

# Possible double magnetic phase transition in $\text{Dy}_5\text{CuPb}_3$

V.H. Tran<sup>a,\*</sup>, L.D. Gulay<sup>b</sup>

<sup>a</sup>W. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 1410, PL-50-950 Wrocław, Poland

<sup>b</sup>Department of General and Inorganic Chemistry, Volyn State University, Volvi Ave 13, UA-43009 Lutsk, Ukraine

Received 14 July 2005; received in revised form 14 November 2005; accepted 20 November 2005

Available online 4 January 2006

## Abstract

We have investigated the magnetic and transport properties of  $\text{Dy}_5\text{CuPb}_3$  by magnetic susceptibility, electrical resistivity, magnetoresistance and thermoelectric power measurements. The compound crystallises in the hexagonal  $\text{Hf}_5\text{CuSn}_3$ -type structure (space group  $P6_3/mcm$ ) and probably undergoes two successive magnetic transitions at  $T_C = 45.0 \pm 0.5$  K and  $T_N = 6.5 \pm 0.5$  K. The experimental data are indicative of a ferri- and antiferromagnetic types of the transitions, respectively. We attribute the double magnetic phase transition and the reduction of the magnetisation values at low temperatures to associate with the two non-equivalent magnetic sublattices of the  $\text{Dy}^{3+}$  ions. We observed a large magnetoresistance value of  $-24\%$  at temperatures in between  $T_N$  and  $T_C$ . The investigated compound has a negative thermoelectric power of  $-17 \mu\text{V/K}$  at 300 K. We interpret the overall behaviour of the  $S(T)$ -curve to two different mechanisms: magnetic and charge carrier diffusion.

© 2005 Elsevier Inc. All rights reserved.

**Keywords:** Localised magnetism; Double magnetic phase transition; Magnetoresistance; Thermoelectric power;  $\text{Dy}_5\text{CuPb}_3$

## 1. Introduction

The series of ternary intermetallic rare-earth compounds  $\text{R}_5\text{TM}_3$  (R = rare earth, T = transition metal, M = Sn, Bi), denoted in the following as 513-type, forms a large family of compounds. The existence of these compounds was discovered more than 40 years ago [1,2]. However, the investigations of their magnetic properties have been performed on a few compounds, namely on  $\text{Ce}_5\text{AgSn}_3$  [3],  $\text{Ce}_5\text{CuSn}_3$  [4,5] and  $\text{Ce}_5\text{CuSb}_3$  [6]. It is worthwhile to mention that the Ag-based compound orders ferromagnetically below 5 K and exhibiting simultaneously an inter-mediated valence state of the cerium ions. Furthermore, the Cu-based ones have been reported to undergo into an antiferromagnetic magnetic phase transition at low temperatures. In addition, the electronic specific heat coefficient of the Ce-based compounds has been found to show a significant enhancement with respect to those of ordinary metals. Therefore, the observation of the intermediate valence and heavy-fermion-like features in the 513-type

compounds investigated so far makes magnetic study of this family of compounds to be highly desired. Recently, a new  $\text{R}_5\text{CuPb}_3$  group was discovered by Gulay et al. [7]. These compounds crystallise in the hexagonal  $\text{Hf}_5\text{CuSn}_3$ -type structure (space group  $P6_3/mcm$ ), as do other series of compounds with Sn [1] or with Bi [2]. To our knowledge, the physical properties of any  $\text{R}_5\text{CuPb}_3$  intermetallic were not explored yet. In this paper we focus first on magnetic phase transition in  $\text{Dy}_5\text{CuPb}_3$ . It is worthwhile to mention that the compounds  $\text{R}_5\text{CuPb}_3$  are formed by filling of octahedral interstices in the crystal structure of binary  $\text{R}_5\text{Pb}_3$  compounds ( $\text{Mn}_5\text{Si}_3$ -type structure, space group  $P6_3/mcm$ ) by the Cu atoms. The relations between the crystal structures of the  $\text{Dy}_5\text{Pb}_3$  and  $\text{Dy}_5\text{CuPb}_3$  compounds are shown in Fig. 1. Empty and filled octahedra [Dy16] and [CuDy16] are shown, respectively. Thus an increase of the volume of the unit cell of  $\text{Dy}_5\text{CuPb}_3$  compared with  $\text{Dy}_5\text{Pb}_3$  is expected. Crystal structure of these compounds has recently been discussed in Ref. [7]. We may mention that since in the unit cell there are two positions for the Dy atoms one should keep in mind that these Dy atoms may have different magnetic sublattices. In turn, one expects complex magnetic phase transitions in

\*Corresponding author. Fax: +48 71 344 1029.

