Journal of Alloys and Compounds, 203 (1994) 55–59
JALCOM 851

New incommensurate structures of the borides $Pr_{41}(Mn_4B_4)_{35}$ and $Pr_7(Re_4B_4)_6$

P.Yu. Zavalij, S.I. Mykhalenko and Yu.B. Kuz'ma*
Department of Analytical Chemistry, L'viv State University, Lomonosov Str. 6, 290005 L'viv (Ukraine)

(Received June 1, 1993)

Abstract

By means of single-crystal X-ray analysis the crystal structures of the ternary borides $Pr_{41}(Mn_4B_4)_{35}$ and $Pr_7(Re_4B_4)_6$ have been investigated and found to be incommensurate. The $Pr_{41}(Mn_4B_4)_{35}$ structure belongs to the incommensurate structure series based on the $NdCo_4B_4$ type. The structure refinements have been carried out separately for the Pr sublattice (space group $I4/mmm$, $c = 0.3422(2)$ nm, $N_{hkl} = 81$, $R = 0.0457$) and the Mn_4B_4 sublattice (space group $P4_2/ncm$, $c = 0.4005(2)$ nm, $N_{hkl} = 34$, $R = 0.0292$). The resultant structure unit cell is described by space group $P4_22_12$, $a = 0.7183(3)$ nm, $c = 14.024(8)$ nm, $N_{hkl} = 134$, $R = 0.087$ (without atomic parameter refinement). The $Pr_7(Re_4B_4)_6$ structure is the first representative of a new incommensurate structure series with lattice parameter $a \approx a_{NdCo_4B_4} \times \sqrt{2}$. The structure refinements have been performed separately for the Pr sublattice (space group $F4/mmm$, $c = 0.3605(2)$ nm, $N_{hkl} = 44$, $R = 0.097$) and the Re_4B_4 sublattice (space group $I4_1/amd$, $c = 0.4201(2)$ nm, $N_{hkl} = 137$, $R = 0.033$) and also for the complete unit cell (space group $P4c2$, $a = 1.0566(6)$ nm, $c = 2.522(2)$ nm, $N_{hkl} = 233$, $R = 0.032$). In both structures the Pr atoms are located in channels formed by four columns of M_4 tetrahedra along the Z axis. The M_4 tetrahedra are rotated relative to one another by an angle around the Z axis. The selection of possible space groups for the incommensurate structures, being derivatives of $NdCo_4B_4$, was made on the basis of the numbers of R and M_4B_4 sublattices.

1. Introduction

Investigations of the $R_\epsilon Fe_4B_4$ (where R is a rare earth metal) boride crystal structures show that all of them are incommensurate, being formed by two mutually interpenetrating sublattices consisting of R atoms and Fe_4B_4 atomic groups respectively [1–7]. These compounds can be described by tetragonal symmetry with approximately the same lattice parameters a (0.700–0.720 nm) but quite different magnitudes of the lattice parameter c. Their compositions are determined by the ratio of the c parameters of the two sublattices, $\epsilon = c_{Fe_4B_4}/c_R$, and can thus be described by the general compositional formula $R_\epsilon Fe_4B_4$. The structure of the $Sm_{11}(Co_4B_4)_{10}$ compound belongs to the same series [8].

On studying the component interactions in the ternary systems (Pr,Nd)–Mn–B [9] and Sm–Mn–B [10], we also obtained ternary compounds with approximately RM_4B_4 composition which had tetragonal symmetry, values of a between 0.720 and 0.730 nm and large values of c. Similar borides exist in the systems R–Re–B too, where R is Y or La [11], Ce [12], Nd [13], Sm [14], Gd [15], Dy [16] or Ho [13]. We observe a similarity between the X-ray powder patterns of all these compounds and they are also quite similar to the patterns of the $R_\epsilon Fe_4B_4$ compounds.

Taking into account the above data, we have performed this study to determine the crystal structure of the $R_\epsilon M_4B_4$ borides, where M is Mn or Re. We have chosen $Pr_\epsilon Mn_4B_4$ and $Pr_\epsilon Re_4B_4$ as the first compounds for investigation.

