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# Low-Temperature Specific Heat and Magnetocaloric Effect in $RCu_2Ge_2$ (R = Dy–Tm) Compounds

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The magnetocaloric effect in $RCu_2Ge_2$ (R = Dy–Tm) was investigated by means of specific heat measurements. The compounds order antiferromagnetically at 6.2 K ($DyCu_2Ge_2$), 5.6 K ($HoCu_2Ge_2$), 3.0 K ($ErCu_2Ge_2$), and 3.9 K ($TmCu_2Ge_2$), and some of them exhibit additional magnetic transitions in the ordered state. In an external magnetic field the low-temperature specific heat changes significantly, which can be attributed to metamagnetic-like transitions. In this temperature region, the investigated samples show distinctly different magnetocaloric effect.

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## 1. Introduction

Ternary $RCu_2Ge_2$ compounds (R = rare earth) crystallise with the body-centred tetragonal crystal structure (space group $I4/mmm$). The constituent R, Cu and Ge atoms occupy 2(a), 4(d) and 4(e) positions, respectively. The structure has a layered character with the monoatomic layers stacked along the $c$-axis in the sequence R–Cu–Ge–Cu–R [1]. For heavy rare-earth based compounds the ordering temperatures are relatively low, namely 12 K in $GdCu_2Ge_2$, 15 K in $TbCu_2Ge_2$, 8 K in $DyCu_2Ge_2$, 6.4 K in $HoCu_2Ge_2$, 3.0 K in $ErCu_2Ge_2$ and 3.9 K in $TmCu_2Ge_2$ [2]. For the Tb-, Dy-, Ho- and Er-based compounds the neutron diffraction data revealed antiferromagnetic structures below the respective Néel temperatures [3–6]. In the case of single crystalline $TbCu_2Ge_2$ some additional magnetic transitions were found just below $T_N$ [7, 8], thus hinting at a possibility of more complex magnetic behaviour in the entire series of phases.

In this paper we present the results of our low-temperature studies of the specific heat of the $RCu_2Ge_2$ (R = Dy–Tm) compounds, which largely corroborate the literature data and the conjecture on subsequent phase transitions. From the obtained $C_p(T,H)$ data, the magnetocaloric effect (MCE) has been derived.

## 2. Experimental details

$RCu_2Ge_2$ (R = Dy, Ho, Er and Tm) polycrystalline samples were synthesised by arc melting stoichiometric amounts of high-purity elements (R of 99.9% purity, Cu and Ge of 99.999% purity) under argon atmosphere. To ensure good homogeneity, the procedure was repeated several times. Subsequently, the buttons were annealed in evacuated quartz tubes at 800 °C for one week. Phase analysis was done by X-ray powder diffraction (XRD) at room temperature using a PANalytical Empyrean diffractometer with Cu $K_\alpha$ radiation. All the diffraction patterns were fully indexed within the tetragonal $ThCr_2Si_2$ structure with the lattice parameters being very close to those reported in the literature [1].

The heat capacity studies were carried out by relaxation method down to 350 mK or 2 K (for different samples) in applied magnetic fields up to 9 T using a Quantum Design PPMS platform.

## 3. Results

As can be inferred from Fig. 1, the specific heat $C_p(T)$ shows distinct $\lambda$-like anomalies at temperatures of 6.2, 5.6, 3.0, and 3.9 K for the compounds with R = Dy, Ho, Er and Tm, respectively. Additional anomalies, likely corresponding to spin reorientations, occur at 2.6 K in $ErCu_2Ge_2$ and 1.7 K in $TmCu_2Ge_2$. Application of magnetic field initially results in shifting the magnetic features towards lower temperatures, as expected for antiferromagnets. In strong magnetic fields, the peaks in $C_p(T)$ are replaced by broad maxima, which systematically move towards higher temperatures with rising the field strength. The observed behaviour arises due to the metamagnetic-like transitions, previously evidenced in the magnetization data of $RCu_2Ge_2$ [2].

Calculations of the adiabatic temperature change upon application of the external magnetic field were performed using formalism described in Refs. [9–11]. At the first

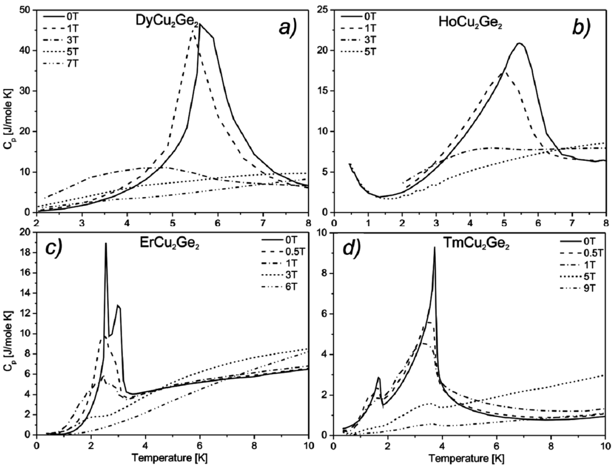

Fig. 1. Specific heat at low temperatures upon applying of external magnetic field for the investigated $RCu_2Ge_2$ compounds.

