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Magnetic Properties of $Dy_{11}Si_4In_6$

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Magnetic and specific heat measurements of $Dy_{11}Si_4In_6$ are reported. This compound crystallizes in the tetragonal $Sm_{11}Ge_4In_6$-type crystal structure (space group $I4/mmm$), in which Dy atoms occupy four different sites. The AC and DC magnetic measurements suggest complex magnetic properties. Below $T_c = 52$ K magnetic ordering has a ferromagnetic component, while below 20 K a change of the properties is observed. Near the Curie temperature the magnetocaloric effect with the magnetic entropy change ΔS_m equal to 16.5 J/(kg K) is observed. The specific heat data indicate only the phase transition at 52 K.

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1. Introduction

The influence of the chemical bonding on the physical properties of the R–M–In ternary systems (R = rare-earth element, M = Ge, Si) have recently attracted great interest. In these systems compounds with different stoichiometries and compositions exist. The compounds are interesting as materials for permanent magnets or the ones with large magnetocaloric effect. The investigated in this work $Dy_{11}Si_4In_6$ compound belongs to the $R_{11}M_4In_6$ family. This compound crystallizes in the tetragonal $Sm_{11}Ge_4In_6$-type structure [1]. This crystal structure is a ternary derivative of the binary $Ho_{11}Ge_{10}$-type one [2]. Preliminary magnetic measurements of the $R_{11}M_4In_6$ (R = Gd–Er; M = Si, Ge) were reported in Ref. [3] suggest complex magnetic properties. The $R_{11}Ge_8In_2$ (R = Gd–Tm) compounds, which crystallize in a similar crystal structure, are ferromagnets and exhibit a large change in the magnetic entropy near the Curie temperature [4]. Here the results of DC and AC magnetic measurements and specific heat data for $Dy_{11}Si_4In_6$ are reported and on their basis the magnetic properties of this compound are determined.

2. Experimental details

The sample was obtained by a standard arc-melting procedure started from the elements with the purity of 99.85% for Dy and 99.99% for Si and In. After melting the sample was annealed at 600 °C for 4 weeks to improve homogeneity.

X-ray powder diffraction patterns recorded at room temperature (PANanalytical X'Pert PRO diffractometer, Cu K_α radiation; Institute of Physics, Jagiellonian University) indicate the tetragonal crystal structure. DC magnetic measurements were carried out using a vibrating sample magnetometer (VSM) option of the Quantum Design PPMS platform. Three types of measurements were performed: at low temperatures in the magnetic field equal to 50 Oe, in the temperature range from 1.9 up to 300 K and the magnetic field equal to 1 kOe and finally, the magnetization curves were measured up to 90 kOe at 1.9 K and in the temperature ranging between 10 and 86 K with the temperature interval $\Delta T = 4$ K. The AC magnetic susceptibility ($\chi_{AC} = \chi' + i\chi''$ where χ' is the real and χ'' — the imaginary component) were measured versus frequency between 10 Hz and 10 kHz and as a function of the magnetic field amplitude H_{AC} between 2 and 10 Oe in the temperature range from 2 up to 80 K. The heat capacity was measured by a relaxation method from 2 up to 80 K using the Quantum Design PPMS platform.

3. Results and discussion

The temperature dependence of the real $\chi'(T, f)$ and imaginary $\chi''(T, f)$ component of the AC magnetic susceptibility measured at several frequencies f from 10 Hz up to 10 kHz and in the temperature range between 2 and 80 K are plotted in Fig. 1a and b. The DC magnetic susceptibility data collected in the magnetic field of 50 Oe (zero field cooling ZFC and field cooling FC) and 1 kOe are shown in Fig. 1c and d (the inset), respectively. The temperature dependence of the χ' component of the AC magnetic susceptibility and the DC magnetic

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susceptibility at 50 Oe have similar character. With increasing temperature both values increase slowly up to 15 K, then undergo a quick rise and show a broad maximum about 49 K and then decrease rapidly down to zero at 52 K. The latter is the evidence of the long-range order disappearance. The temperature dependence of the DC magnetic susceptibility measured at 1 kOe is different: here a broad maximum below 50 K is observed and above 52 K magnetic susceptibility χ_{DC} obeys the Curie–Weiss law with the paramagnetic Curie temperature equal to 23.7 K and effective magnetic moment per Dy atom equal to 10.61 μ_{B}. The values of χ'' decrease to zero at 52 K but their temperature dependence changes significantly with the applied frequency.