2. Experimental details

The single crystals for the investigation were extracted from annealed ingots with the compositions $PrMn_4B_4$ and $PrRe_4B_4$. These ingots were prepared by direct arc melting of the pure elements, with certified purities of 99.7 wt.% for Pr, 99.5 wt.% for electrolytic Mn, 99.4 wt.% for Re and 99.4 wt.% for microcrystalline boron powder, under an argon atmosphere. The single-crystal X-ray diffraction study was carried out by means of photographic methods: Laue, rotations and photography of the reciprocal lattice, followed by automated single-crystal diffractometry (DARCH-1, graphite-monochro-

---

*Author to whom correspondence should be addressed.

SSDI 0925-8388(93)00851-O

mated Mo Kα radiation, $2\theta_{max}=80°$). All computations were performed using a CSD programme package [17].

3. Results

The fact that two different sets of layers were seen on the rotation photographs of the borides $Pr_\epsilon Mn_4B_4$ and $Pr_\epsilon Re_4B_4$ around the [001] axis, corresponding to two different substructures, confirmed our assumption about possible incommensurateness of the structures of the compounds.

3.1. $Pr_{41}(Mn_4B_4)_{35}$ structure

The single-crystal investigation showed that the compound crystallizes in the tetragonal crystal system and the observed reflections correspond to two sublattices with the same parameter $a=0.7183(3)$ nm but different parameters c. We have registered the intensities of 239 reflections, of which 146 were independent. By analogy with the incommensurate structures of iron- or cobalt-containing borides, we assumed that one sublattice is formed by Pr atoms ($c_{Pr}=0.3422(2)$ nm) and the second contains Mn and B atoms ($c_{Mn_4B_4}=0.4005(5)$ nm). The unit cell parameter ratio $c_{Mn_4B_4}/c_{Pr}$ is approximately 41:35; hence the fully refined lattice parameter of the structure $Pr_\epsilon Mn_4B_4$ seems to be $c=14.024(8)$ nm, so that the compound composition may be described by the formula $Pr_{41}(Mn_4B_4)_{35}$.

The separate refinement of atomic coordinates and their thermal parameters for the Pr sublattice has been carried out using 81 *hkl* reflections (without *hk*0 reflections which are common to both sublattices) in space group *I*4/*mmm*, where the Pr atoms occupy the site position 2(*a*) 000; $B_{eq}=0.98(3)\times10^{-2}$ nm², $B_{11}=B_{22}=1.02(5)\times10^{-2}$ nm², $B_{33}=0.91(7)\times10^{-2}$ nm², final residual $R=0.0457$. The atomic parameters for the Mn_4B_4 sublattice have been refined using 34 *hkl* reflections in space group $P4_2/ncm$ down to $R=0.0292$. The atomic positions occupied here are described with the coordinates *xxz* (site position 8(*j*)): $x_1=0.1268(3)$, $z_1=0.133(3)$, $B_{iso}=0.73(4)\times10^{-2}$ nm² and $x_2=0.069(3)$, $z_2=0.630(19)$, $B_{iso}=1.1(3)\times10^{-2}$ nm², where x_1, z_1 and x_2, z_2 are the coordinates of Mn and B atoms respectively.

The model of the incommensurate structure of the boride may be constructed by combining 41 Pr sublattices and 35 Mn_4B_4 sublattices to give the formula $Pr_{41}(Mn_4B_4)_{35}$ ($Z=2$, $\rho_{calc}=6.88(1)$ g cm^{-3}). The space group $P4_22_12$ was obtained from the symmetries of the Pr and Mn_4B_4 sublattices taking into account the numbers of each type of sublattice present (41 and 35 respectively). The atomic coordinates of the structure $Pr_{41}(Mn_4B_4)_{35}$ were derived from the atomic coordinates of the two sublattices and are summarized in Table 1. The reflection array for the calculation of the whole structure was obtained by combining the two reindexed arrays of the Pr and Mn_4B_4 sublattices. Because the total number of independent reflections was only 146, the refinement of 325 free parameters of the $Pr_{41}(Mn_4B_4)_{35}$ structure was impossible. The residual without parameter refinement was $R=0.087$.