E-mail address: [vhtran@int.pan.wroc.pl](mailto:vhtran@int.pan.wroc.pl) (V.H. Tran).

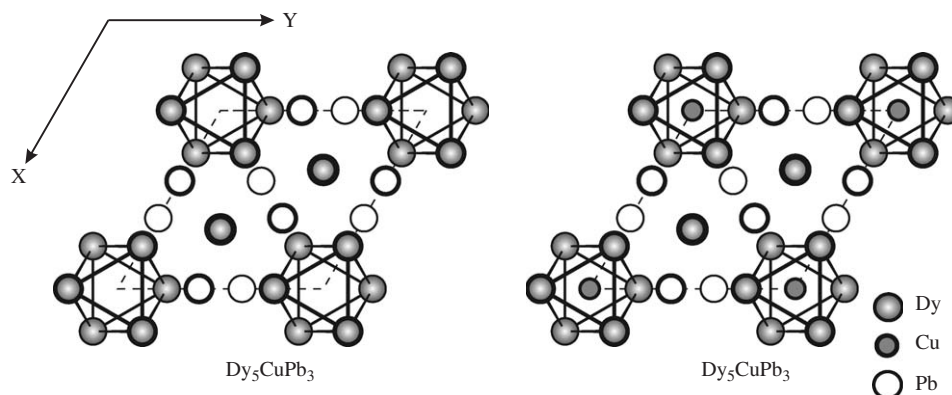


Fig. 1. Empty and filled octahedra [Dy16] and [CuDy16] in the structures of the  $\text{Dy}_5\text{Pb}_3$  and  $\text{Dy}_5\text{CuPb}_3$  compounds, respectively.

this compound. Besides, in contrast to the case of cerium based compounds, where the magnetic properties are usually interpreted in terms of the Kondo lattice model [8], the magnetism in  $\text{Dy}_5\text{CuPb}_3$  would be expected due to the long-range Ruderman–Kittel–Kasuya–Yosida interaction combined with crystal field anisotropy.

## 2. Experimental details

Samples with a total mass of about 1 g each were prepared by arc melting of pure metals (the purity of the ingredients was better than 99.9 wt.%) in a high-purity argon atmosphere. The alloys were remelted several times to ensure homogeneity. The mass losses after the melting were less than 0.5 wt.%. The obtained samples were sealed in evacuated quartz ampoules and annealed at 1070 K during 100 h. After annealing the ampoule with the samples was quenched in air.

X-ray powder diffraction patterns of the samples were recorded using a Siemens D5000 powder diffractometer ( $\text{CuK}\alpha$  radiation,  $10^\circ$ – $80^\circ$ , step scan mode with a step size of 0.05 and counting time of 5 s per data point). The experiments indicated that the obtained samples are single-phased. Lattice parameters of  $\text{Dy}_5\text{CuPb}_3$  calculated based on the observed Bragg reflections are  $a = 9.060(3)$  and  $c = 6.578(2)$  Å. These are consistent with the previously reported data [7]. The composition of the samples was confirmed using EDX and microstructure analyses.

DC magnetisation,  $M$ , was measured by means of a SQUID (Quantum Design) magnetometer in fields up to 5 T and in the temperature range 2–400 K. The magnetisation data were collected in zero-field cooling (ZFC) and in field-cooling (FC) modes. Electrical resistivity,  $\rho(T)$ , was measured using a four-probe DC-technique in the temperature range 2–300 K. The samples were rectangular with typical dimensions  $0.5 \text{ mm} \times 0.5 \text{ mm} \times 5 \text{ mm}$ . Transverse magnetoresistance data,  $MR$ , were collected in two different ways: iso-field data in a fixed magnetic field of 8 T on zero-field cooled samples and isothermal data in fields up to 8 T at several selected temperatures below 50 K. We define the magnetoresistance as  $\Delta\rho/\rho(0) = \frac{\rho(T,B) - \rho(0)}{\rho(0)}$ . Thermoelectric power was measured using the differential

method in the temperature range 4–300 K. The sample with a dimension  $1 \times 1 \times 2 \text{ mm}^3$  was clamped between two spring-loaded Pt blocks provided with heater and a pair of Au–Fe/chromel thermocouple. The temperature gradient of about 1 K was applied across the sample length.

