

# Magnetocaloric and Thermal Properties of $\text{Ho}(\text{Co}_{1-x}\text{Si}_x)_2$ Compounds

Vladimír Sechovský, Denys Vasylyev, and Jan Prokleška

Department of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5, 121 16 Prague 2, Czech Republic

Reprint requests to V. Sechovsky. Fax: +420-2-21911617. E-mail: sech@mag.mff.cuni.cz

*Z. Naturforsch.* **2007**, 62b, 965–970; received April 6, 2007

*Dedicated to Dr. Bernard Chevalier on the occasion of his 60<sup>th</sup> birthday*

The specific heat and thermal conductivity of  $\text{HoCo}_2$  and  $\text{Ho}(\text{Co}_{0.95}\text{Si}_{0.05})_2$  were measured as functions of temperature in several constant magnetic fields up to 8 T. From a specific-heat data analysis the isothermal entropy change and the magnetocaloric effect (MCE) have been evaluated in a wide temperature range for several values of the applied magnetic field. The considerable values of the magnetocaloric effect in the vicinity of the magnetic ordering transition are qualifying both compounds as suitable for magnetic refrigeration purposes. The magnetic phase transition temperature ( $T_C$ ) increases from 77 K for  $\text{HoCo}_2$  to 103 K for  $\text{Ho}(\text{Co}_{0.95}\text{Si}_{0.05})_2$  while the large MCE in the vicinity of  $T_C$  is maintained, which demonstrates ways of tuning the operating temperatures of the magnetic refrigerant.

**Key words:**  $\text{HoCo}_2$ , Magnetic Phase Transition, Specific Heat, Magnetocaloric Effect, Thermal Conductivity

## Introduction

A large magnetocaloric effect (MCE) around a magnetic phase transition gives rise to a potential application of materials for the use in magnetic cooling [1], which offers a more ecological alternative to present cooling systems. Knowledge of thermal transport properties and thermopower of intermetallic compounds is very important from the point of view of thermoelectric power generators and of the development of thermocouples. Since the available information pool in this field is rather insufficient, concerted investigations of magnetocaloric and thermal transport phenomena in certain magnetic materials are highly desirable.

The Laves-phase rare earth (RE) intermetallic compounds  $\text{RECo}_2$  are presently the subject of intensive studies. Results of these investigations bring fundamental knowledge on the wide topics of the 4*f* localized and 3*d* itinerant magnetism. These materials were chosen because of their sensitivity to an external magnetic field or to partial substitution by other elements leading to intrinsic changes. An important feature of these compounds is a large magnetic entropy change in the vicinity of a magnetic phase transition and consequently a large MCE. For the  $\text{RECo}_2$  systems, substitution of one element by another can change the elec-

tron configuration and density of states at the Fermi surface, thus modifying the magnetic properties of the  $\text{RECo}_2$  compounds. Under the condition of the fixed volume, the estimation of the hybridization between the Co *d* states and Si *p* states can contribute to a better understanding of the nature of the 3*d* magnetism.

The aim of the present work was to study the MCE of  $\text{HoCo}_2$  and  $\text{Ho}(\text{Co}_{0.95}\text{Si}_{0.05})_2$  compounds around the magnetic ordering phase transition occurring as a result of the application of various magnetic fields. Results of a simultaneous study of thermal transport measurements are also presented.

## Experimental Section

Polycrystalline samples of  $\text{HoCo}_2$  and  $\text{Ho}(\text{Co}_{0.95}\text{Si}_{0.05})_2$  were prepared by arc-melting of the elements of at least 3N5 purity in the nominal composition. The obtained ingots were wrapped in Ta foil and sealed in a quartz tube under high vacuum and annealed at 950 °C for 50 h. Both samples crystallize in the  $\text{MgCu}_2$ -type (C15) structure with lattice parameters which are in good agreement with literature data [3].