TABLE 1. Atomic coordinates of $Pr_{41}(Mn_4B_4)_{35}$ superstructure (space group $P4_22_12$) calculated from initial atomic coordinates of Pr (space group *I*4/*mmm*) and Mn_4B_4 (space group $P4_2/ncm$) sublattices

Atom	Coordinates[a]			*i*
	x	*y*	*z*	
Pr1	0	0	0	
Pr2–21	0	0	$i/41$	1–20
Mn1–35	x_1	$\frac{1}{2}+x_1$	$(z_1+i)/35$	0–34
B1–35	$\frac{1}{4}-x_2$	$\frac{3}{4}-x_2$	$(z_2+i)/35$	0–34

[a] x_1, z_1 and x_2, z_2 are atomic coordinates of Mn and B in Mn_4B_4 sublattice respectively.

TABLE 2. Interatomic distances (δ) in Mn_4B_4 sublattice of $Pr_{41}(Mn_4B_4)_{35}$ structure

Atoms	δ (nm)	Atoms	δ (nm)
Mn–1Mn	0.2788(7)	B–2Mn	0.222(2)
4Mn	0.2673(13)	1Mn	0.220(2)
1Mn	0.2503(3)	1Mn	0.210(7)
2B	0.222(2)	1Mn	0.208(7)
1B	0.220(4)	1B	0.175(7)
1B	0.210(7)		
1B	0.208(7)		

The interatomic distances (δ) in the Mn_4B_4 sublattice are listed in Table 2; they are close to the sums of the atomic radii.

3.2. $Pr_7(Re_4B_4)_6$ structure

The single-crystal X-ray analysis showed that the structure of this compound is also tetragonal but with $a=1.0586(6)$ nm, which is $\sqrt{2}$ times larger than the *a* parameter of all known $R_\epsilon M_4B_4$ structures where M is Mn, Fe or Co. We have registered 392 reflections, 233 of them being independent. The sublattices of Pr atoms and Re_4B_4 groups are characterized by lattice parameters $c_{Pr}=0.3605(2)$ nm and $c_{Re_4B_4}=0.4201(2)$ nm respectively. Their ratio corresponds to 7:6, so that the composition of the compound can be described by the formula $Pr_7(Re_4B_4)_6$ and its final parameter $c=2.522(1)$ nm ($Z=4$, $\rho_{calc}=13.42(2)$ g cm^{-3}).

The Pr sublattice may be described by the space group *F*4/*mmm*. The refinement of atomic coordinates has been carried out using 83 reflections (44 of them were independent) down to $R=0.097$. The Pr atoms

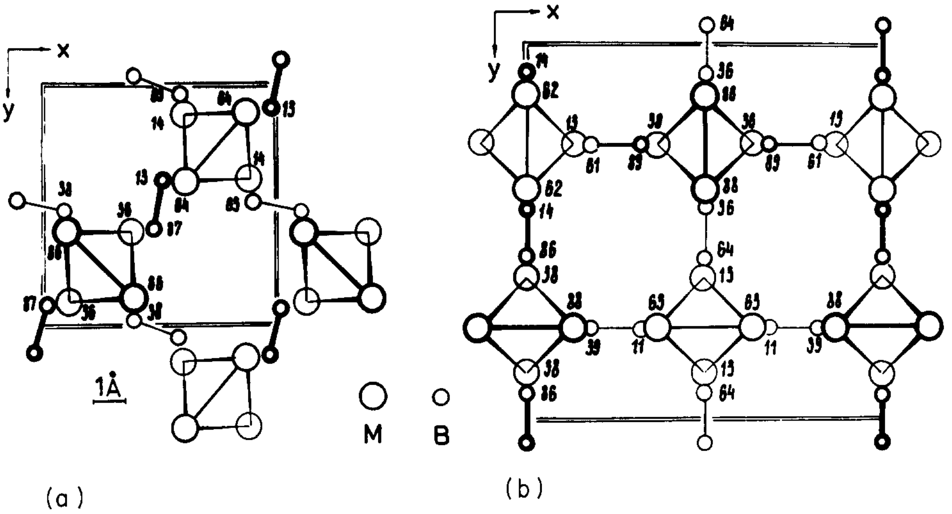

Fig. 1. Accommodation of M_4 tetrahedra and B_2 pairs in (a) $NdCo_4B_4$ and (b) $Pr_7(Re_4B_4)_6$ structures. The numbers indicate the atomic *z* coordinates.

occupy the site position 4(*a*) 000, $B_{eq}=0.9(2)\times10^{-2}$ nm², $B_{11}=B_{22}=0.5(2)\times10^{-2}$ nm², $B_{33}=1.8(6)\times10^{-2}$ nm².