## 3. Results

In Fig. 2 we show the reciprocal magnetic susceptibility  $\chi^{-1}(T)$  of  $\text{Dy}_5\text{CuPb}_3$  measured at a field of 0.5 T and in the inset the product  $\chi T$  as a function of temperature. One can see in this figure that the  $\chi(T)$  dependence exhibits the Curie–Weiss (CW) behaviour above 100 K. From the CW law fitting of the magnetic susceptibility data we obtained effective moment  $\mu_{\text{eff}} = 10.84 \mu_B/\text{Dy}$  and paramagnetic Curie temperature  $\Theta_p = 50.5(5)$  K. Clearly, the  $\mu_{\text{eff}}$ -value agrees well with the theoretical value expected for the  $\text{Dy}^{3+}$  ions with the electronic configuration  ${}^6\text{H}_{15/2}$  ( $10.64 \mu_B$ ). This fact implies that in  $\text{Dy}_5\text{CuPb}_3$  the magnetic  $\text{Dy}^{3+}$  ions are mainly responsible for the magnetism. A ferromagnetic-type interaction in the paramagnetic state is dominating since the positive value of  $\Theta_p$  estimated from the experimental data is relatively large.

However, the ferromagnetic interaction does not lead the compound to undergo a transition to a ferromagnetic order. As one can infer from the inset of Fig. 2 the magnetic phase transition at 45 K appears to be complex. At a field of 0.5 T, the magnetisation shows a broad maximum between 10–40 K. We argue below that such a behaviour is the result of the competition between ferromagnetic and antiferromagnetic (AF) interactions. The evidence for the latter interaction is supported by the temperature dependence of the product  $\chi T$ , shown in inset b of Fig. 2.

Considering the data at low temperatures shown in Fig. 3 we see that at a low field of 0.1 T the ZFC magnetisation shows two anomalies at  $T_N = 6.5$  and  $T_C = 45.0$  K, respectively. These anomalies are defined as an extremum point of the temperature derivative of the magnetic susceptibility (see inset of Fig. 3). If we apply a higher field strength the anomalies shift in the opposite directions. For instance, at 0.5 T the position of maximum

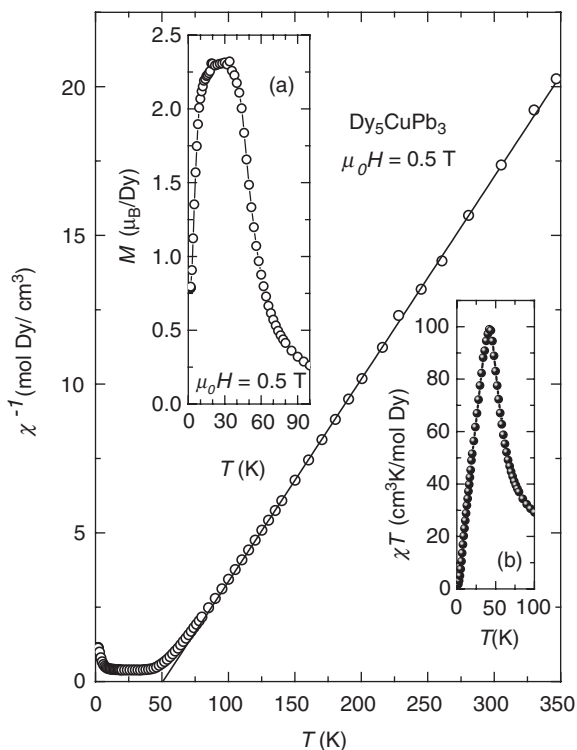


Fig. 2. Temperature dependence of the reciprocal magnetic susceptibility. The dashed line is the fit of the experimental data to the Curie–Weiss law. Inset a shows the low-temperature magnetisation. Inset b shows the product  $\chi T$  as a function of temperature.

