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Crystallographic, magnetic and calorimetric studies of $Ho_5Si_2Ge_2$

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Abstract

Following the discovery of a giant magnetocaloric effect in $Gd_5(Si,Ge)_4$, attention has been extended to $R_5(Si,Ge)_4$ with R being other rare-earth elements. In this work, X-ray structural analyses, low- and high-field magnetization measurements and zero-field calorimetric measurements were carried out on $Ho_5Si_2Ge_2$. Specific heat data were also obtained for nonmagnetic $Lu_5Si_2Ge_2$ as a reference material. In contrast to the general trend of having a ferromagnetic order in the $R_5(Si,Ge)_4$ series, $Ho_5Si_2Ge_2$ actually becomes antiferromagnetically ordered with a Néel temperature T_N near 25 K. Moreover, an anomalous behavior below T_N also prevails in the temperature dependence of both magnetization and specific heat, suggesting further transitions from the antiferromagnetic to other complex magnetic structures.

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Keywords: Specific heat; Antiferromagnetic ordering; Crystallographic structure; Magnetic structure

1. Introduction

Since the discovery of a giant magnetocaloric effect (GMCE) in $Gd_5Si_2Ge_2$ [1,2], this compound has taken the central stage of research activities on magnetic refrigeration materials. A preliminary study on the $R_5Si_2Ge_2$ series with other rare earths (R) completely replacing Gd revealed quite interesting magnetic ordering phenomena. It has been shown that, similar to $Gd_5(Si,Ge)_4$, Tb-based compounds also undergo ferromagnetic transitions with T_c near room temperature, along with a GMCE in its vicinity [3,4]. Meanwhile, other R-based compounds order at lower temperatures and show complex magnetic structures [3]. As an extension of this line of research, we report here on crystallographic, magnetic and calorimetric studies of $Ho_5Si_2Ge_2$. To delineate the thermal

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property into lattice and magnetic contributions, calorimetric measurements were also made on $Lu_5Si_2Ge_2$ as a nonmagnetic reference.

2. Experimental

The $Ho_5Si_2Ge_2$ and $Lu_5Si_2Ge_2$ samples were prepared by arc-melting a stoichiometric mixture of Ho/Lu (3 N), Si (5 N) and Ge (4 N) in a pure Ar atmosphere. The resulting ingots were turned over and remelted several times to ensure sample homogeneity. The overall weight loss was less than 0.6%. Whereas the as-melted $Lu_5Si_2Ge_2$ ingot was directly used for measurements, the $Ho_5Si_2Ge_2$ ingot was further sealed in a quartz ampoule with pure Ar atmosphere and annealed for 7 days at 1000°C, followed by water quenching. The crystallographic structure and the sample quality were studied using X-ray diffraction and electron probe microanalysis (EPMA). The magnetic properties of $Ho_5Si_2Ge_2$ between 2 and 300 K were determined with a 5 T SQUID magnetometer. Further magnetization measurements in high fields up to 40 T were carried out at the Amsterdam High Field Installation. The specific heat of $Ho_5Si_2Ge_2$ and $Lu_5Si_2Ge_2$ was measured in the temperature range of 0.6–40 K by using a microcalorimeter as described elsewhere [5].

3. Results and discussion

The room-temperature XRD-patterns of the $Ho_5Si_2Ge_2$ and $Lu_5Si_2Ge_2$ samples are presented in Fig. 1. For $Ho_5Si_2Ge_2$, the analysis indicates a single phase of the orthorhombic structure, space group Pnma, with unit cell parameters of $a = 7.501$ Å, $b = 14.510$ Å, and $c = 7.599$ Å. In reconfirming this by the EPMA analysis, the matrix of the EPMA image in the inset of Fig. 1 corresponds to the main phase having an exact composition of $Ho_5Si_{1.6}Ge_{2.1}$. The dark phase in the image represents an "impurity" phase of the composition $Ho_5Si_{2.8}Ge_{1.6}$, which amounts to only a few percent in volume. For $Lu_5Si_2Ge_2$, an orthorhombic structure was determined with

