Non-collinear antiferromagnetic structure in PrCuAl

P. Javorský¹, J. Kaštıl¹ and O. Isnard²
¹ Charles University, Faculty of Mathematics and Physics, Department of Condensed Matter Physics, Ke Karlovu 5, 121 16 Prague 2, The Czech Republic
² Institut Néel, CNRS associé à l’Université J. Fourier, Boîte F, BP 166, 38042 Grenoble cedex 9, France
E-mail: javor@mag.mff.cuni.cz

Abstract. We report on the magnetic structure in PrCuAl as determined by powder neutron diffraction. This compound crystallizes in the hexagonal ZrNiAl-type structure and the bulk measurements indicated an antiferromagnetic order in PrCuAl below $T_N = 7.9$ K. Our neutron-diffraction data confirmed the antiferromagnetic order below $T_N$ and revealed the propagation vector $(1/3, 1/3, 1/3)$. The Pr magnetic moments lie within the basal plane and form a triangular structure. This magnetic structure differs from antiferromagnetic structures observed in other $R$CuAl or $RNiAl$ compounds that are mostly characterized by $(1/2, 0, q)$ propagation.

1. Introduction
PrCuAl belongs to a large group of the $RTX$ ($R =$ rare earth, $T =$ transition metal, $X =$ p-metal) ternary compounds crystallizing in the hexagonal ZrNiAl-type structure. Most of these compounds order magnetically at low temperatures. The magnetic structures are often characterized by existence of frustrated magnetic moments as a consequence of a triangle-like arrangement of the rare-earth atoms within the basal plane [1]. Very interesting and surprising development of magnetic behavior was observed in the $RNi_{1-x}Cu_xAl$ series with $R =$ Tb [2], Er [3] and Dy [4]. The transition between the magnetic order in $RNiAl$ and $RCuAl$ is rather complex and unusual. Especially the loss of the long-range magnetic order in the concentration range between $x \simeq 0.6$ and $x \simeq 0.8$ was observed in all the three series. It arouses questions about the nature of exchange interactions in these materials, namely how the itinerant 3$d$ electrons brought in the system by Ni enter in the exchange interaction game [2, 5].

There are some indications that the behavior in the $PrNi_{1-x}Cu_xAl$ series could be different. PrCuAl orders antiferromagnetically below $T_N = 7.9$ K [6, 7] in contrast to ferromagnetic $RCuAl$ compounds with the heavy rare earth (Gd-Er). The $RCuAl$ compounds containing light rare earth $R =$ Pr, Nd and Sm are also rather exceptional concerning their ordering temperatures that are relatively very high: two times higher than expected from the scaling using de Gennes factor and the ordering temperature of GdCuAl [6]. The de Gennes scaling is nevertheless preserved in the PrCuAl-NdCuAl-SmCuAl sequence. The enhanced ordering temperature might eventually indicate different exchange mechanisms in the $RCuAl$ compounds containing the light rare-earth atoms. The antiferromagnetic order is reported also for PrNiAl with the magnetic structure already determined [1]. The aim of the present paper is to study the magnetic structure in PrCuAl using neutron powder diffraction.
Table 1. Atomic positions in PrCuAl

| atomic site | x, y, z | x, y, z | x, y, z |
|-------------|--------|--------|--------|
| 3Pr in 3(g) | (x_Pr, 0, 1/2) | (0, x_Pr, 1/2) | (-x_Pr, -x_Pr, 1/2) |
| 3Al in 3(f) | (x_Al, 0, 0) | (0, x_Al, 0) | (-x_Al, -x_Al, 0) |
| 2Cu in 2(c) | (1/3, 2/3, 0) | (2/3, 1/3, 0) | |
| 1Cu in 1(b) | (0, 0, 1/2) | | |

2. Experimental
The polycrystalline PrCuAl sample was prepared by arc-melting the stoichiometric compositions of pure elements (3N for Pr, 4N5 for Cu and 5N for Al) in mono-arc furnace under protection of argon atmosphere. The samples were turned and remelted several times to achieve better homogeneity.