The atomic coordinates in the Re_4B_4 sublattice were refined using 250 reflections (137 of them were independent) in space group $I4_1/amd$ down to $R=0.033$. The atoms occupy the site position 16(*h*) 0*xz*: $x_1=0.3781(1)$, $z_1=0.6250(5)$, $B_{eq}=0.64(2)\times10^{-2}$ nm², $B_{11}=1.24(6)\times10^{-2}$ nm², $B_{22}=0.11(4)\times10^{-2}$ nm², $B_{33}=0.58(3)\times10^{-2}$ nm² and $x_2=0.432(4)$, $z_2=0.144(10)$, $B_{iso}=0.8(5)\times10^{-2}$ nm², where x_1, z_1 and x_2, z_2 are the coordinates of Re and B atoms respectively.

As is known, the prototype of incommensurate structures of the series $R_\epsilon M_4B_4$ (M≡Mn, Fe, Co) is the commensurate structure $NdCo_4B_4$ [18] in which the Co atoms form columns of empty tetrahedra parallel to the *Z* axis. Four of these columns form a channel in which the Nd atoms are located. Since $a_{Pr_7(Re_4B_4)_6}\approx a_{NdCo_4B_4}\times\sqrt{2}$, we suggest that the structure of $Pr_7(Re_4B_4)_6$ be constructed similarly, meaning that the Pr atoms be placed in the channels formed by the columns of Re_4 tetrahedra (Fig. 1b).

The refinement of atomic coordinates in a complete unit cell of the $Pr_7(Re_4B_4)_6$ structure was performed in space group $P\bar{4}c2$, using 392 reflections down to $R=0.032$. Final values of the atomic coordinates are given in Table 3. Figure 2 confirms our assumption about how the Pr atoms and Re_4 tetrahedra columns are arranged in the structure $Pr_7(Re_4B_4)_6$.

The atomic coordination for the $Pr_7(Re_4B_4)_6$ structure remains the same as in previously investigated incommensurate structures of the $R_\epsilon Fe_4B_4$ series. All the Pr atoms are characterized by a coordination number (CN) of 18, while the Re atoms have CN = 14 (for Re1, 3, 4 and 7) or CN = 13 (for all other Re atoms). The boron atoms have CN = 8, except for B10 which has CN = 9. The boron atom environments are $[BRe_5Pr_2]$ distorted pentagonal bipyramids with additional Pr and B atoms (for B10) or with one additional boron atom (for all other B atoms). Thus all the boron atoms are

TABLE 3. Final atomic coordinates and isotropic thermal parameters[a] for $Pr_7(Re_4B_4)_6$ structure (space group $P\bar{4}c2$)

Atom	*x/a*	*y/b*	*z/c*
Pr1	0.250(2)	*x*	$\frac{3}{4}$
Pr2	0.249(2)	0.252(3)	0.3230(6)
Pr3	0.252(3)	0.252(3)	0.4681(6)
Pr4	0.247(3)	0.250(2)	0.5972(5)
Re1	−0.0183(12)	0.1294(12)	0.0407(8)
Re2	−0.009(2)	0.1286(11)	0.2066(7)
Re3	0.0164(13)	0.1284(12)	0.3772(6)
Re4	0.1282(11)	0.490(2)	0.0847(6)
Re5	0.1282(11)	0.4868(14)	0.2496(11)
Re6	0.1277(11)	0.489(2)	0.4156(7)
Re7	0.489(2)	0.3718(12)	0.1239(7)
Re8	0.506(3)	0.3722(11)	0.2927(8)
Re9	0.511(2)	0.3722(11)	0.4590(8)
Re10	0.3729(11)	0.007(3)	−0.0004(11)
Re11	0.3726(11)	−0.009(2)	0.1674(7)
Re12	0.3724(11)	−0.009(2)	0.3328(7)
B1	0.5002	0.1844	0.4993
B2	0.3161	0.9988	0.9177
B3	0.3162	0.0010	0.0838
B4	0.9995	0.1850	0.2928
B5	0.3153	0.5006	0.2902
B6	0.4988	0.1835	0.6653
B7	0.5018	0.1834	0.3330
B8	0.3157	0.4983	0.1241
B9	0.0017	0.1845	0.1268
B10	0.3173	0.0016	0.2509
B11	0.3161	0.5013	0.4530
B12	0.9988	0.1839	0.4594

