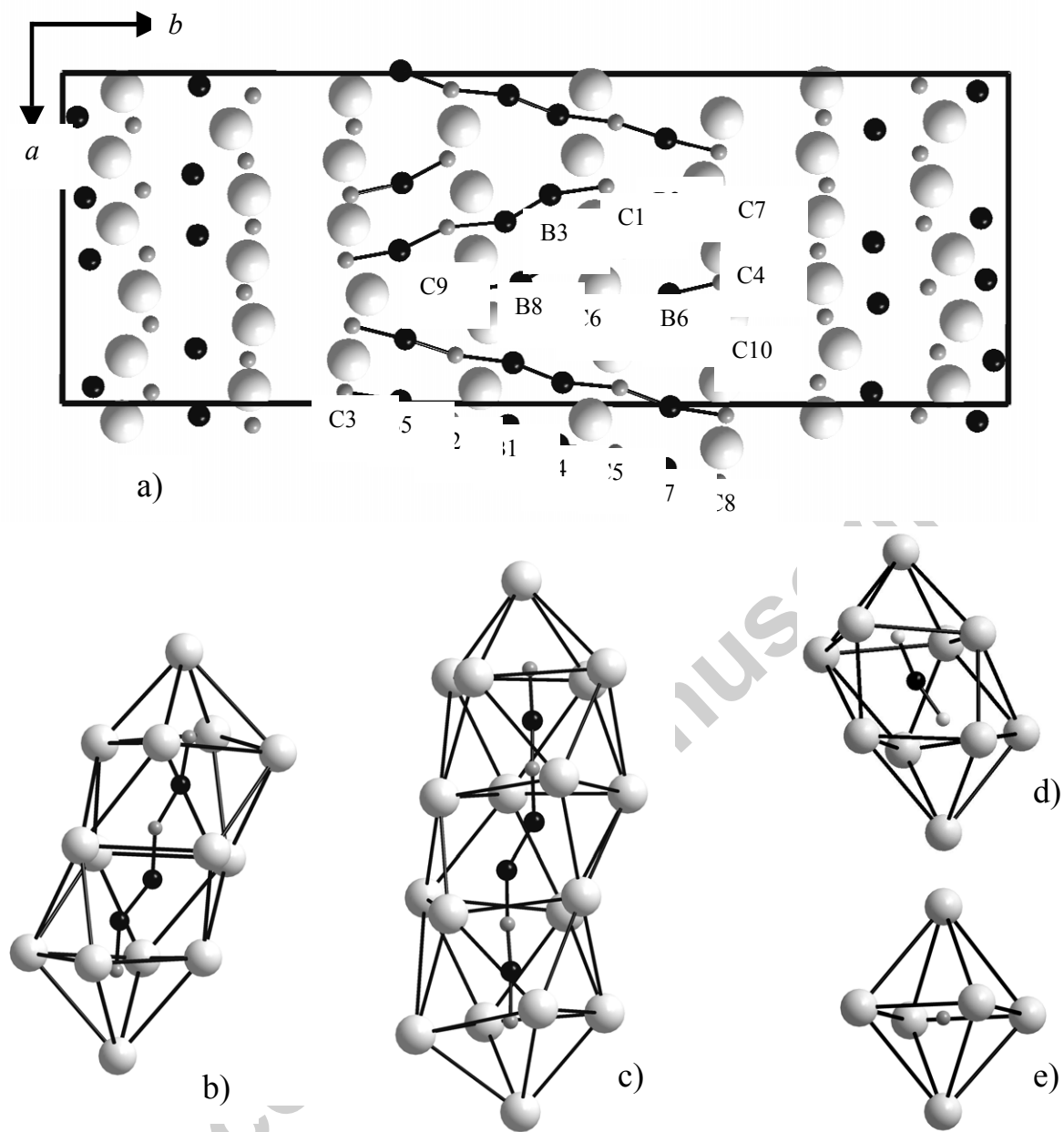


Fig. 1.