of  $d(M/H)/dT$  amounts to 4.3 K whereas the inflection point 47.0 K. In the inset of Fig. 3 we show the temperature dependences of  $d(M/H)/dT$  for several magnetic fields. Such field dependencies of the extrema in the  $M(T)$ -dependencies point to antiferromagnetic and ferromagnetic type transitions at  $T_C$  and  $T_N$ , respectively. One of characteristic behaviour of the studied material is the irreversibility of the magnetisation. For  $Dy_5CuPb_3$  this phenomenon is due to an interplay between the thermal energy and anisotropy energy. The hexagonal  $Hf_5CuSn_3$ -type structure ensures for a highly anisotropic character of magnetic interactions of the  $Dy^{3+}$  ions.

In Fig. 4 we show the magnetisation data collected at several temperatures below 60 K. We observe that the initial magnetisation at 2 K is linear with the applied field and at a critical field of  $\sim H_{cr} = 1.5$  T the  $M(H, 2$  K) curve shows a metamagnetic transition. These characteristics support the AF ground state of the compound. Typically for an antiferromagnet,  $H_{cr}$  shifts down to lower values with increasing temperature. In the induced ferromagnetic state, i.e., above  $H_{cr}$ ,  $M$  tends to saturate with a value of  $7\mu_B/Dy$  at 5 T. Upon decreasing magnetic field the magnetisation exhibits a hysteresis loop and relatively large remanent magnetisation is found. A free powder-magnetisation at 5 T and 2 K reaches a little larger value of  $8\mu_B/Dy$ . Thus, at 2 K the observed magnetisation is significantly lower than the theoretical moment  $10\mu_B/Dy$  of the free  $Dy^{3+}$  ions. Such a disagreement between these

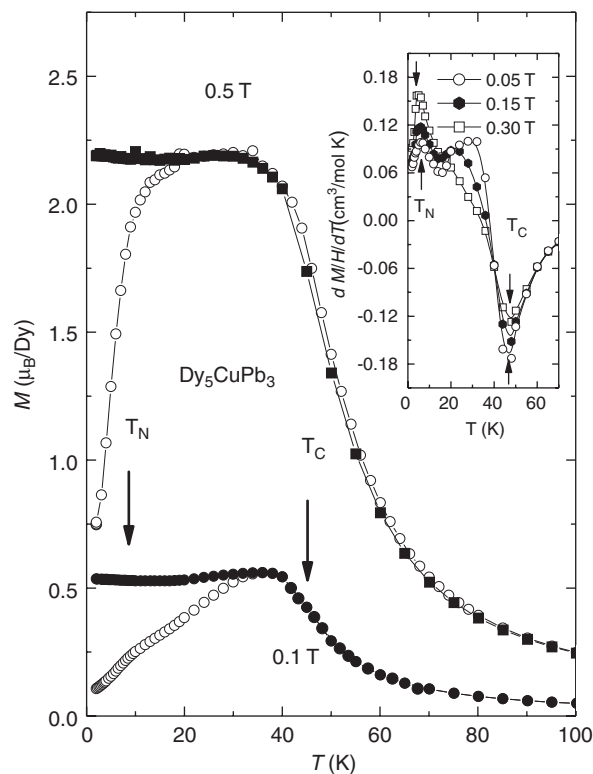


Fig. 3. Temperature dependence of the magnetization of  $Dy_5CuPb_3$  measured at 0.1 and 0.5 T. The data collected in zero-field cooling mode are presented as open symbols, data in field-cooling mode closed symbols. Inset: Temperature dependence of the derivative of  $d(M/H)/dT$  for magnetisation measured at 0.05, 0.15 and 0.3 T.

two values suggests that the moments in different magnetic sublattices are somewhat compensated, and a higher magnetic field is needed to orientate all magnetic moments. Alternative interpretation is due to a strong anisotropy of the material. Considering the fact that the saturation moment observed in a powder is  $\pi/4$  of the easy plane value in an easy plane system or equal to  $1/2$  of the easy axis value in an easy axis system, one suspects that the studied compound could be an easy plane magnetisation magnet.