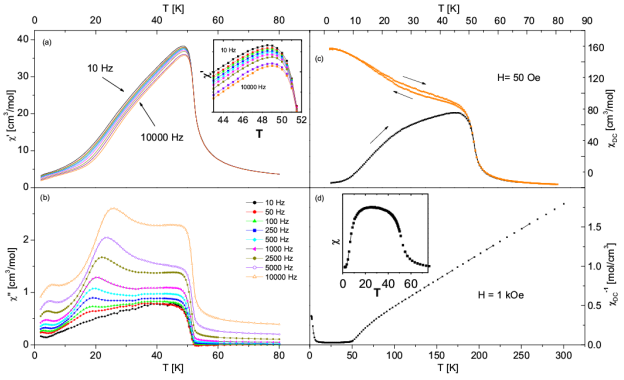

Fig. 1. Temperature dependence of the real χ'_{AC} (a) and imaginary χ''_{AC} (b) component of the AC magnetic susceptibility for the frequencies varying between 10 Hz and 10 kHz. The temperature dependence of the DC magnetic susceptibility at $H = 50$ Oe (c) and at $H = 1$ kOe ((d), the inset). The temperature dependence of the reciprocal DC magnetic susceptibility at 1 kOe (d).

For the frequency of 10 Hz the temperature dependence of χ'' is similar to those obtained for χ' (Fig. 1) where only one broad maximum about $T_0 = 50$ K is observed. With increasing frequency two additional maxima appear at T_1 and T_2 below 30 K (e.g. for $f = 50$ Hz, $T_1 = 3$ K and $T_2 = 20$ K) and a significant change in the values of χ'' is observed close to T_2. The temperatures T_1 and T_2 increase with increasing frequency. These suggest that the process is dynamical. The dependence of $1/f$ versus $1/T_i$ could be described by the formula $\tau = \tau_0 \exp(E_{\mathrm{a}}/k_{\mathrm{B}}\mathrm{T})$ where τ_0 is the characteristic time and E_{a} — activation energy. Numerical analysis of the above data leads to $\tau_0 = 1.9 \times 10^{-6}$ s and $E_{\mathrm{a}} = 24(2)$ K for T_1 and $\tau_0 = 1 \times 10^{-8}$ s and $E_{\mathrm{a}} = 243(22)$ K for T_2. The peak position at T_0 is frequency independent both in χ' and χ'' which indicates a ferromagnetic state.

Figure 2 shows the temperature dependence of the real χ' and imaginary χ'' part of the AC magnetic susceptibility measured in different magnetic fields ($H_{\mathrm{AC}} = 2$, 4, 6, 8, 10 Oe) at one chosen frequency $f = 2.5$ Hz. The results are similar to the above described frequency dependences plotted in Fig. 1.

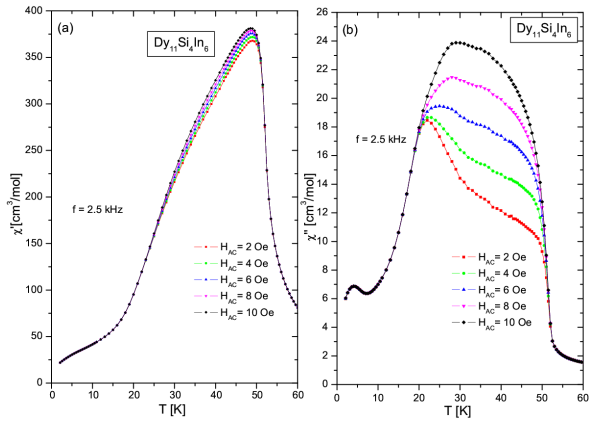

Fig. 2. Temperature dependence of the real χ'_{AC} (a) and imaginary χ''_{AC} (b) part of the AC magnetic susceptibility measured in different magnetic fields ($H_{\mathrm{AC}} = 2$, 4, 6, 8, 10 Oe) at one chosen frequency $f = 2.5$ Hz.

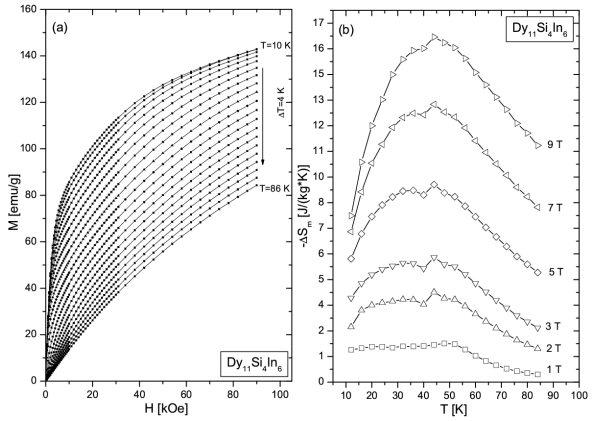

Fig. 3. Magnetization versus magnetic field at different temperatures between 10 and 86 K (a) and entropy ΔS_{m} change plotted versus temperature at different magnetic field (b).