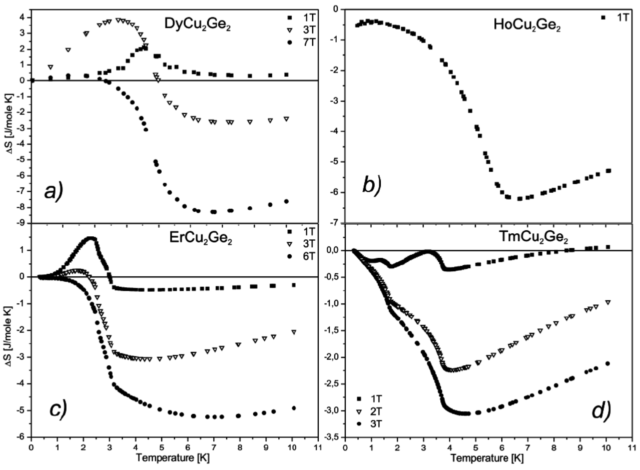

Fig. 2. Entropy change upon applying of external magnetic field for the investigated compounds.

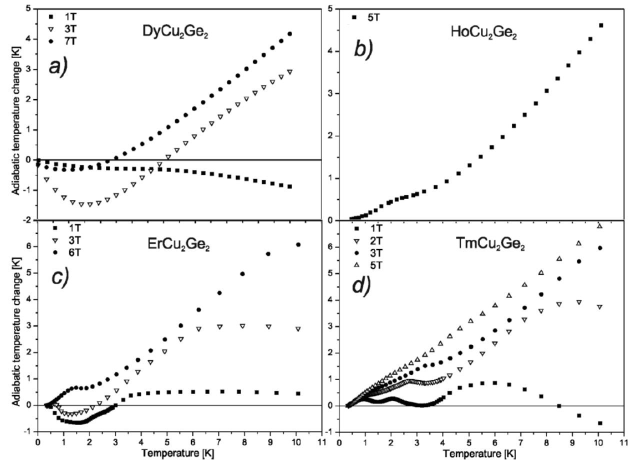

Fig. 3. Magnetocaloric effect for the investigated $RCu_2Ge_2$ samples.

step, for each magnetic field, the total entropy was calculated as $S(T,H) = \int_0^T \frac{C_p(T^*,H)}{T^*}\,\mathrm{d}T^*$. Then, the entropy change $\Delta S$ and adiabatic temperature change $\Delta T_{\mathrm{ad}}$ were derived.

In Fig. 2 calculated entropy changes upon change of the external magnetic field are presented. As expected, a maximum value of $\Delta S$ occurs at vicinity of the phase transition, at least at low magnetic fields, where the metamagnetic transitions do not affect the data. It must be emphasized that the MCE remains quite large well above the transition temperatures. This behaviour originates in the Schottky contribution arising from the rare-earth's ground multiplet splitting in the presence of the crystal field. The observed changes of $\Delta S$'s sign are accompanied usually to antiferromagnetic transitions, where magnetic field shifts the specific heat anomalies towards the lower temperatures. Consequently, a larger entropy can be gained at presence of magnetic field than in zero field and hence positive value of $\Delta S$ is visible. On the other hand, applying magnetic field large enough to induce a metamagnetic transition leads to opposite phenomenon. This behaviour is very apparent for Dy- and Er-based compounds (see Fig. 2a,c).

As may be inferred from Fig. 3, the so-obtained $\Delta T_{\mathrm{ad}}$ coefficient does not exhibit any universal behaviour within the $RCu_2Ge_2$ series. In magnetic fields weaker than the respective critical value for the metamagnetic transition, both the sign of $\Delta T_{\mathrm{ad}}$ and the shape of the $\Delta T_{\mathrm{ad}}(T)$ function is different for different compounds. Above the metamagnetic transition, more uniform behaviour is observed, namely $\Delta T_{\mathrm{ad}}$ is largely positive and systematically increases with increasing temperature, reaching values of about 5–7 K at $T = 10$ K.

The magnetic phase transitions are hardly discernible on the $\Delta T_{\mathrm{ad}}(T,H)$ curves. Though some features can be recognized for $H = 1$ T, their positions on the temperature scale do not correspond neither to $T_{\mathrm{N}}$'s nor to the spin-reorientation anomalies derived from the specific heat data. Most likely, straight identification of the antiferromagnetic phase transitions is hampered by the metamagnetic-like behaviours in all the compounds studied.

According to the literature [12, 13], some anomalies in $\Delta T_{\mathrm{ad}}(T,H)$ usually form at the temperatures $T_x$, at which the specific heat curves measured in zero and finite magnetic field cross each other. Around these singular points, MCE is expected to exhibit either a minimum or a maximum. Sometimes, such crossings in the $C_p(T_x,H)$ curves are associated with changes in the MCE sign [13]. In the present case of the $RCu_2Ge_2$ phases, such kind of correlations can indeed be recognized when comparing Fig. 1 and Fig. 3, however their detailed discussion appears difficult because of the occurrence of the metamagnetic behaviour.

## 4. Summary

The low-temperature specific heat of $RCu_2Ge_2$ (R = Dy, Ho, Er and Tm) was found to be strongly dependent on the external magnetic field. In concert with the magnetization data [2], the $C_p(T,H)$ functions revealed metamagnetic-like anomalies in all the compounds investigated. The latter effect greatly influences the magnetocaloric behaviour of these materials, quantified by the entropy change $\Delta S$ and adiabatic temperature change functions $\Delta T_{\mathrm{ad}}(T)$. In the state of magnetic field-induced ferromagnetic alignment of the rare-earth magnetic moments $\Delta T_{\mathrm{ad}}$ is mostly positive and reaches the values of 5–7 K far above the respective Néel temperatures.

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