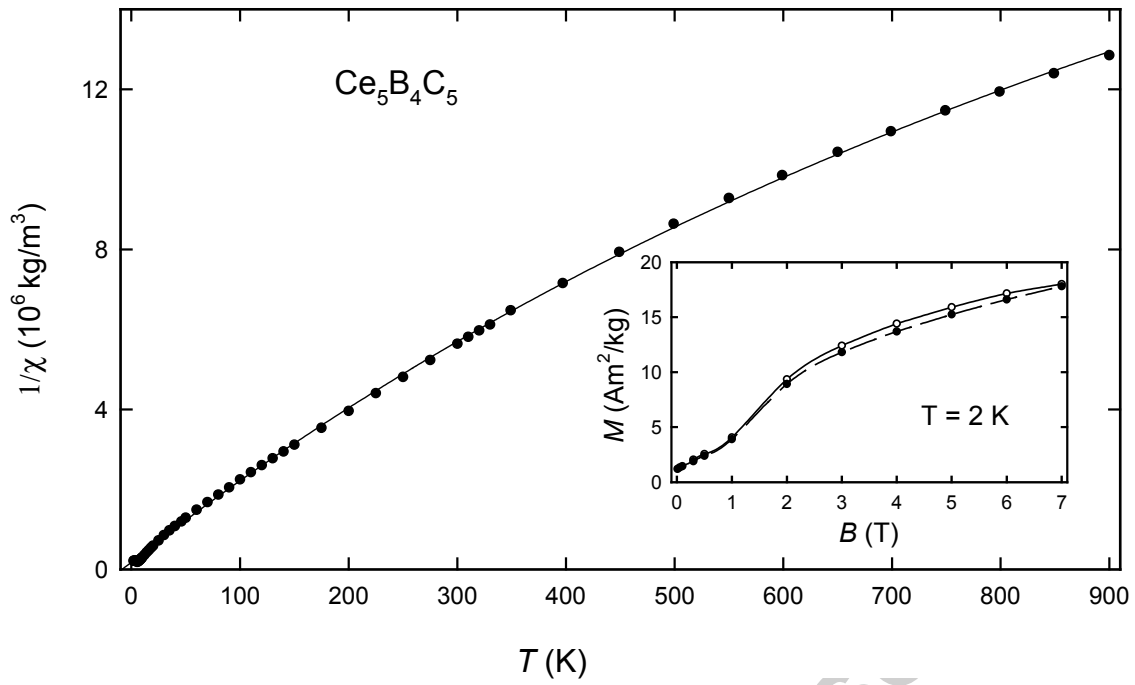


Fig.2

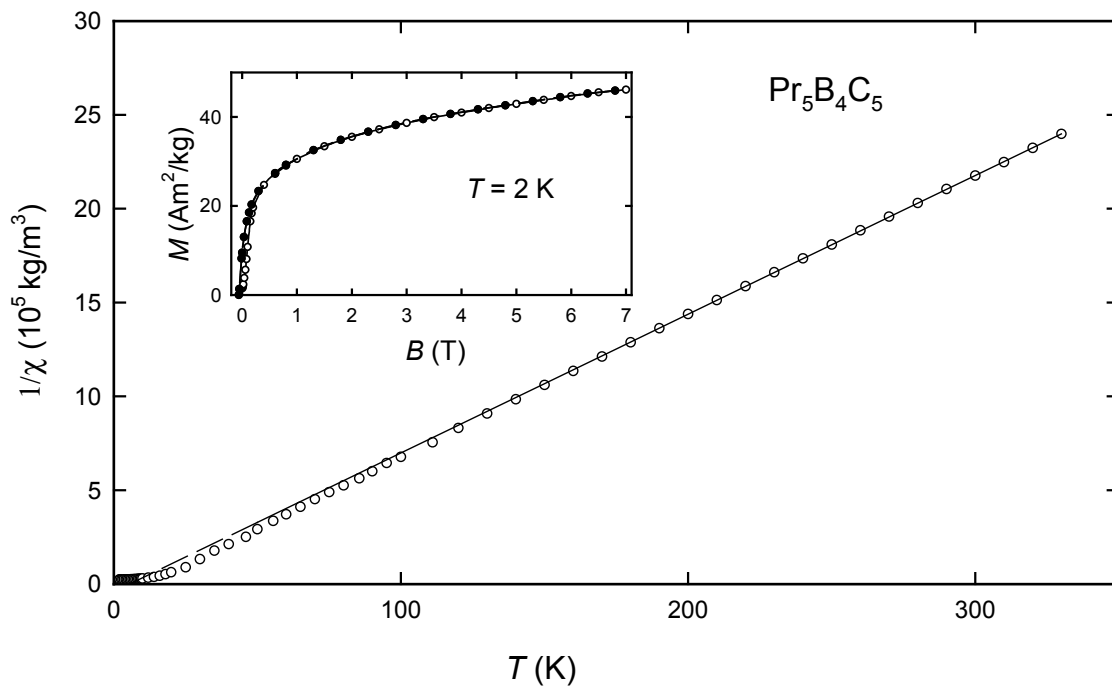


Fig.3

