Magnetocaloric Effect and Transition Order in $HoAl_2$

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Magnetic measurements of $HoAl_2$ are reported. The compound crystallizes in the cubic $MgCu_2$-type crystal structure. $HoAl_2$ exhibits two successive magnetic transitions: below $T_c = 29$ K a ferromagnetic order is formed while anomaly at $T_t = 20$ K is related to reorientation of magnetic moment. Near transition temperatures a magnetocaloric effect with magnetic entropy changes $-\Delta S_m$ equal to 6.3 J/(mol K) at T_c and 5.0 J/(mol K) at T_t for an external field $\mu_0 H = 9$ T is observed.

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1. Introduction

The magnetocaloric effect (MCE) is of great interest nowadays [1], especially for its potential application in new generation of refrigerators. The $HoAl_2$ intermetallic compound crystallizes in the $MgCu_2$-type cubic Laves structure (space group O_h^7, respectively $Fd3m$). $HoAl_2$ is a ferromagnet with Curie temperature of 28 K as reported from specific heat data [2] or 33 K found from magnetic susceptibility measurements [3]. At about 20 K easy direction of magnetization changes from ⟨110⟩ to ⟨100⟩ direction [3, 4]. Magnetocaloric effect in $HoAl_2$, determined from magnetic measurements on polycrystalline sample in magnetic field of 5 T, is reported in Refs. [5–7]. The MCE curve has a maximum at T_c. The experimental value is smaller than theoretical prediction 6.6 J/(mol K) at $H = 5$ T [7].

In the present paper we report results of magnetization measurements on bulk $HoAl_2$ sample between 1.9 and 300 K in magnetic fields up to 9 T. From these measurements we determine temperature variation of magnetic entropy change ($-\Delta S_m$) from $M(H, T)$ curves.

2. Experimental methods and results

The $HoAl_2$ sample was prepared from 3N pure Ho and 4N pure Al. The stoichiometric amounts of the metal were melted in arc under argon atmosphere. Next, the sample was annealed at 1073 K for one week in evacuated quartz tube. Powder X-ray diffraction measurements performed with Cu K_α radiation indicate that the compound crystallizes in cubic system of the $MgCu_2$-type. The determined lattice parameter equal to 7.838(3) Å is in good agreement with the values reported in literature. Magnetic measurements were performed in temperature range from 1.9 K to 300 K and in external magnetic fields up to 9 T using a vibrating sample magnetometer (VSM) option of the PPMS Quantum Design platform.

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The results of magnetic measurements of $HoAl_2$ are shown in Fig. 1. The Curie temperature $T_c = 29$ K has been defined as temperature at which $|d\chi/dT|$ reaches its maximum for the zero field cooling (ZFC) and field cooling (FC) curves. Below T_c a ferromagnetic order with Ho magnetic moment equal to 7.5 μ_B at 1.9 K is observed. The hysteresis loop at 1.9 K, presented in lower inset in Fig. 1, reveals presence of a very small coercivity, less than 60 Oe, which is favorable for magnetocaloric materials.

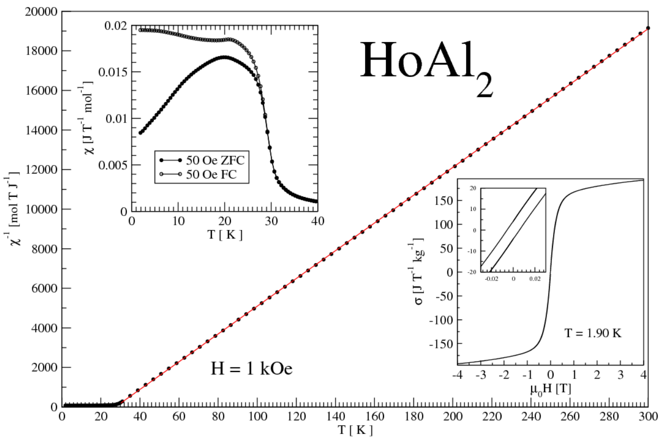

Fig. 1. Temperature dependence of $HoAl_2$ reciprocal magnetic susceptibility. The solid line shows the Curie–Weiss law fit. The upper inset presents magnetic susceptibility (ZFC and FC curves) at low temperature while the lower one — hysteresis loop at 1.9 K with low-field region being enlarged.