Specific heat and thermal conductivity measurements were performed using the PPMS 14 T apparatus (Quantum Design) in the JLMS, Prague. The specific heat was measured over the temperature range from 1.9 to 300 K in zero

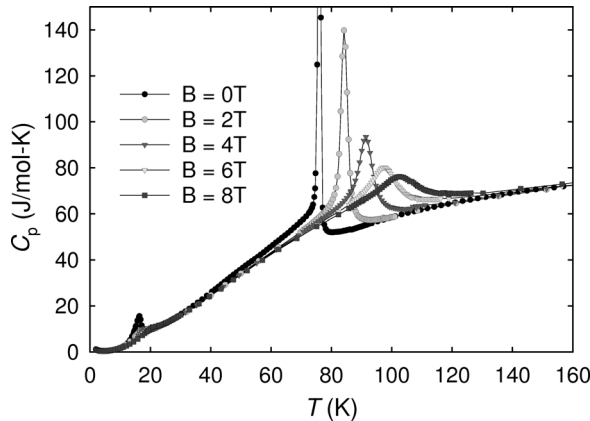


Fig. 1. Temperature dependence of the specific heat of  $\text{HoCo}_2$  below 160 K measured in different magnetic fields up to 8 T.

magnetic field. In the magnetic fields 2, 4, 6 and 8 T the samples were measured over the temperature range 1.9–160 K.

For thermal transport measurements a four-probe lead configuration was used for mounting the sample. The four leads were attached individually by means of a small amount of silver-filled H20E epoxy from Epoxy Technology and were baked about 5 min at a temperature of  $\sim 150^\circ\text{C}$ . The size of the  $\text{HoCo}_2$  and  $\text{Ho}(\text{Co}_{0.95}\text{Si}_{0.05})_2$  samples was  $10.5 \times 0.65 \times 0.8$  and  $8.97 \times 1.2 \times 1.05 \text{ mm}^3$ , respectively. The emissivity values of both materials were equal to 0.3. The continuous measurement mode was applied for both samples. The thermal conductivity was measured in the temperature interval from 1.9 to 350 K without magnetic field, and at temperatures between 1.9 and 160 K in the magnetic fields of 4 and 8 T.

## Results

### Magnetocaloric effect

Figs. 1 and 2 show the temperature dependence of the specific heat of  $\text{HoCo}_2$  and  $\text{Ho}(\text{Co}_{0.95}\text{Si}_{0.05})_2$  measured in magnetic fields up to 8 T. The Curie temperatures are  $T_C = 77 \text{ K}$  for  $\text{HoCo}_2$  and  $103 \text{ K}$  for  $\text{Ho}(\text{Co}_{0.95}\text{Si}_{0.05})_2$ , respectively. Both compounds exhibit pronounced symmetric peaks in the  $C_p$  vs.  $T$  plots in the vicinity of the magnetic transition. In other words, the transition from the high-temperature paramagnetic state to low-temperature magnetic ordering is accompanied by a sudden change of magnetic entropy at  $T_C$ . When applying a magnetic field, the sharp anomaly in the  $C_p$  vs.  $T$  dependence at  $T_C$  is shifted to higher temperatures and becomes rapidly smeared out with increasing the field value, but nevertheless it remains rather symmetric.

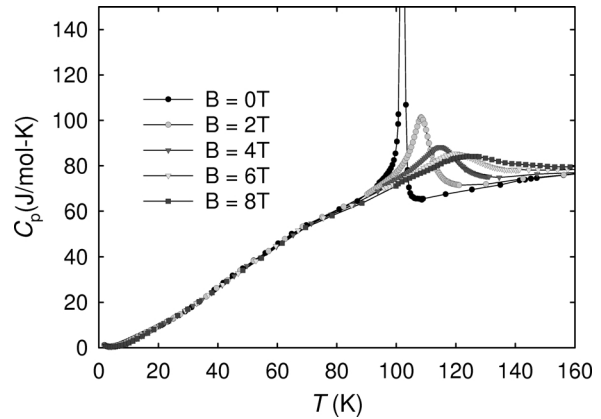


Fig. 2. Temperature dependence of the specific heat of  $\text{Ho}(\text{Co}_{0.95}\text{Si}_{0.05})_2$  below 160 K measured in different magnetic fields up to 8 T.