[a] Isotropic thermal parameters: $B_{Pr}=0.57\times10^{-2}$ nm², $B_{Re}=0.37\times10^{-2}$ nm², $B_B=1.0\times10^{-2}$ nm².

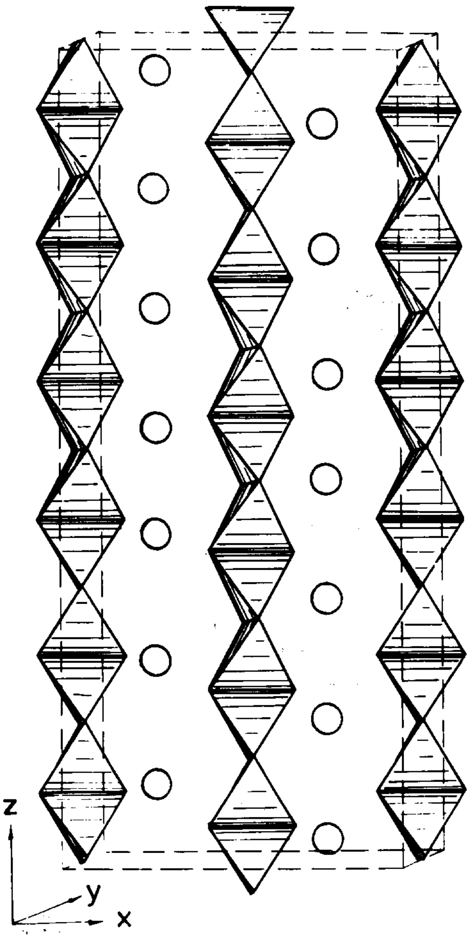

Fig. 2. Columns of Re_4 tetrahedra and Pr atoms in $Pr_7(Re_4B_4)_6$ structure. The rotation of the tetrahedra is indicated.

TABLE 4. Minimum interatomic distances (δ) in $Pr_7(Re_4B_4)_6$ structure

Atoms	δ (nm)
Pr3–Pr4	0.326(20)
Pr3–Re10	0.301(6)
Pr4–B6	0.274(3)
Re11–Re11	0.270(2)
Re7–B11	0.203(2)
B7–B8	0.177

connected in B_2 pairs. Moreover, δ_{B-B} is in the range from 0.1842 nm (between B1 and B11 atoms) to 0.1770 nm (between B7 and B8 atoms). There are no strong compressions in the structure $Pr_7(Re_4B_4)_6$. The minimum interatomic distances are listed in Table 4.

Our investigation of the crystal structure of the $Pr_7(Re_4B_4)_6$ compound shows that a new series of incommensurate boride structures exists, its lattice parameter (a_2) being related to that of the previously investigated series $R_\epsilon Fe_4B_4$ (a_1) by the relation $a_2 = a_1\sqrt{2}$.

4. Discussion

In the investigation of incommensurate structures of $R_\epsilon M_4B_4$ borides, a problem of space group selection arises in describing the complete structures. It is known that these structures consist of two sublattices: one of them is formed by R atoms (space group $I4/mmm$), the other by M_4B_4 units (space group $P4_2/ncm$). The two sublattices have different c lattice parameters, their ratio defining the superstructure lattice and its common lattice parameter c. Investigators either describe such structures in space group $P4_2/n$, as in the commensurate (normal) compound $NdCo_4B_4$ [1, 2, 4, 6], or adopt lower crystal symmetry ($Pccn$) [3]. Such uncertainty regarding the space group selection is due to the presence of complete lattice supersymmetry.

