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Magnetic Phase Transitions and Thermal Properties of $Ho(Co_{1-x}Si_x)_2$ Compounds

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The specific heat of $HoCo_2$ and $Ho(Co_{0.95}Si_{0.05})_2$ was measured as a function of temperature in several constant magnetic fields up to 8 T. A data analysis allowed us to determine the isothermal entropy change and the magnetocaloric effect in a wide temperature range. 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 $HoCo_2$ to 103 K for $Ho(Co_{0.95}Si_{0.05})_2$ while the large magnetocaloric effect in the vicinity of TC is maintained, which demonstrates possible ways of tuning the operating temperatures of the magnetic refrigerant.

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1. Introduction

A large magnetocaloric effect (MCE) near a magnetic phase transition (MPT) makes some materials suitable for the use in magnetic cooling [1] — a more ecological alternative to present cooling systems. Since the available information pool in this field is still rather insufficient, further investigations of magnetocaloric phenomena in various materials are highly desirable.

The Laves-phase rare-earth (RE) intermetallic compounds $RECo_2$ were chosen because of their sensitivity to an external magnetic field and to partial substitution by other elements leading to intrinsic changes of magnetic parameters and modifications of electronic properties related to magnetism. These compounds exhibit a large magnetic entropy change in the vicinity of MPT and consequently a large MCE. The present work is devoted to a specific-heat MCE study of $HoCo_2$ and $Ho(Co_{0.95}Si_{0.05})_2$ compounds [2] in various magnetic fields and to a data analysis, which allows determination of the MCE around the MPT between paramagnetic state and magnetic ordering.

2. Experiment, results, and discussion

Polycrystalline samples of $HoCo_2$ and $Ho(Co_{0.95}Si_{0.05})_2$ were prepared by arc-melting of elements of at least 3N5 purity in the nominal composition. The obtained ingots were wrapped in a Ta foil, sealed in a quartz tube under high vacuum and annealed at 950°C for 50 h. Both samples have been found by X-ray powder diffraction to crystallize in the cubic Laves-phase $MgCu_2$-type ($C15$) structure with lattice parameters, which are in good agreement with literature data [3]. Specific-heat measurements were performed using the PPMS 14 T apparatus (Quantum Design). The specific heat was measured over wide temperature intervals around T_C in the magnetic fields of 2, 4, 6, and 8 T.

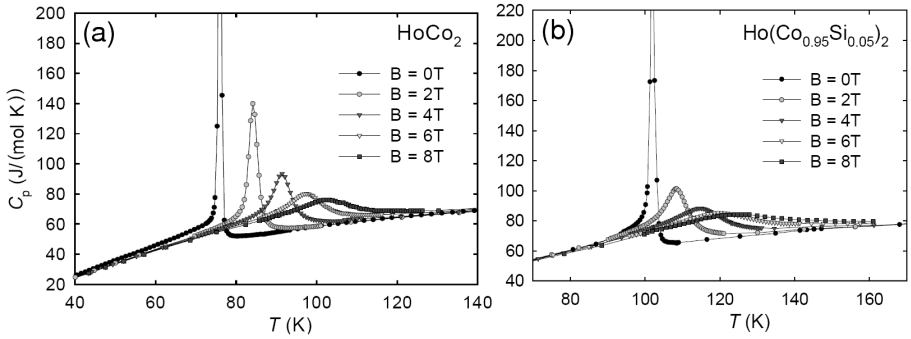

Fig. 1. Temperature dependences of the specific heat of $HoCo_2$ (a) and $Ho(Co_{0.95}Si_{0.05})_2$ (b) measured in different magnetic fields up to 8 T.

The position of the sharp anomaly (a pronounced symmetric peak) on the $C_p(T)$ dependence for $B = 0$ T displayed in Fig. 1 determines the Curie temperature $T_C = 77$ K for $HoCo_2$ and 103 K for $Ho(Co_{0.95}Si_{0.05})_2$. When applying a magnetic field, the anomaly is shifted to higher temperatures and becomes rapidly smeared out with increase in the field value. The specific heat data measured in different magnetic fields allowed us to determine the isothermal entropy change (IEC):

$$S(T)_{B_i} = \int_0^T \frac{C(T', B_i)}{T'} \mathrm{d}T' + S_{0,B_i}, \tag{1}$$