The specific heat data measured in different magnetic fields allow to determine the MCE and the isothermal entropy change of  $\text{HoCo}_2$  and  $\text{Ho}(\text{Co}_{0.95}\text{Si}_{0.05})_2$ .

$$S(T)_{H_i} = \int_0^T \frac{C(T', H_i)}{T'} dT' + S_{0, H_i} \quad (1)$$

where  $i = 0, 1, \dots$ ;  $C(T, H_i)$  is the specific heat measured in magnetic fields  $H_0$  and  $H_i$ , and  $S_{0, H_i}$  is equal to zero at 0 K in a condensed system [4]. The magnitude of the magnetocaloric effect and the isentropic temperature change  $\Delta T_{\text{ad}}(T)$  have been derived from the vertical between the  $S(T)_0$  and  $S(T)_{H_i}$  curves [5].

The isothermal entropy change  $\Delta S(T)$  is displayed in Figs. 3 and 4 as a function of temperature.  $-\Delta S(T)$  increases very sharply to a maximum value at approximately 80 K and 106 K for  $\text{HoCo}_2$  and  $\text{Ho}(\text{Co}_{0.95}\text{Si}_{0.05})_2$ , respectively, whereas it decays much more slowly with further increasing temperature. With increasing the magnetic field, the high-temperature decay becomes gradually slower. The maximum  $|\Delta S(T)|$  value is found at  $8 \text{ J mol}^{-1} \text{ K}^{-1}$  for  $\text{HoCo}_2$  and at  $6 \text{ J mol}^{-1} \text{ K}^{-1}$  for  $\text{Ho}(\text{Co}_{0.95}\text{Si}_{0.05})_2$  for the magnetic field of 8 T.

Our results of  $-\Delta S(T)$  seem to be in reasonably good agreement with data calculated from magnetization curves measured at corresponding temperatures by N. H. Duc *et al.* [6] using the Maxwell relation (2)

$$\left( \frac{\partial T}{\partial H} \right)_T = \left( \frac{\partial M}{\partial T} \right)_H \quad (2)$$

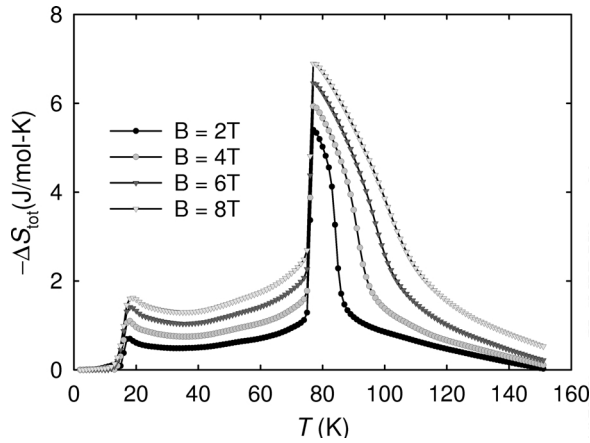


Fig. 3. Entropy change for various magnetic fields for  $\text{HoCo}_2$  determined from specific heat data.

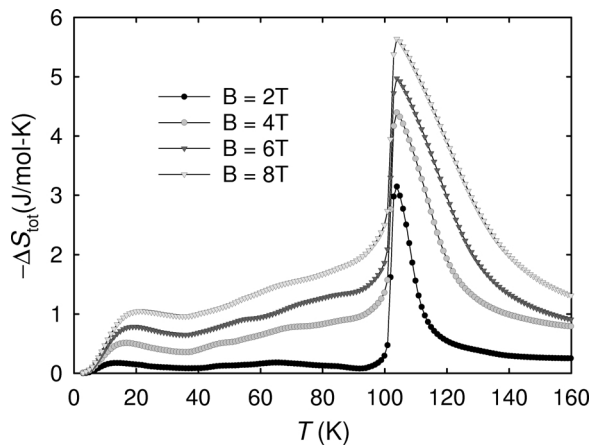


Fig. 4. Entropy change for various magnetic fields for  $\text{Ho}(\text{Co}_{0.95}\text{Si}_{0.05})_2$  determined from specific heat data.

yielding

$$\Delta S(T) = \int_0^H \frac{\partial M}{\partial T} dH. \quad (3)$$

The disagreement between the corresponding values of the magnetic entropy change in lower magnetic fields taken from the two different experiments (specific heat and magnetization) can be understood by taking into consideration that the Maxwell relation does not hold for the first-order metamagnetic transition, which appears in our compounds in a narrow range of temperatures above  $T_C$  (see Fig. 5).