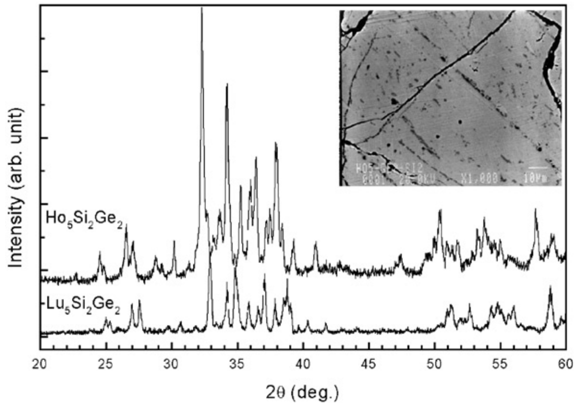

Fig. 1. Room-temperature XRD-patterns of $Ho_5Si_2Ge_2$ and $Lu_5Si_2Ge_2$ powders. The inset shows an EPMA image of the $Ho_5Si_2Ge_2$ sample.

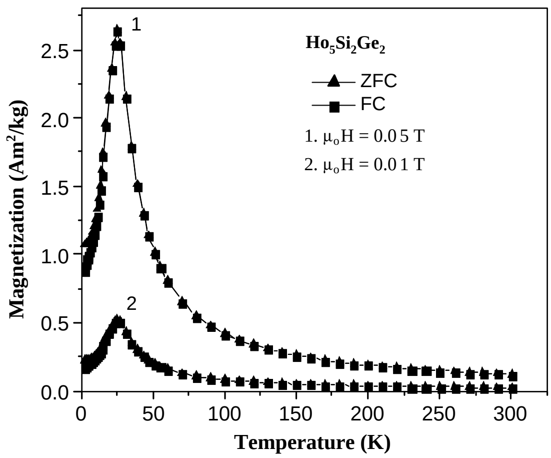

Fig. 2. Temperature dependence of FC- and ZFC-magnetization of $Ho_5Si_2Ge_2$ in a field of 0.01 and 0.05 T.

lattice constants $a = 7.386$ Å, $b = 14.262$ Å and $c = 7.456$ Å.

The temperature dependence of the magnetization of $Ho_5Si_2Ge_2$ is given in Fig. 2. A magnetic order sets in at a much lower temperature than that in $Gd_5Si_2Ge_2$ [1]. Judging from the occurrence of a peak in the figure, the transition is of an antiferromagnetic type. The peak corresponding to the Néel temperature, $T_N \approx 25$ K, is nearly unchanged with increasing applied field. The susceptibility shown in Fig. 3 follows a Curie–Weiss relation $\chi = C/(T - \theta)$ with a paramagnetic Curie temperature $\theta = 17$ K. The effective Ho-

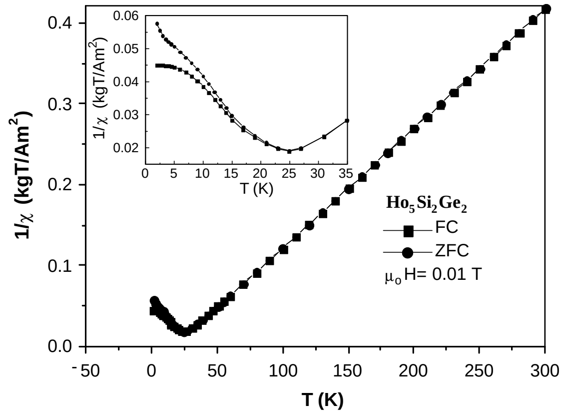

Fig. 3. Temperature dependence of the inverse susceptibility, as calculated from the magnetization data in Fig. 2, of $Ho_5Si_2Ge_2$ in a field of 0.01 T. The inset shows a split between FC- and ZFC-data at the low-temperature region.