Apart from divergence between ZFC and FC curves appearing below T_c there is additional anomaly observed in both the curves about 20 K. Above T_c the reciprocal magnetic susceptibility obeys the Curie–Weiss law with paramagnetic Curie temperature equal to 27 K and effective magnetic moment of 10.7 μ_B which is close to the free Ho^{3+} ion value (10.61 μ_B).

Figure 2a shows magnetization curves measured in applied magnetic field up to 9 T and temperature ranging from 10 to 40 K with temperature step $\Delta T = 2.5$ K. On the basis of these data, isothermal magnetic entropy changes were calculated from the relation

$$\Delta S_{\mathrm{m}}(T) = \sum_j \frac{\sigma_{i+1}(H_j) - \sigma_i(H_j)}{T_{i+1} - T_i}(H_j - H_{j-1}), \quad (1)$$

where magnetic field $H_0 = 0$ and $H_{j\,\max} = H$ with $j = 1$, ..., $j_{\max}$ while σ_i and σ_{i+1} were the values of magnetization at temperature T_i and T_{i+1}, respectively [8]. Magnetic entropy change vs temperature, for several external magnetic fields, is shown in Fig. 2b. The entropy curves have a maximum at $T = 28$ K. The maximal entropy change increases with increasing external magnetic field reaching 6.3 J/(mol K) at 9 T.

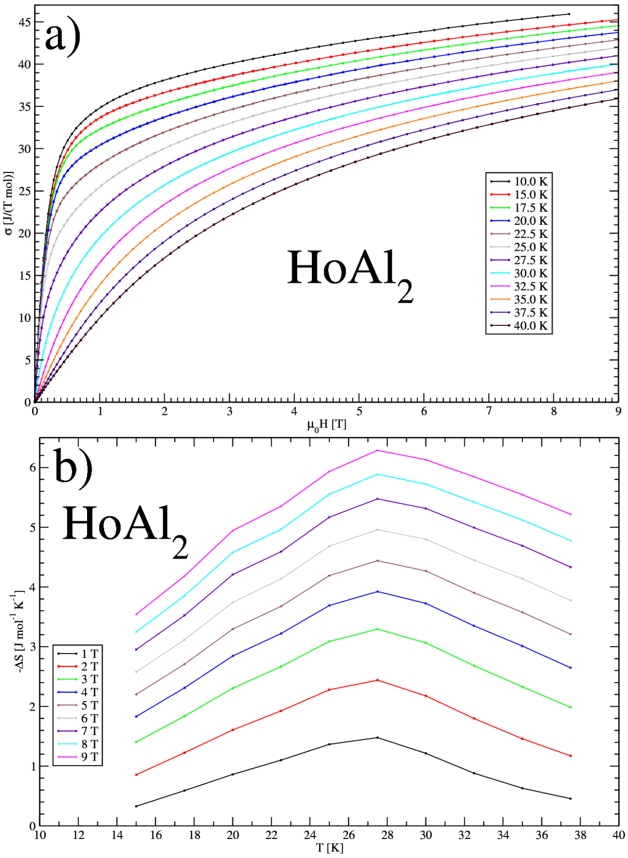

Fig. 2. (a) Magnetization versus magnetic field at different temperatures between 10 and 40 K and (b) entropy change $-\Delta S$ plotted versus temperature at different magnetic fields up to 9 T.

Refrigerant capacity (RC) can be calculated by the expression $\mathrm{RC} = \Delta S_{\mathrm{m}}(T_{\mathrm{h}} - T_{\mathrm{c}})$ where $-\Delta S_{\mathrm{m}}$ is a maximal entropy change at selected field, T_{c} is a temperature at which entropy change reaches its maximum equal to $-\Delta S_{\mathrm{m}}$ while T_{h} is a temperature at which ΔS equals $\frac{1}{2}\Delta S_{\mathrm{m}}$ [9]. The refrigerant capacity calculated from experimental data equals about 95 J/mol at 9 T.