The powder neutron diffraction experiment was performed at the Institute Laue-Langevin, using the D1B instrument. The diffraction patterns were measured with a wavelength of $\lambda = 2.52$ Å over an angular range of 80° using a multidetector with a step of 0.2° between each of the 400 $^3$He detection cells. We collected diffraction patterns with a large statistics at 12 and 2 K. Additionally, diffraction patterns with lower statistics were measured during continuous heating from 2 K to 12 K to map the temperature development. We used randomly-oriented powder with the mass of about 10 g placed into the cylindrical vanadium holder with a diameter of 8 mm. The measured data were analyzed by Rietveld refinement method, using the Fullprof program [8].

3. Results and discussion
Our neutron-diffraction pattern collected in the paramagnetic state at 12 K (see Fig.1) confirmed the ZrNiAl-type structure of PrCuAl. This crystal structure, shown in Fig.2a), consists of two types of layers at $z = 0$ and 1/2 with the atomic positions given in Table 1.

The refined lattice parameters and the atomic-position parameters, $x_{Pr}$ and $x_{Al}$, are given in Table 2 and the corresponding fit is shown in Fig.1a). The values of both lattice parameters at low temperatures are surprisingly slightly higher than those obtained at the room temperature [6]. Therefore it could be interesting to investigate their temperature dependence in more details.

The temperature development of the diffraction pattern, shown in Fig.1b), reveals additional magnetic intensities that appear below $\sim 7$ K, in agreement with $T_N = 7.9$ K derived from the specific heat and magnetization [7]. These magnetic peaks can be indexed by a propagation vector $k = (1/3, 1/3, 1/3)$.

The best agreement with the data measured at 2 K was obtained for the magnetic structure

Table 2. Results of the refinement of the crystal and magnetic structure at 12 and 2 K. The parameters of atomic positions at 2 K have been fixed to values obtained at 12 K.

| a (pm) | c (pm) | $x_{Pr}$ | $x_{Al}$ | $\mu_{Pr}$ ($\mu_B$) | $R_B$ | $R_{mag}$ |
|--------|--------|----------|----------|-----------------------|-------|-----------|
| 12 K   | 722.5(6) | 415.7(4) | 0.579(3) | 0.225(6) | 2.7 | - |
| 2 K    | 722.2(5) | 415.5(3) | 0.579 | 0.225 | 3.0(2) | 2.8 | 15.5 |
| 300 K [6] | 717.1 | 414.8 | | | | |
Figure 1. a) Neutron diffraction patterns of PrCuAl at $T = 12$ and 2 K. The small circles represent the measured data, line is the fit described in the text, the line in the bottom is the difference between experiment and the fit for 2 K data. The vertical bars mark the reflections related to structural (top) and magnetic (bottom) part. b) The temperature dependence of diffraction pattern measured during continuous heating from 2 to 12 K. The pattern was recorded with a temperature step of 0.3 K. The most intense magnetic peaks are marked by a star.

displayed in Fig.2b). All the Pr magnetic moments lie within the basal plane and create a triangular antiferromagnetic structure. Moments on all the three rare-earth crystallographic sites are fully equivalent and the maximum size reaches $3.0 \mu_B$, close to the Pr$^{3+}$ free-ion value of $3.2 \mu_B$. We note that the agreement factor $R_{mag}$ is relatively high for the magnetic phase because the corresponding intensities are relatively weak and many of them overlap with other higher peaks.

The proposed magnetic structure of PrCuAl is, to our best knowledge, unique among the RTX compounds with the ZrNiAl-type crystal structure studied up to now. The magnetic-structure periodicity of 1/3 along the c-axis was not observed yet. The same propagation within

Figure 2. a) ZrNiAl-type hexagonal crystal structure and b) magnetic structure of PrCuAl: projection into the basal plane. The arrows represent magnetic moments located on the Pr sites. The arrow size corresponds to the moment size.
the basal plane \((k = (1/3, 1/3, 0))\) has been reported for DyAgGe, HoAgGe, HoAgSi or DyAgSi [9, 10] and also FeCrAs [11], but the proposed magnetic-moment arrangement in the RAgGe and RAgSi compounds is different. The presence of \(3k\) wave vectors, suggesting square modulated magnetic structures, was observed in DyAgGe and HoAgGe [9]. In the PrCuAl pattern, we do not see any peaks that would correspond to \(3k\) but we should note that these peaks would be very small because of a small Pr magnetic moment compared to Dy or Ho moments. Neutron diffraction study on a single crystal would be highly desirable to confirm the proposed magnetic structure of PrCuAl and possibly reveal further details.