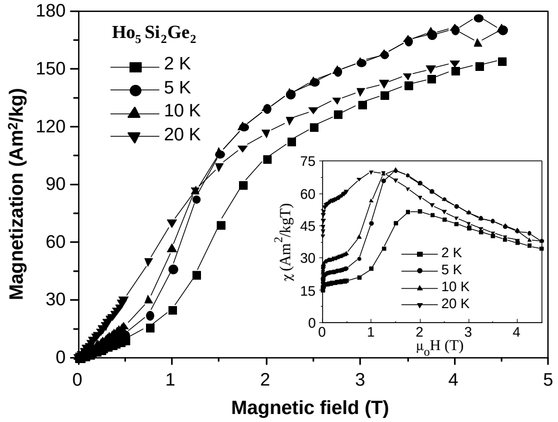

Fig. 4. Low-field magnetization of $Ho_5Si_2Ge_2$ as a function of field at different temperatures below T_N. The inset shows the field dependence of the susceptibility as extracted from the corresponding magnetization curves.

moment derived from these data is 9.7 μ_B, compared with $g_J[J(J+1)]^{1/2}\mu_B = 10.60\,\mu_B$ for free Ho^{3+}. Also revealed in the inset of Fig. 3 is a split of the temperature dependence of the inverse susceptibility between the zero-field-cooled (ZFC) and field-cooled (FC) curves at $T = 15$ K, as well as an anomaly near 2 K.

Below the Néel temperature, magnetization data at different temperatures in low fields up to 5 T in Fig. 4 exhibit a metamagnetic transition. As can be seen in the inset showing the field dependence of the susceptibility, the critical field decreases with increasing temperature. The metamagnetic transition might be related to a field-induced transformation from the antiferromagnetic to some other magnetic configurations yet to be identified. This appears to be consistent with the magnetization data at 4.2 K in high fields up to 38 T in Fig. 5. They approach saturation very slowly, suggesting a quite large magneto-crystalline anisotropy and/or a complex ordered spin structure at low temperatures. By extrapolating the magnetization data to an infinite field based on $M = M_s + aH^{-1}$, the saturation magnetization moment at 4.2 K is estimated to be 10.18 μ_B per Ho^{3+} ion. This is in good agreement with the theoretical value of $g_J J = 10\,\mu_B$. Data not shown here from magnetic hysteresis loop measurements at different temperatures below T_N gave negligible coercivity values.

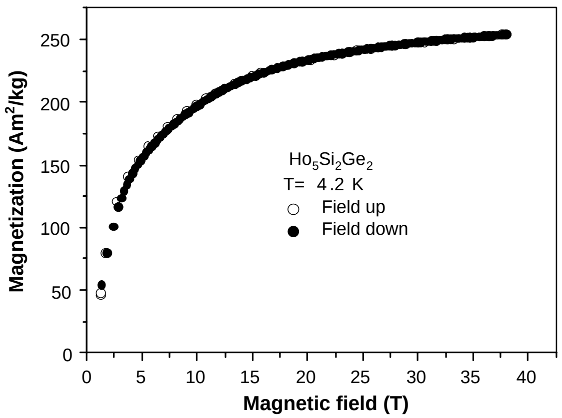

Fig. 5. High-field magnetization of $Ho_5Si_2Ge_2$ as a function of field at 4.2 K.

Figs. 6 and 7 present specific heat data in terms of the temperature dependence of C and C/T for $Ho_5Si_2Ge_2$ and $Lu_5Si_2Ge_2$, respectively. The smooth and monotonically increasing values for nonmagnetic $Lu_5Si_2Ge_2$ in Fig. 7 are fitted to a polynomial function, which is then assumed to represent the lattice component to the measured specific heat of $Ho_5Si_2Ge_2$. The difference of these plots represents the expected magnetic contributions, at least for temperatures above 5 K, below which C/T rises steeply as part of a nuclear Schottky term as observed in holmium [6] and Ho-based compounds [7].