The magnetisations taken between 20–60 K vary in a manner typical of material with a strong ferromagnetic correlation. The values of  $M$  at 5 T decrease steadily with increasing temperature and there is no evidence of the spontaneous magnetisation. This behaviour is illustrated in the panel c of Fig. 4, where the Arrott plot is shown. At relatively high fields, the squared magnetisation versus  $\mu_0 H/M$  for data below 45 K has positive values of both the slope and intercept to the  $M^2$  axis. From the deduced values one can conclude that an induced ferromagnetism by magnetic fields appears below 47 K. Because of the absence of any spontaneous magnetisation, the magnetic phase transition at  $T_C = 45.0$  K referred from the low field measurement, is presumably of ferrimagnetic type.

The temperature dependence of the electrical resistivity in zero field is shown in Fig. 5. Due to a lot of microcracks in the sample we were not able to determine the absolute

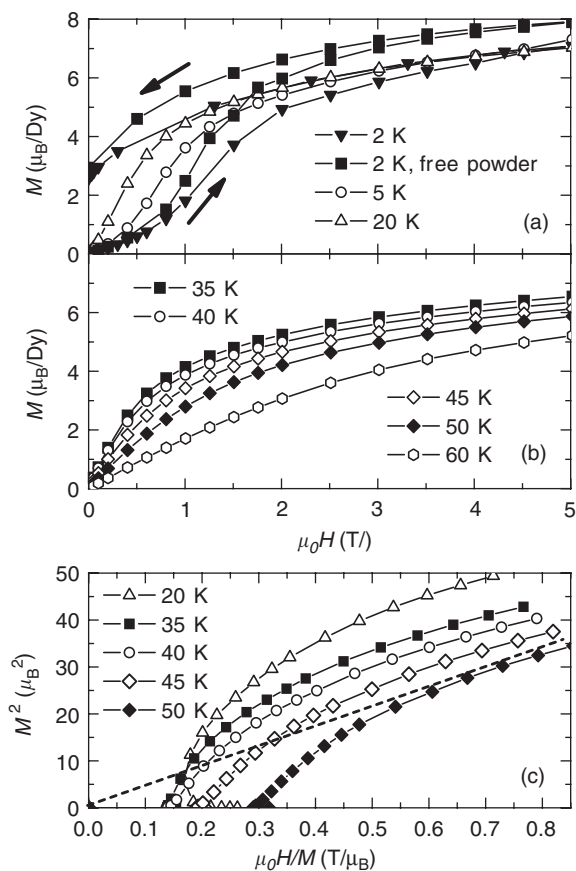


Fig. 4. (a) and (b) Magnetisation of  $\text{Dy}_5\text{CuPb}_3$  measured at several temperatures below 60 K. The arrows indicate increasing or decreasing magnetic field strength for the 2 K magnetisation data. The free powder magnetisation at 2 K is also shown. (c) Magnetisation of  $\text{Dy}_5\text{CuPb}_3$  in the form of the Arrott plot. The solid lines are guides for the eyes. The dashed line hints an induced ferromagnetism below 47 K.

resistivity value. However, one can analyse the experimental data with the help of the Bloch–Grüneisen function [9]  $\rho(T) = \rho(0) + kT\left(\frac{T}{\Theta}\right)^4 \int_0^{\Theta/T} \frac{z^5 dz}{(e^z - 1)(1 - e^{-z})}$  with the Debye temperature of  $\Theta = 220$  K (dashed line in Fig. 5).  $\rho_0$  is the residual resistivity and  $k$  is a constant. From the fitting data one can see that, the sample exhibits the  $\rho(T)$ -dependence of a phonon behaviour above 60 K.

In the temperature range 40–60 K, the  $\rho(T)$  shows an increase with decreasing temperature. It is noticed that  $T_C$  deduced from the magnetic measurement 45.0 K locates quite far above maximum of the resistivity (37 K). A similar maximum in the  $\rho(T)$ -curves has already been observed in ferromagnetic GMR materials [10], for which one of the possible mechanisms is the formation of magnetic polarons. Maximum in the resistivity near the Curie temperatures was also found in metallic  $\text{RNi}_5$  compounds [11], in which the magnetic moments fluctuation time is believed to be comparable to the relaxation time of conduction electrons. With further decreasing temperature below maximum, the reduction of spin