The plot of the  $\Delta T_{ad}(T)$  data determined in this paper (see Figs. 6 and 7) also exhibits a sharp peak in

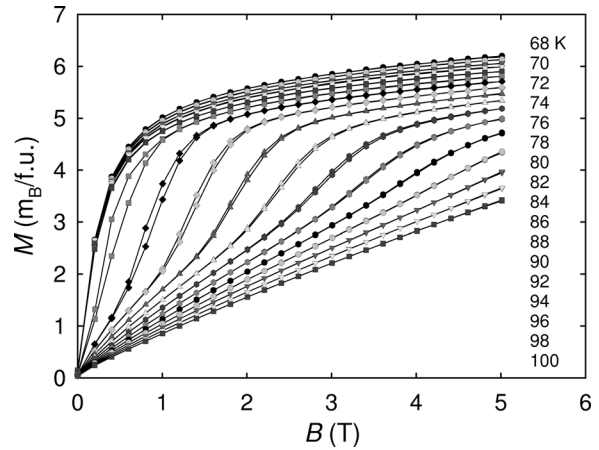


Fig. 5. Magnetization isotherms of  $\text{HoCo}_2$  at temperatures above  $T_C$ .

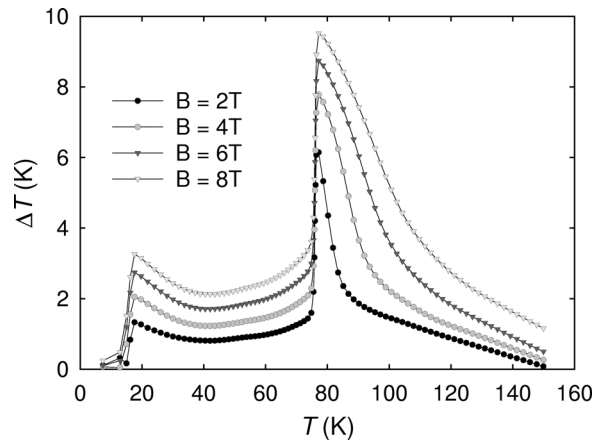


Fig. 6. Magnetocaloric effect  $\Delta T_{ad}(T)$  for an isoentropic process in magnetic fields up to 8 T (with respect to zero initial field) for  $\text{HoCo}_2$  as derived from specific heat data.

the vicinity of  $T_C$  and a broad peak at low temperatures for both compounds. The plot of  $\Delta T_{ad}(T)$  shows peaks around 83 K (106 K for  $\text{Ho}(\text{Co}_{0.95}\text{Si}_{0.05})_2$ ) for different fields and temperatures, and the maximum of the peaks is nearly independent of the value of the applied magnetic field. The size of MCE on the other hand naturally increases with increasing field and the maximum values are  $\Delta T_{ad}(T) = 10$  K for  $\text{HoCo}_2$  and 8 K for  $\text{Ho}(\text{Co}_{0.95}\text{Si}_{0.05})_2$  in the magnetic field of 8 T.

The anomalies observed in the specific heat and magnetocaloric properties below 20 K are connected with an order-to-order magnetic phase transition based on the easy-magnetization direction of the Ho magnetic moment.