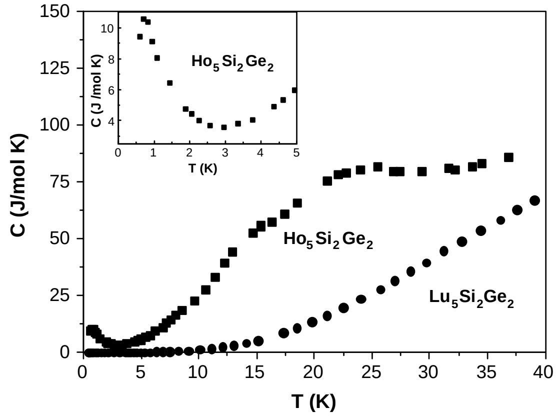

Fig. 6. Temperature dependence of the specific heat of $Ho_5Si_2Ge_2$ and $Lu_5Si_2Ge_2$. The inset shows the lowest temperature part of the $C(T)$ curve of $Ho_5Si_2Ge_2$.

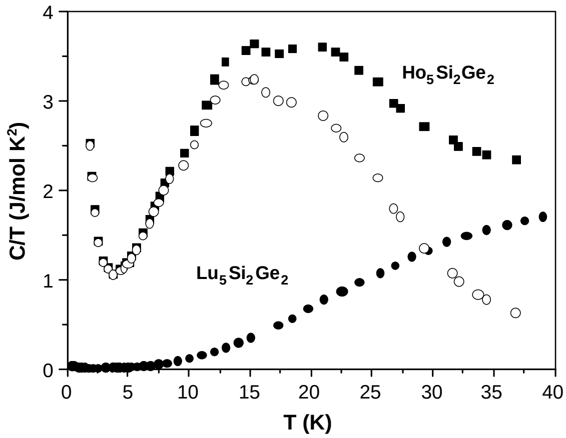

Fig. 7. Temperature dependence of C/T of $Ho_5Si_2Ge_2$ and $Lu_5Si_2Ge_2$. The difference plot (open circles) represents mainly the magnetic contributions above 5 K and a nuclear Schottky term at the lower temperatures for $Ho_5Si_2Ge_2$.

There appear to be two identifiable magnetic anomalies. In conjunction with the magnetic data in Fig. 2, the broad C/T-peak near 20 K is obviously caused by the antiferromagnetic ordering. For the second peak around 15 K, a clue can be obtained from Fig. 8, which plots the magnetic entropy of $Ho_5Si_2Ge_2$ above 5 K as derived by area integration of the calorimetric data in Fig. 7, $S_m(T) - S_m(5K) = \int (C_m/T)\,dT$. By neglecting the expectedly small value of

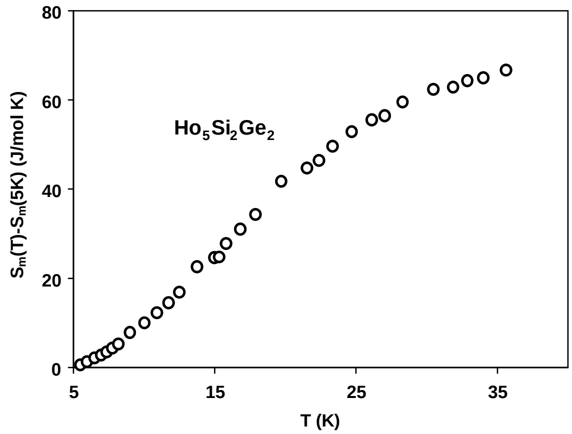

Fig. 8. Temperature dependence of the magnetic entropy of $Ho_5Si_2Ge_2$ above 5 K.

$S_m(5\,K)$, the magnetic entropy for $Ho_5Si_2Ge_2$ reaches over 60 J/mol K above T_N, where the magnetic ordering could have vanished completely. In comparison, a magnetic entropy of only $5R\ln 3 = 46$ J/mol K is expected for a simple order–disorder process, assuming a ground state triplet of Ho^{3+} ions. Under this consideration, the nature of the second anomaly at 15 K is difficult to establish. The entropy change points in a direction of more states involved than only the triplet ground state, complicating the magnetic phase diagram.

In conclusion, both magnetic and calorimetric measurements on $Ho_5Si_2Ge_2$ reveal an antiferromagnetic ordering at 25 K, followed by a second phase transition at 15 K of so far unknown nature. Further studies such as neutron diffraction and specific heat measurements in magnetic field are necessary to clarify the magnetic structure of both phases below 25 K.

Acknowledgements

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