We have carried out a selection of possible space groups for derivatives of the $NdCo_4B_4$ structure, considering that the R and Mn_4B_4 sublattices are described in space groups $I4/mmm$ and $P4_2/ncm$ respectively. The Laue class has also been taken into account. These data are combined in Table 5. In accordance with this, the structure of the $Sm_{11}(Co_4B_4)_{10}$ boride can be assigned to space group $P\bar{4}2_1c$ [8] and the $Ho_{20}(Fe_4B_4)_{17}$ boride structure to $P\bar{4}c2$ [7]. It is worth noting that the $Nd_{19}(Fe_4B_4)_{17}$ structure does not belong to space group $P4_2/n$ as the authors of ref. 6 assumed, but to $P4_42_12$.

An analogous selection of possible space groups has been carried out for the new incommensurate structure series represented by $Pr_7(Re_4B_4)_6$. Its Re_4B_4 sublattice is built on diagonals along [110] and [$\bar{1}$10] of the $NdCo_4B_4$ structure, while the Pr sublattice remains the same. There is only one representative known for this structure series and no analogous commensurate structure has been found so far. However, because many compounds with the composition $R_\epsilon Re_4B_4$ were discovered in R–Re–B systems, new representatives of this incommensurate structure series can be expected to be found.

It was noted in ref. 6 that a particular rotation of M_4 tetrahedra and B_2 pairs around the [001] axis (along Z) takes place. We have examined $Ho_{20}(Fe_4B_4)_{17}$ [7] and $Sm_{11}(Co_4B_4)_{10}$ [8] which were investigated earlier

TABLE 5. Selection of space groups for incommensurate structure series based on initial structures $Nd_x(Co_4B_4)_y$ and "$Pr_x(Re_4B_4)_y$"

x	y	Series $Nd_x(Co_4B_4)_y$		Series "$Pr_x(Re_4B_4)_y$"	
		Space group	Representative	Space group	Representative
$2n+1$	$2n+1$	$P4_22_12$	$Pr_{41}(Mn_4B_4)_{35}$	$P\bar{4}n2$	–
$2n+1$	$2n$	$P\bar{4}2_1c$	$Sm_{11}(Co_4B_4)_{10}$	$P\bar{4}c2$	$Pr_7(Re_4B_4)_6$
$4n+2$	$2n+1$	$P\bar{4}c2$	$Ho_{20}(Fe_4B_4)_{17}$	$I\bar{4}2d$	–
$4n$	$2n+1$			$I4_122$	–

by us. These structures also show a distinct Mn_4 tetrahedra rotation around the fourth-order axis. As can be seen in Fig. 3, the M_4 tetrahedra in the $Sm_{11}(Co_4B_4)_{10}$ structure are rotated by a larger angle than in the $Ho_{20}(Fe_4B_4)_{17}$ structure. The tetrahedra columns with centres at the positions $\frac{3}{8}\ \frac{1}{8}\ z$ and $\frac{5}{8}\ \frac{1}{8}\ z$ are seen to be rotated in opposite directions. This tetrahedra rotation is also observed in $Pr_7(Re_4B_4)_6$ (Fig. 2). Moreover, the rotation angle is almost the same as in $Sm_{11}(Co_4B_4)_{10}$ (Fig. 3).

The above results indicate that the $R_\epsilon M_4B_4$ ($M \equiv Mn$, Fe, Co, Re) borides form two series of incommensurate structures constructed by identical principles. It is very likely that new incommensurate structures can also be obtained in other R–M–B systems where M is a noble metal. This is quite possible because compounds of the approximate composition ROs_4B_4 exist in the R–Os–B systems. They have tetragonal structures which have not yet been determined and have lattice parameters similar to those of the $R_\epsilon M_4B_4$ compounds. For instance, for the YOs_4B_4 compound it has been found that $a = 0.74650$ nm and $c = 3.28160$ nm [19]. A more detailed study of these boride structures would increase the number of new incommensurate structures.