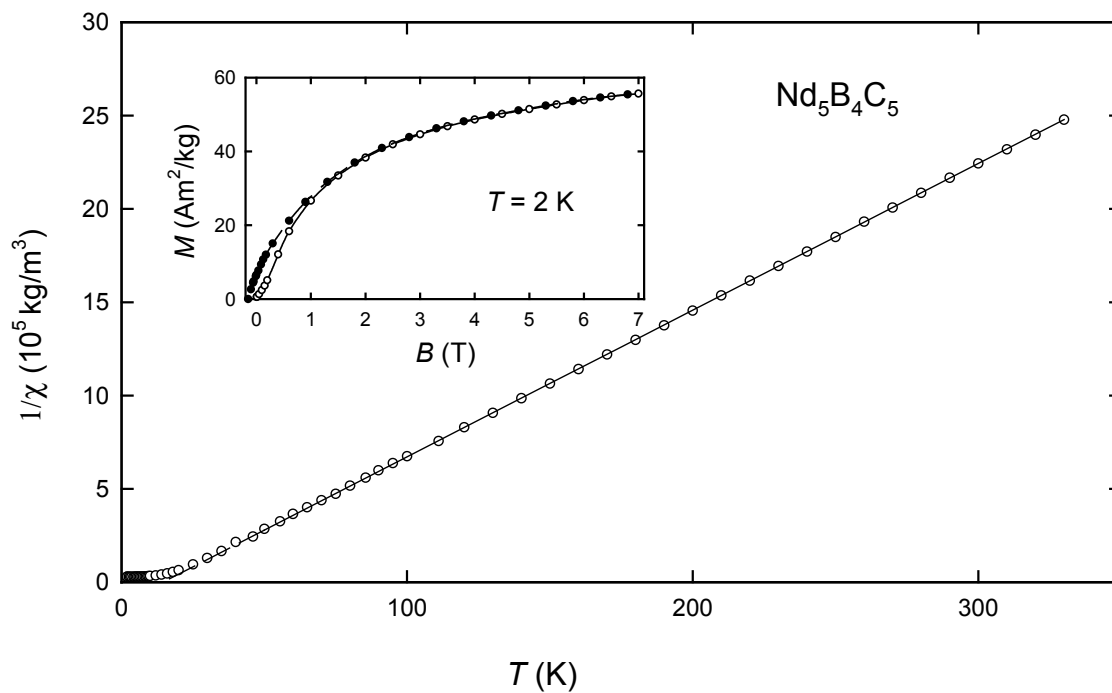


Fig. 4

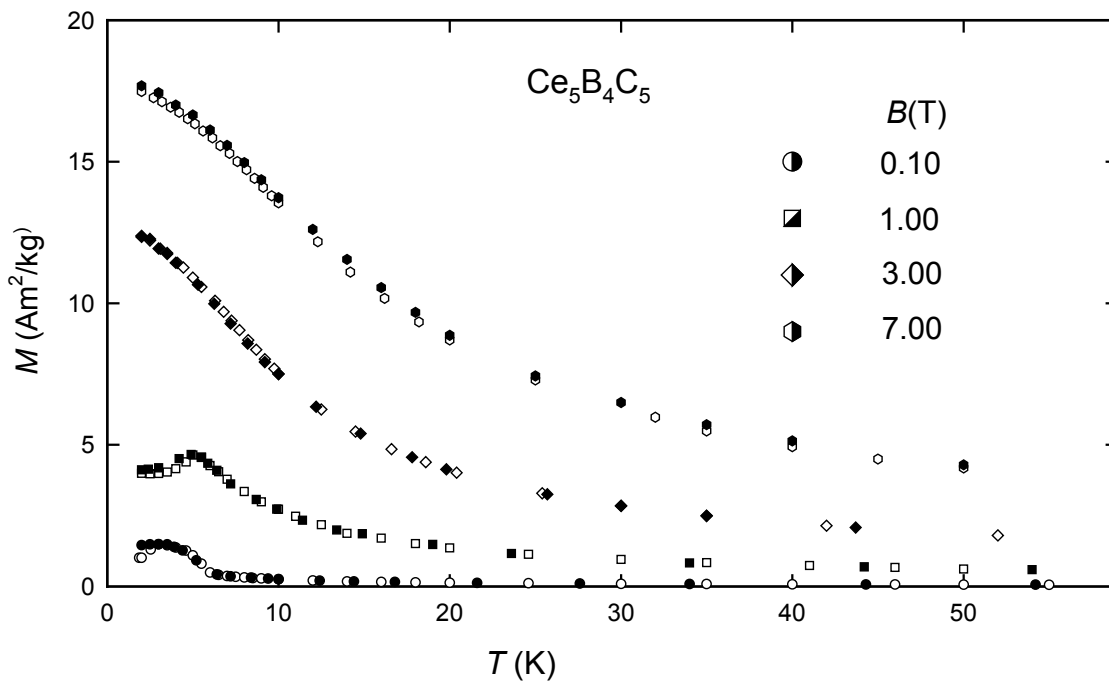


Fig. 5