where $i = 0, 1\ldots$; $C(T, B_i)$ is the specific heat measured in magnetic fields B_0 and B_i and $S_{0,B_i} = 0$ at 0 K in a condensed system [4]. The MCE, which is the adiabatic temperature change $\Delta T_{ad}(T)$, can be determined from the horizontal distance between the $S(T)_0$ and $S(T)_{0,B_i}$ curves [5]. The plots of the $\Delta T_{ad}(T)$ dependences shown in Fig. 2 for $HoCo_2$ and $Ho(Co_{0.95}Si_{0.05})_2$, respectively, exhibit a sharp peak near T_C, namely at 83 and 106 K, respectively. The temperature of the $\Delta T_{ad}(T)$ maximum is almost magnetic field invariant. The size of MCE on the other hand naturally increases with increasing field and the maximum values are $\Delta T_{ad}(T) = 10$ K and 8 K, respectively.

To compare our results with literature, we calculated also the values of the isothermal entropy change $\Delta S(T)$. Our results of $-\Delta S(T)$ at higher magnetic fields are in reasonably good agreement with data calculated from magnetization curves using the Maxwell relation [6]. The observed discrepancies observed in lower magnetic fields can be understood when considering lack of validity of the Maxwell relation in close vicinity of a first order magnetic phase transition, which is the case of the studied compounds. Measurement of specific heat data or direct measurement of MCE is inevitable for correct evaluation of magnetocaloric characteristics.

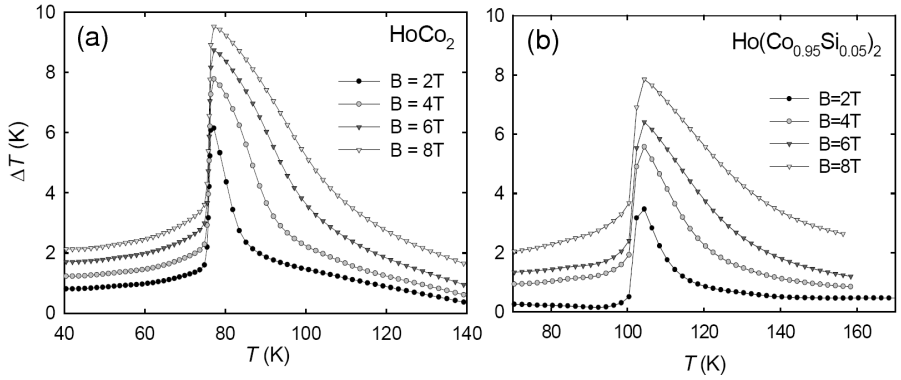

Fig. 2. MCE in magnetic fields up to 8 T (with respect to zero initial field) in $HoCo_2$ (a) and $Ho(Co_{0.95}Si_{0.05})_2$ (b) derived from specific-heat data.

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 considerable induced magnetic moments due to exchange interactions with the ferromagnetically ordered $4f$ moment sublattice of Ho [7]. The $C_p(T)$ data for $HoCo_2$ in the paramagnetic region well above T_{C} are practically independent of magnetic field. Also electrical resistivity investigations performed on the pseudobinary $(Ho_{1-x}Y_x)Co_2$ [8] have shown that the $\rho(T)$ dependence for $T \gg T_{\mathrm{C}}$ 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 resistivity [9].

For the $RE(Co,Si)_2$ systems (RE = Dy, Er, and Ho), electronic properties strongly change when Co is partly replaced by Si. Under the condition of the fixed volume, the hybridization between the Co d states and the Si p states plays an important role for the $3d$ magnetism. Two possible mechanisms governing the increase in T_{C} exist: (1) enhancement of the $4f-3d$ exchange interaction and (2) enhancement of the Co susceptibility and a concomitant increase in the 3d moment. It means that increase in T_{C} can be tentatively attributed to an

additional contribution of exchange interaction mediated by the $5d$(RE)–$3p$(Si) and $3d$(Co)–$3p$(Si) hybridization.

In conclusion, specific-heat measurements of $HoCo_2$ and $Ho(Co_{0.95}Si_{0.05})_2$ up to 8 T were performed and a first-order magnetic phase transition between high-temperature paramagnetic and low-temperature ferrimagnetic states has been observed at $T_C = 77$ and 103 K, respectively. The sharp anomaly in the temperature dependence of the specific heat is only slightly altered for the Si doped compound. The MCE determined in the vicinity of T_C 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 by small Si doping of the Co sublattice, while maintaining the large MCE values only weakly altered, enhances the application potential of these materials.

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