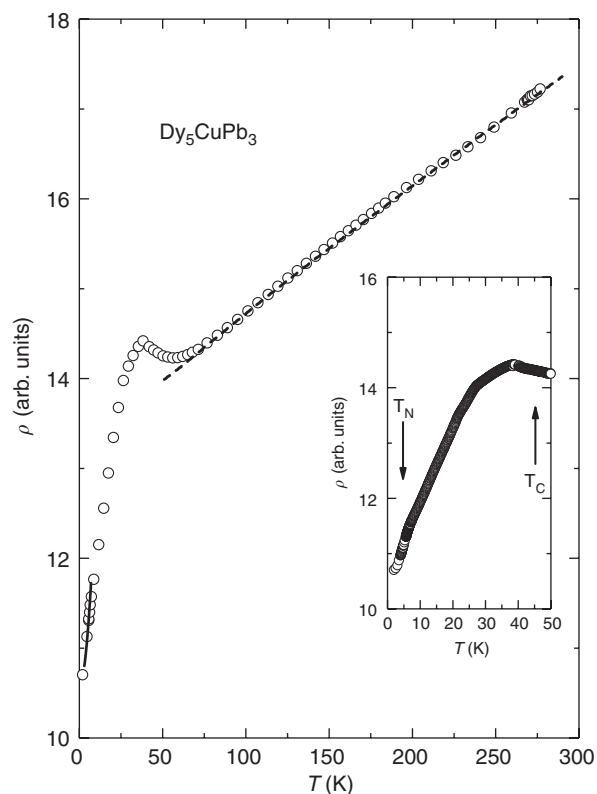


Fig. 5. Temperature dependence of the electrical resistivity of  $\text{Dy}_5\text{CuPb}_3$ . The dashed line represents the Debye function. The solid line is a hint of the  $T^2$  dependence. The inset shows the low-temperature data.

disorder scattering leads to a sharp decrease in the resistivity. Inspecting the low temperature data shown in the inset of Fig. 5 one observes an anomaly at 6.0 K, which is consistent with the phase transition inferred from the magnetic measurement data. Below about 5 K we have attempted to fit the data to the  $T^2$  dependence, expected for electron–electron or/and electron–magnon scattering. The solid line in Fig. 5 is an illustration of such a fit.

The application of an external magnetic field leads to a decrease in the resistivity (Fig. 6a), resulting in a large negative magnetoresistance. Interestingly, the largest  $MR$  occurs neither at  $T_N$  nor at  $T_C$  (see Fig. 6b) but in between  $T_N$  and  $T_C$ . This fact implies that the fluctuation of the magnetic Dy moments associated with a spin reorientation is the dominant mechanism.

In Fig. 7 we show the field dependence of the magnetoresistance measured at 4, 10 and 20 K. The data clearly indicate that as the temperature is varied there are also qualitative changes in the  $\Delta\rho/\rho(0)$ -curves. For the 4 K  $MR$  curve one can recognise the occurrence of a positive plateau at low fields. Near 1.5 T, the field derivative of the  $MR$  shows minimum, corresponding to spin flip process, which already observed in the magnetisation measurement (Fig. 4a). In the case of data at 10 K, the  $MR$  curve exhibits