Magnetic entropy vs. applied magnetic field dependence can be analyzed numerically at temperatures close to T_{c}. Within the molecular field approximation [10], the dependence $\Delta S(T, H) \sim H^n$ is predicted. Figure 3 shows

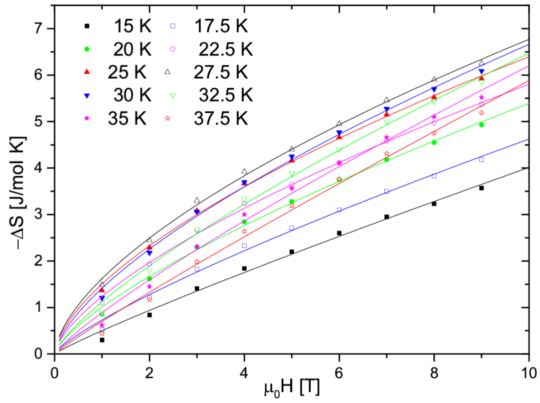

Fig. 3. Magnetic entropy vs. applied magnetic field dependence.

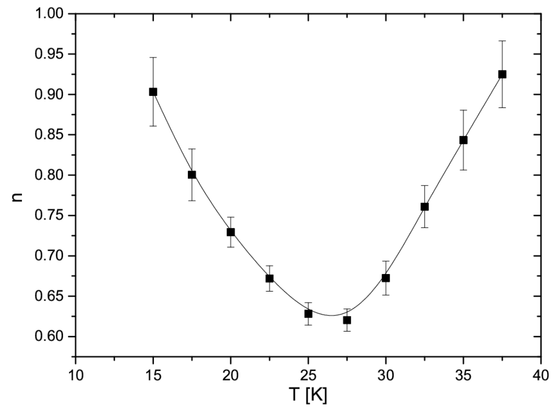

Fig. 4. Temperature dependence of power n determined from relation $\Delta S(T, H) \sim H^n$.

both the experimental and fitted data of ΔS while the obtained values of n are presented in Fig. 4. n changes with temperature reaching a minimum equal to 0.62 at $T = 26$ K which is close to the theoretical value of $^2/_3$ (0.667) [10]. While receding from the critical temperature n increases, however, it does not reach either 1.0 or 2.0 as predicted theoretically for low- and high-temperature limit, respectively. Such a result indicates that analyzed temperature range was relatively narrow.

3. Summary

In the present work dc magnetization measurements of polycrystalline $HoAl_2$ sample are reported. On basis of experimental data, magnetocaloric effect is investigated. Temperature dependences of magnetization and magnetic susceptibility are in agreement with the previous data assuming that the compound is ferromagnetic with magnetic moments localized on Ho^{3+} ions.

The new result is a large thermo-magnetic irreversibility between ZFC and FC curves which is a typical feature associated with a large anisotropy of a ferromagnet.

The calculated magnetic entropy at $\mu_0 H = 9$ T and T_c equals 6.3 J/(mol K) and is comparable with previously reported data [6, 7].

Close to T_c, ΔS behaves as H^n thus confirming molecular field approximation predictions. Also the obtained values of n are in agreement with theory.

During the time of our experiment a new paper reporting data on magnetocaloric effect in $HoAl_2$ single crystal was published [11]. The paper reports on temperature dependence of magnetization for $HoAl_2$ single crystal measured along [100] and [110] directions. On the basis of experimental data a thermal variation of magnetic entropy change ($-\Delta S_m$) is calculated. Both the ΔS_m curves, along [100] and [110] directions, have a maximum at T_c and similar dependence above the Curie point. Below T_c a large divergence between the curves is observed: the curve along [110] direction has only small anomaly at T_t, similar to that observed in this work, while the curve along [100] direction has a minimum at T_t. The value of $-\Delta S_m$ reported in Ref. [11] equals 6.5 J/(mol K) at $\mu_0 H = 7$ T and is similar to the one reported in this work. For comparison, specific heat data for polycrystalline sample yield 5.5 J/(mol K) at $\mu_0 H = 5$ T [8]. Theoretical predictions for MCE in $HoAl_2$ show influence of spin reorientation from [110] to [100] direction on magnetocaloric effect [12].

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