The three Pr sites are magnetically equivalent in PrCuAl. It is not very common for compounds with this crystal structure. Significant frustration of moments on one of the three sites and/or their different propagation with respect to the remaining two sites is frequently observed, including Pr-based compounds PrNiAl [1] and PrPdAl [12] or TmCuAl [13] what is another antiferromagnet among the \(R\)CuAl group. The magnetic structure in PrCuAl remains also relatively stable in magnetic fields. When applying external magnetic field, \(T_N\) shifts considerably to lower temperatures, but there is no sign of any metamagnetic transition up to 6 T [6, 7].

The pure antiferromagnetic order in both PrNiAl and PrCuAl, relatively high transition temperatures compared to heavy rare-earth counterparts and the magnetic structure of PrCuAl, considerably different from other \(RCuAl\) and \(RNiAl\) compounds, evoke the idea that Pr(Ni,Cu)Al series could show a different behavior than \(R\)\((Ni,Cu)Al\) studied up to now.

4. Conclusions

Using powder neutron diffraction experiment we have confirmed the antiferromagnetic order in PrCuAl below \(T_N = 7.9\) K suggested from bulk property studies. The proposed magnetic structure is characterized by the propagation vector \(k = (1/3, 1/3, 1/3)\). The praseodymium magnetic moments are arranged within the basal plane in a triangular structure, the maximum moment size reaches 3.0 \(\mu_B\).

Acknowledgments

The work was supported by the Grant Agency of the Czech Republic under the Grant No. 202/08/0711 and is a part of the research program MSM 0021620834 financed by the Ministry of Education of the Czech Republic. We would like to acknowledge also the ILL for the beam time allocation and support during the measurement.

References

[1] Ehlers G and Maletta H 1996 Z. Phys. B 101 317.
[2] Ehlers G, Ahlert D, Ritter C, Miekeley W and Maletta H 1997 Europhys. Lett. 37 269.
[3] Prchal J, Javorský P, Sechovský V, Dopita M, Isnard O and Jurek K 2004 J. Magn. Magn. Mater. 283 34.
[4] Prchal J, Javorský P, Detlefs B, Danis S and Isnard O 2007 J. Magn. Magn. Mater. 310 e589.
[5] Prchal J, Javorský P, Dopita M, Isnard O and Sechovský V 2006 J. Alloys and Compounds 408-412 155.
[6] Javorský P, Havela L, Sechovský V, Michor H and Jurek K 1998 J. Alloys and Compounds 264 38.
[7] Javorský P, Sechovský V, Havela L and Michor H 1998 J. Magn. Magn. Mater. 177-181 1052.
[8] Rodriguez-Carvajal J 1993 Physica B 192 55.
[9] Baran S, Hofmann M, Leciejewicz J, Penc B, Ślaski M and Szytula A 1998 J. Alloys and Compounds 281 92.
[10] Baran S, Hofmann M, Leciejewicz J, Penc B, Ślaski M, Szytula A and Zygmunt A 2001 J. Magn. Magn. Mater. 222 277.
[11] Wu W, McCollam A, Swainson I, Rourke P M C, Rancourt D G and Julian S R 2009 EPL 85 17009.
[12] Keller L, Dünnl A, Kitazawa H, Tang J, Fauth F and Zolliker M 1998 Physica B 241-243 660.
[13] Javorský P, Gubbens P C M, Mulders A M, Prokeš K, Stüsser N, Gortenmulder T J and Hendrikx R W A 2002 J. Magn. Magn. Mater. 251 123.