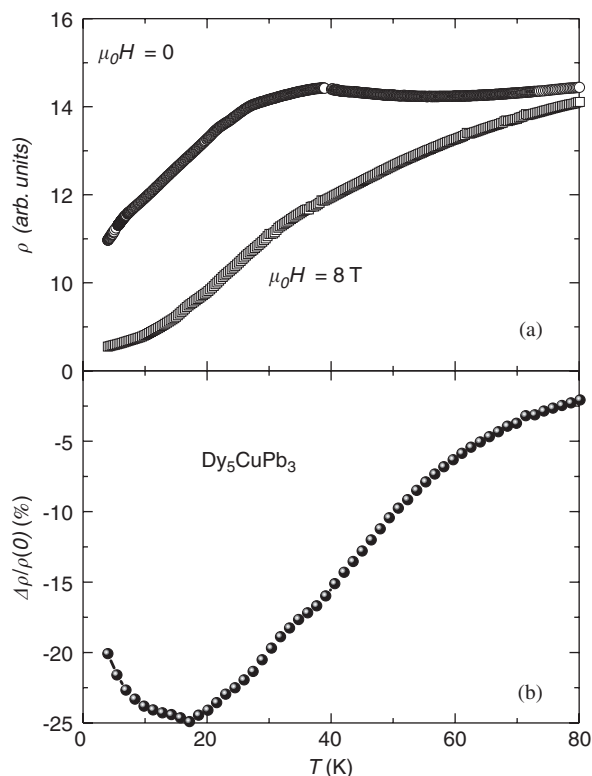


Fig. 6. (a) Temperature dependence of the resistivity measured at 0 and at 8 T. (b) The magnetoconductance at 8 T as a function of temperature.

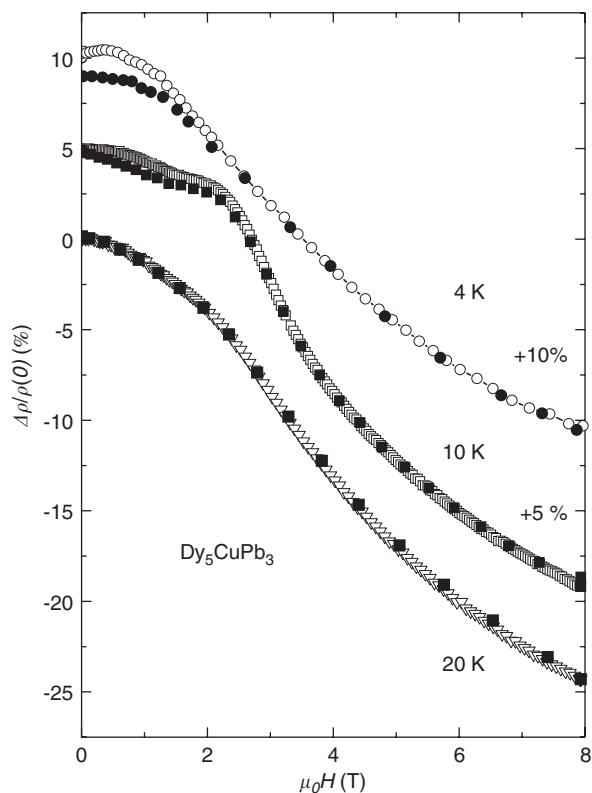


Fig. 7. Magnetoconductance at 4, 10 and 20 K versus applied field strength. For the sake of clarity, the data at 4 and 10 K are shifted by 10 and 5%, respectively. The open and closed symbols indicate the data collected with increasing and decreasing field strength, respectively.

a knee situated at about 2.5 T. For both 4 and 10 K  $MR(H)$ -curves a small hysteresis is observed below 1.5 T. One important point should be noted that at temperatures 10 and 20 K the  $MR(H)$  reaches a relatively large value of  $-24\%$  at a field of 8 T, but it does not show any indication of saturation. This means that the spin-alignment mechanism leading spins towards the applied field direction still persists at high fields.

The thermoelectric power  $S$  of  $Dy_5CuPb_3$  is negative at room temperature and shows the linear decrease down to  $T_C$  (Fig. 8). Below 37 K there is a step-like increase providing to a positive maximum in the neighbourhood of  $T_N$ . The thermopower behaviour of the studied compound must be the result of a combined effect of magnetic and charge carrier diffusion components. Any maximum at  $\sim\Theta/10$  usually connected with the phonon drag mechanism is not observed.

#### 4. Concluding remarks

In conclusion, the compound  $Dy_5CuPb_3$  crystallises in the hexagonal  $Hf_5CuSn_3$ -type structure (space group  $P6_3/mcm$ ). The bulk measurements suggest that the compound orders magnetically below  $45.0 \pm 0.5$  K with an additional magnetic phase transition at  $6.5 \pm 0.5$  K. Magnetisation and magnetoconductance measurements imply that the lower phase transition in  $Dy_5CuPb_3$  is antiferromagnetic in origin, while the higher temperature