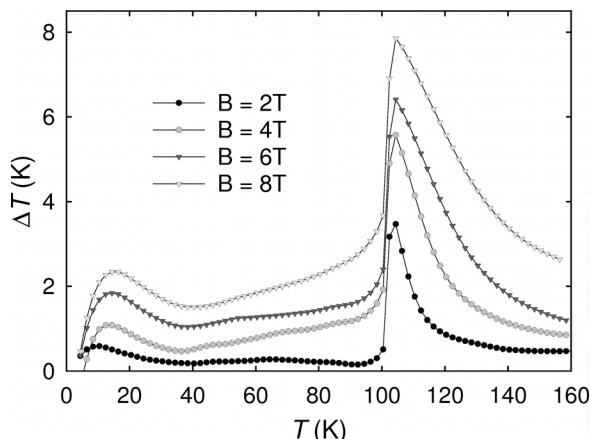


Fig. 7. Magnetocaloric effect  $\Delta T_{\text{ad}}(T)$  for an isentropic process in magnetic fields up to 8 T (with respect to zero initial field) for  $\text{Ho}(\text{Co}_{0.95}\text{Si}_{0.05})_2$  as derived from specific heat data.

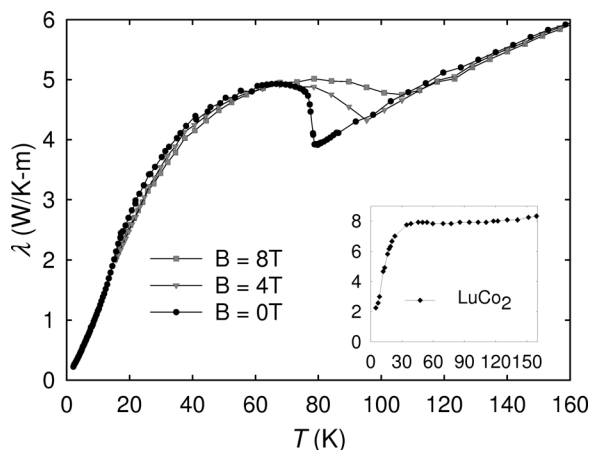


Fig. 8. Thermal conductivity  $\lambda$  versus  $T$  in various magnetic fields up to 8 T around the phase transition temperature for  $\text{HoCo}_2$ . Inset: Thermal conductivity  $\lambda$  versus  $T$  for  $\text{LuCo}_2$ .

#### Thermal conductivity

Figs. 8 and 9 show the temperature dependence of the heat conductivity  $\lambda(T)$  for  $\text{HoCo}_2$  and  $\text{Ho}(\text{Co}_{0.95}\text{Si}_{0.05})_2$ , respectively. A negative step ( $\sim -25\%$ ) is observed in zero magnetic field around  $T_C = 77$  K for  $\text{HoCo}_2$ . In high magnetic fields the anomaly at  $T_C$  smears out. The thermal conductivity behavior of  $\text{Ho}(\text{Co}_{0.95}\text{Si}_{0.05})_2$  in the critical region of the magnetic phase transition is much less pronounced. The  $\lambda(T)$  plot shows a tiny step at  $T_C = 103$  K, by far not as sharp as for  $\text{HoCo}_2$ . This  $\lambda(T)$  anomaly is shifted to higher temperatures and smeared out in magnetic fields. Both compounds show almost no field de-

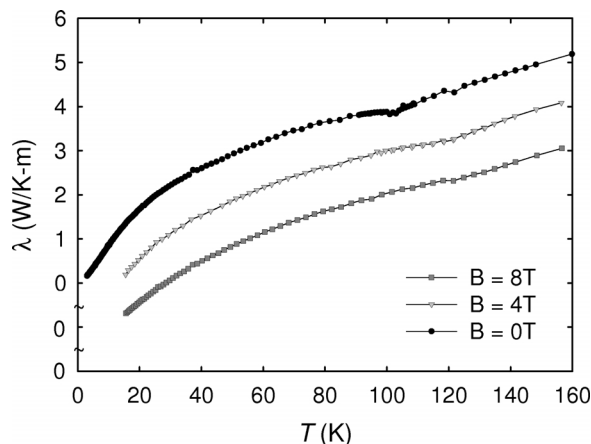


Fig. 9. Thermal conductivity  $\lambda$  versus  $T$  in various magnetic fields up to 8 T around the phase transition temperature for  $\text{Ho}(\text{Co}_{0.95}\text{Si}_{0.05})_2$ .