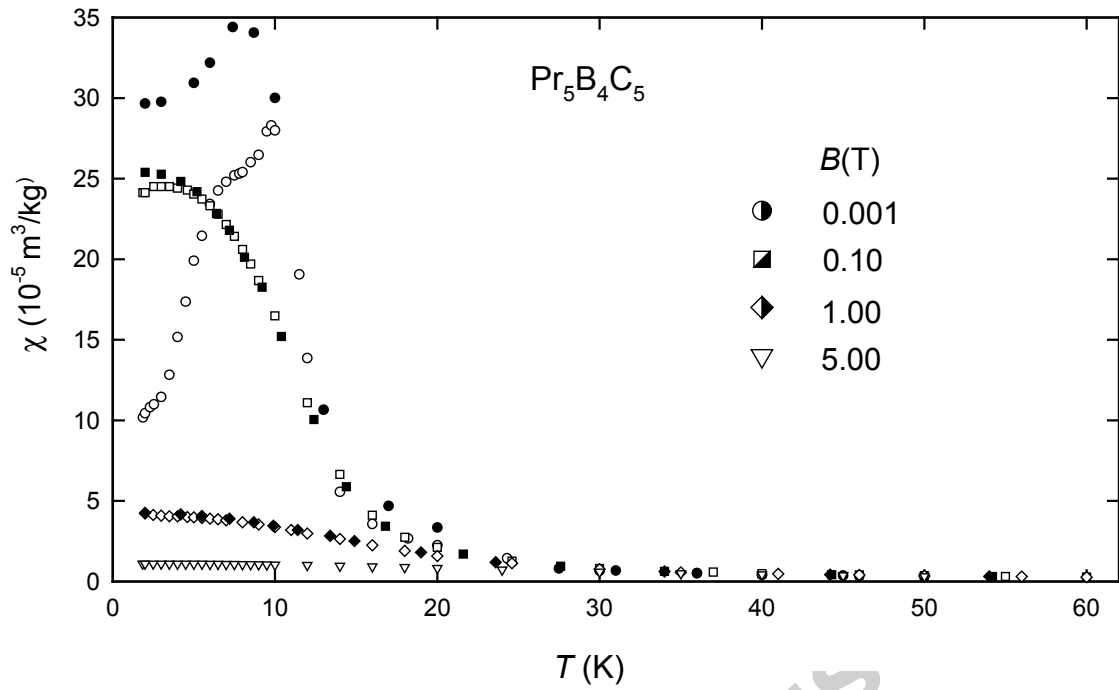


Fig. 6

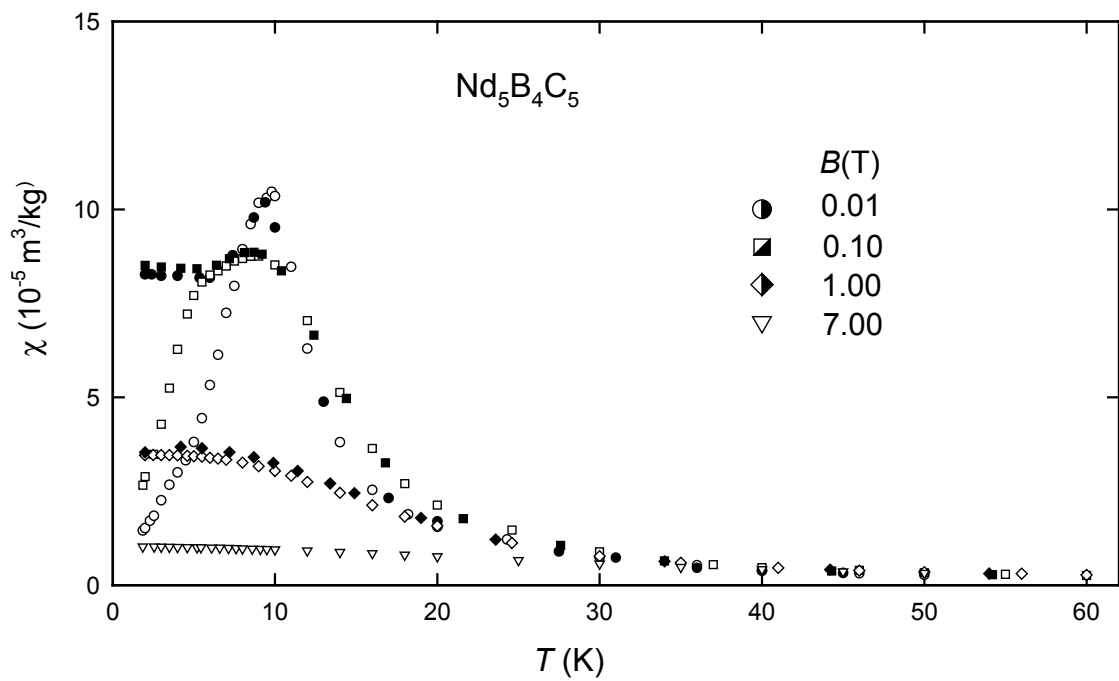


Fig. 7