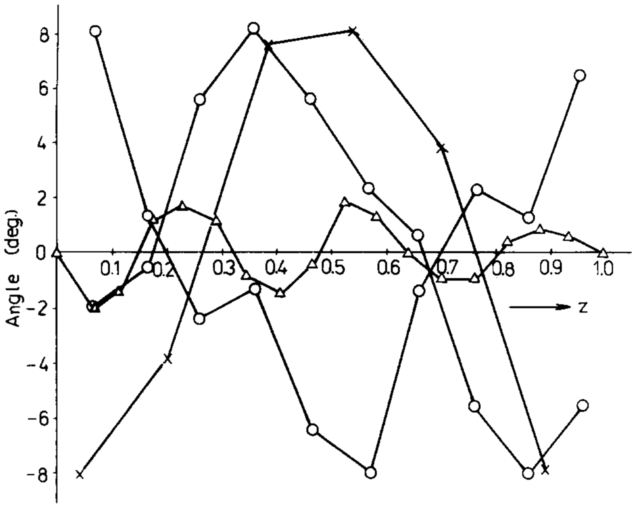

Fig. 3. Rotation of the M_4 tetrahedra angle in $R_\epsilon M_4B_4$ structures: △, $Ho_{20}(Fe_4B_4)_{17}$; ○, $Sm_{11}(Co_4B_4)_{10}$; ×, $Pr_7(Re_4B_4)_6$.

References

1 E. Parthé and B. Chabot, *Handbook on the Physics and Chemistry of Rare Earths,* Vol. 6, North-Holland, Amsterdam, 1984, p. 113.
2 A. Bezinge, N.F. Braun, J. Muller and K. Yvon, *Solid State Commun., 55*(2) (1985) 131.
3 D. Givord, J.M. Moreau and P. Tenaud, *Solid State Commun., 55*(4) (1985) 303.
4 D. Givord, J.M. Moreau and P. Tenaud, *J. Less-Common Met., 123* (1986) 109.
5 D. Niarchos, G. Zonganelis, A. Kostikas and A. Simopoulos, *Solid State Commun., 59* (1986) 389.
6 A. Bezinge, K. Yvon, H.F. Braun and J. Muller, *Phys. Rev. B, 36*(3) (1987) 1406.
7 I.B. Gubych, P.Yu. Zavalij and Yu.B. Kuz'ma, *Neorg. Mater., 29*(2) (1993) 289.
8 P.Yu. Zavalij, Yu.B. Kuz'ma and L.V. Zavalij, *Russ. Crystallogr., 35*(3) (1990) 638.
9 S.I. Mykhalenko, Yu.B. Kuz'ma and T.D. Chuchman, *Izv. Akad. Nauk USSR, Neorg. Mater., 26*(11) (1990) 2295.
10 S.I. Mykhalenko and Yu.B. Kuz'ma, *Izv. Akad. Nauk USSR, Neorg. Mater., 27*(10) (1991) 2109.
11 S.I. Mykhalenko, Yu.B. Kuz'ma and A.S. Sobolev, *Poroshk. Met.,* (1) (1977) 48.
12 S.I. Mykhalenko, Yu.B. Kuz'ma and M.S. Nalyvajko, *High Temperature Borides and Silicides,* Naukova Dumka, Kiev, 1978, p. 72.
13 Yu.B. Kuz'ma, S.I. Mykhalenko and N.F. Chaban, *Investigation and Application of Refractory Metals Alloys,* Nauka, Moscow, 1983, p. 5.
14 S.I. Mykhalenko, Yu.B. Kuz'ma and O.S. Shchur, *Poroshk. Met.,* (9) (1982) 50.
15 N.F. Chaban, S.I. Mykhalenko and Yu.B. Kuz'ma, *Poroshk. Met.,* (2) (1989) 56.
16 S.I. Mykhalenko, *Vest. L'vov Gos. Univ., Ser. Chem., 23* (1981) 52.
17 L.G. Akselrud, Yu.N. Gryn, P.Yu. Zavalij, V.K. Pecharsky and V.S. Fundamensky, *Collected Abstracts Twelfth Eur. Crystallographic Meeting, Moscow, August 1989,* Izv. Akad. Nauk SSSR, Vol. 3, Moscow, 1989, p. 155.
18 Yu.B. Kuz'ma and N.S. Bilonizhko, *Dopov. Akad. Nauk Ukr. RSR. Ser. A,* (3) (1978) 276.
19 Yu.B. Kuz'ma and N.F. Chaban, *Binary and Ternary Systems Containing Boron,* Metallurgiya, Moscow, 1990.