pendence in the paramagnetic region at high temperatures. The experimental value of the Lorenz number, defined as  $L = \frac{\lambda \rho}{T}$ , ( $\rho$  is the electrical resistivity – measured and published by Cuong *et al.* [2] for  $\text{RE}(\text{Co}_{1-x}\text{Si}_x)_2$ ) is constant in the paramagnetic region in agreement with the Wiedemann-Franz law. By contrast, the Lorenz number is strongly temperature-dependent in the neighborhood of the magnetic phase transition. It seems that the spin fluctuation scattering causes a deviation of  $L$  from the value of  $L_0$  (the theoretical value of the Lorenz number  $L_0$  for the free electron gas equals to  $2.45 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$ ). For comparison we present the temperature variation of the thermal conductivity of the nonmagnetic material  $\text{LuCo}_2$ , as published by Gratz *et al.* [8], as an inset of Fig. 8. A negative curvature below 50 K is connected with the spin fluctuating scattering mechanism [8–10].

#### Discussion

The physical properties like specific heat, MCE, and transport characteristics of the studied compounds in the region of the magnetic phase transition are strongly determined by the behavior of the Co 3d electrons, which below  $T_C$  carry induced magnetic moments due to interactions with the ferromagnetically ordered 4f moment sublattice of Ho [11]. The  $C_p(T)$  and  $\lambda(T)$  curves for  $\text{HoCo}_2$  in the paramagnetic region are practically independent of the magnetic field. Further, the  $\rho(T)$  and  $\lambda(T)$  curves have nearly the same temperature dependence in the paramagnetic temperature range. Resistivity investigations performed on

the pseudobinary  $(\text{Ho}, \text{Y})\text{Co}_2$  (see for example [12]) have also shown that the temperature dependence of  $\rho$  for  $T \gg T_C$  is the same in all the compounds independent of the amount of Ho substituted by Y. In this case disordered localized magnetic  $4f$  moments cause a temperature-independent contribution to the electrical and thermal resistivity [13].

The thermal and electrical transport properties become anomalous when approaching  $T_C$ . For the specific heat and MCE this is connected with a change in entropy of the system in the vicinity of the phase transition. The thermal conductivity depends on one hand on the conduction electron behavior and on the other hand on the variety and nature of scattering centers. In our case, the magnetic ordering leads to a sudden decrease of the number of scattering processes of conduction electrons on disordered moments yielding the anomaly of the thermal conductivity.

The anomalies observed in the  $C_p(T)$  and  $\lambda(T)$  curves at 17 K on  $\text{HoCo}_2$  can be attributed to the reorientation of the easy-magnetization axis. It corresponds, in fact, to an anomaly observed by Lemaire [14] at the same temperature in the thermal variation of the low field magnetization. This anomaly is also seen in the MCE vs.  $T$  curve at nearly the same temperature for  $\text{Ho}(\text{Co}_{0.95}\text{Si}_{0.05})_2$ .

For the  $RE(\text{Co}, \text{Si})_2$  systems ( $RE = \text{Dy}, \text{Er}$  and  $\text{Ho}$ ), electronic properties strongly change when Co is partly replaced by Si. Under the condition of fixed volume, the hybridization between Co  $d$  states and Si  $p$  states plays an important role for the  $3d$  magnetism. Two possible mechanisms governing the increase of  $T_C$  exist: i) increase of the  $4f-3d$  exchange interaction, and ii) enhancement of the Co susceptibility with a concomitant increase of the  $3d$  moment. The  $4f-3d$  exchange interaction is almost constant with increasing Si substitution up to  $x = 0.15$  [15, 16]. This means that the increase of  $T_C$  can be tentatively attributed to an additional contribution of exchange interactions from the  $5d(RE)-3p(\text{Si})$  and  $3d(\text{Co})-3p(\text{Si})$  hybridization.

The thermal conductivity behavior of  $\text{HoCo}_2$  is greatly modified by substituting Co by Si. At temperatures well above  $T_C$ , the  $\lambda(T)$  data are practically invariant of the magnetic field. In the vicinity of the magnetic phase transition anomalies are observed. The anomalies are gradually reduced with the magnetic field. This effect may be connected with an evolution of the induced Co moment. Note that the temperature range of magnetic ordering is extended in an applied magnetic field.