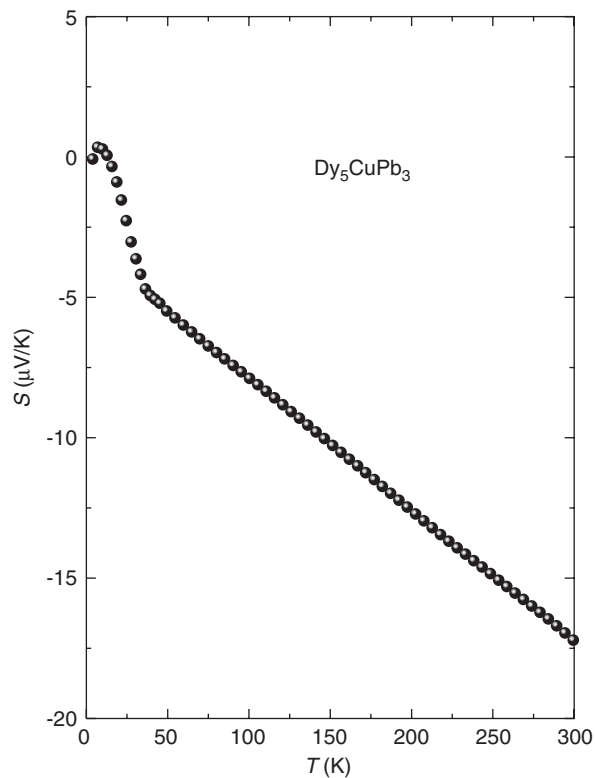


Fig. 8. Temperature dependence of the thermoelectric power of  $Dy_5CuPb_3$ .

transition is of ferrimagnetic type. The magnetic properties of  $\text{Dy}_5\text{CuPb}_3$  may be described in a localised electron magnetism picture. The low-temperature magnetic behaviour, i.e., the double magnetic phase transition and a reduction of magnetic moments at low temperatures, can be understood assuming two magnetic  $\text{Dy}^{3+}$  sublattices. We suppose that the change in the magnetic structures with lowering temperature from  $T_C$  to  $T_N$  is accompanied with an enhancement of fluctuation of the magnetic moments, leading to a decrease of the relaxation time of the conduction electrons and it results in the occurrence of the resistivity maximum below  $T_C$ . An applied magnetic field suppresses the moments fluctuation, giving rise to a giant magnetoresistance ( $-24\%$ ) at temperatures below  $T_C$ . Since the thermoelectric power is linear with temperature, i.e., due to the diffusion component, we may propose that the considerably large value of the thermoelectric power ( $-17\mu\text{V/K}$ ) at room temperature lies in a low charge carrier nature of the compound. Further investigations, notably measurements of specific heat and neutron diffraction are planned to clarify the nature of the observed phase transitions.

## Acknowledgments

The work has been supported by the Polish State Committee Grant no. 4T08A 045 24.

## References

- [1] K. Schubert, H.G. Meissner, M. Poetzschke, W. Rossteutscher, E. Stolz, *Naturwissenschaften* 49 (1962) 57; W. Rieger, E. Parthé, *Monat. Chem.* 99 (1968) 291.
- [2] D. Hohnke, E. Parthé, *J. Less-Common Methods* 17 (1969) 291.
- [3] P. Boulet, D. Mazzone, H. Noël, P. Riani, P. Rogl, R. Ferro, *Intermetallics* 7 (1999) 931.
- [4] V.H. Tran, *J. Alloys Comp.* 383 (2004) 281.
- [5] V.H. Tran, *Czech. J. Phys.* 54 (2004) D411.
- [6] V.H. Tran, *Phys. Rev. B* 70 (2004) 094424.
- [7] L.D. Gulay, J. Stępień-Damm, M. Wołczyr, *J. Alloys Comp.* 319 (2001) 148.
- [8] S. Doniach, in: R.D. Parks (Ed.), *Valence Instabilities and Related Narrow Band Phenomena*, Plenum, New York, 1977, p. 169; S. Doniach, *Physica (Amsterdam)* 91B (1977) 231.
- [9] J.M. Ziman, *Electrons and Phonons*, Oxford University Press, Oxford, UK, 1960.
- [10] A.P. Ramirez, *J. Phys.: Condens. Matter* 9 (1997) 8171.
- [11] J.A. Blanco, D. Gignoux, D. Schmitt, A. Tari, F.Y. Bang, *J. Phys.: Condens. Matter* 6 (1994) 4335.