Figure 3a shows magnetization measured in the applied magnetic field up to 90 kOe in the temperature range between 10 and 86 K with the temperature step $\Delta T = 4$ K. On the basis of these data the isothermal entropy changes were calculated using the Maxwell relation [5]. The results (Fig. 3b) indicate that the biggest change in the entropy calculated from the relation $\Delta S(T)_{\mathrm{m}} = \sum_i \frac{M_{i+1}-M_i}{T_{i+1}-T_i}\delta_H$, where δ_H is the change in the magnetic field value and M_i and M_{i+1} are the values of magnetization at temperatures T_i and T_{i+1}, respectively, occurs at the Curie temperature.

The temperature dependence of the specific heat C_p shows only a small anomaly at 52 K (Fig. 4). This is in good agreement with the magnetic measurements which indicate a phase transition from paramagnetic to ordered state at this temperature.

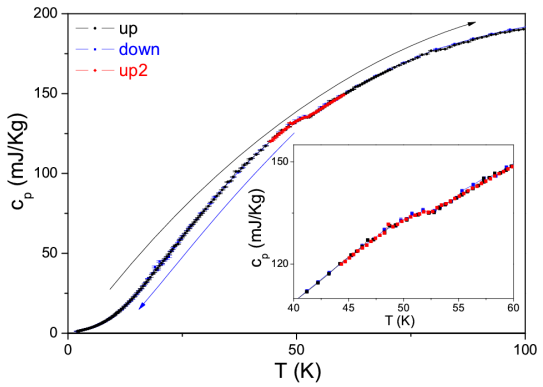

Fig. 4. Temperature dependence of the specific heat C_p. Inset shows dependence near Curie temperature.

4. Summary and conclusions

The reported magnetic data indicate complex magnetic properties of $Dy_{11}Si_4In_6$ resulting from the complex crystal structure in which dysprosium atoms occupy four nonequivalent sites. Magnetic data show that above 52 K the compound is a paramagnet with magnetic moments localized on the Dy atoms. The value of the effective magnetic moment is close to the free Dy^{3+} ion value. Positive sign of the paramagnetic Curie temperature suggests that the ferromagnetic interactions are dominant. Below $T_c = 52$ K the Dy magnetic moments order with a ferromagnetic component. The data collected at low temperatures indicate complex magnetic properties including a metastable or a spin-glass state. The specific heat data show only a small anomaly at 52 K (Fig. 4).

The presented data are similar to those reported for $Dy_{11}Ge_8In_2$ [5]. Both compounds crystallize in the same tetragonal crystal structure but the occupation of the 16m site is different: in $Dy_{11}Ge_8In_2$ the Wyckoff position 16m is occupied by Ge atoms while in $Dy_{11}Si_4In_6$ by In ones. Magnetic data indicate that $Dy_{11}Ge_8In_2$ is a ferromagnet with $T_c = 76$ K. Below T_c, at 60 and 34 K, a change in the magnetic properties is observed.

To clarify the temperature dependence of the magnetic properties of the studied compound additional neutron diffraction measurements are planned.

Acknowledgments

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References

[1] Y.B. Tyvanchuk, C.Y. Miliyanchuk, V.I. Zaremba, J. Stępień-Damm, Y.M. Kalychak, *Ukrain. J. Chem.* **67**, 15 (2001).

[2] G.S. Smith, Q. Johnson, A.G. Tharp, *Acta Crystallogr.* **23**, 640 (1967).

[3] Yu. Tyvanchuk, R. Duraj, S. Baran, T. Jaworska-Gołąb, Ya. Kalychak, J. Przewoźnik, A. Szytuła, *Intermetallics* **25**, 18 (2012).

[4] Y.Y. Janice Cheung, V. Svitlyk, Y. Mozharivskyj, *Intermetallics* **19**, 276 (2010).

[5] A.M. Tishin, Y.L. Spichkin, *The Magnetocaloric Effect and its Applications*, Institute of Physics Publ., Bristol 2003, p. 480.