## Conclusions

Specific heat and thermal conductivity measurements of  $\text{Ho}(\text{Co}_{1-x}\text{Si}_x)_2$  compounds with  $x = 0$  and  $0.05$  up to 8 T were performed.  $\text{HoCo}_2$  and  $\text{Ho}(\text{Co}_{0.95}\text{Si}_{0.05})_2$  undergo transitions at 77 and 103 K, respectively, as first-order magnetic phase transitions between high-temperature paramagnetic and low-temperature ferromagnetic states. The transitions are accompanied by a sharp anomaly in thermal, transport and lattice properties. The sharp anomaly in the temperature dependence of the specific heat is only slightly altered for the Si-doped compound, whereas the thermal conductivity in the vicinity of the magnetic phase transition clearly differs between  $\text{HoCo}_2$  and  $\text{Ho}(\text{Co}_{0.95}\text{Si}_{0.05})_2$ .

The magnetocaloric effect observed in the vicinity of the magnetic-ordering transition reaches a considerable magnitude which qualifies both compounds as suitable media for magnetic refrigeration purposes. The possibility to tune the operating temperature region with high MCE values in the neighborhood of  $T_C$  by small doping of the Co sublattice with Si, while keeping the large MCE values only weakly altered, increases the application potential of these materials.

## Acknowledgements

This work is a part of the research program MSM 0021620834 that is financed by the Ministry of Education of the Czech Republic. It was supported also by the Czech National Foundation within the grant # 101/07/1173.

- 
- [1] K. A. Gschneidner Jr., V. K. Pecharsky, *Phys. Rev. Lett.* **1997**, 78, 4494–4407.
  - [2] T. D. Cuong, L. Havela, V. Sechovský, Z. Arnold, J. Kamarád, N. H. Duc, *J. Alloys Comp.* **1997**, 262–263, 141–146.
  - [3] O. Syshchenko, T. Fujita, V. Sechovský, M. Diviš, H. Fujii, *J. Magn. Magn. Mater.* **2001**, 226–230, 1062–1067.
  - [4] M. Foldeaki, R. Chaine, B. R. Gopal, T. K. Bose, X. Y. Liu, J. A. Barclay, *J. Appl. Phys.* **1998**, 83, 2727–2734.
  - [5] M. W. Zemansky, *Heat and Thermodynamics*, McGraw-Hill, New York, **1968**.
  - [6] N. H. Duc, D. T. Kim Anh, *J. Magn. Magn. Mater.* **2002**, 242–245, 873–875.
  - [7] A. Giguere, M. Foldeaki, W. Schnelle, E. Gmelin, *J. Phys.: Condens. Matter* **1999**, 11, 6969–6981.

- [8] E. Gratz, R. Reselt, A.T. Burkoe, E. Bauer, A.S. Markosyans, A. Galatanut, *J. Phys.: Condens. Matter* **1995**, 7, 6687–6706.
- [9] B. Coqblin, J.R. Iglesias-Sicardi, R. Jullien, *Contemp. Phys.* **1978**, 19, 327–450.
- [10] J.M. Fournier, E. Gratz in: *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 17 (Eds.: K.A. Gschneidner Jr., L. Eying, G.H. Lander, G.R. Chopin), North-Holland, Amsterdam, **1993**, chapter 115, p. 409.
- [11] J. Inoue, M. Shimizu, *J. Phys. F* **1982**, 12, 1811–1819.
- [12] W. Steiner, E. Gratz, H. Ortbauer, H.W. Camen, *J. Phys. F* **1978**, 8, 1525–1537.
- [13] E. Gratz, G. Hilscher, H. Kirchmayr, H. Sassik, *The Rare Earths in Science and Technology*, Plenum, New York, **1980**, p. 327.
- [14] R. Lemaire, *Cobalt* **1966**, 33, 201–211.
- [15] T.D. Cuong, L. Havela, V. Sechovský, Z. Arnold, J. Kamarád, *Kovové Materiály* **1998**, 36, 53–60.
- [16] S. Khmelevskiy, P. Mohn, *J. Phys.: Condens. Matter* **2000**, 12, 9453–9464.