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MAGNETOCALORIC EFFECT IN POLYCRYSTALLINE $\mathrm{DyAl_2}$ FOR CRYOGENIC GAS LIQUEFACTION STUDIED IN MAGNETIC FIELDS UP TO 3T

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In recent years, natural gas has acquired an increasing geopolitical importance as a source of energy transported over long distances for consumption in many different sectors of the economy. However, modern technologies for the liquefaction of hydrocarbons are very complex and expensive. Taking into account the significant progress in the field of modern superconducting magnetic field sources, magnetic cooling is becoming an alternative to traditional vapor-gas cooling. In the cryogenic temperature range, the Laves phases are among the most effective materials with a magnetocaloric effect. This article is devoted to the study of the magnetocaloric effect in magnetic fields up to 3 T in $\mathrm{DyAl_2}$. In these magnetic field the change of the magnetic entropy in this intermetallic compound is $\Delta S_m = -9.26$ J/(kg·K) and is achieved near the Curie temperature $T_C = 55\,\mathrm{K}$.

Keywords: *magnetocaloric effect, magnetic cooling, Laves phase, natural gas liquefaction, ferromagnet.*

Introduction

Natural gas is one of the main sources of energy nowadays and in the near future. Currently, there is a trend towards a rapid growth in the production and consumption of this type of energy in all market segments, including methane, hydrogen, oxygen, etc. The use of natural gas in liquefied form allows to optimize storage and provides the possibility to transport it even to hard-to-reach places far from main arteries of gas pipelines. The first attempts to liquefy natural gas were made in the early 20th century and were crowned with success in the United States in 1917, but industrial production of liquefied natural gas did not begin until the mid-1960s.

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Liquid natural gas (LNG) is a promising and developing market. According to a special report by Royal Dutch Shell analysts (2018), LNG accounts for about 40% of global gas exports. In 2018, 18 countries, including Russia, are involved in the export of liquefied natural gas. According to the International Energy Agency, by 2040 the supply of natural gas in liquefied form will exceed the volume of gas supplied by traditional pipeline transport.

The liquefaction process requires complex, energy-intensive compressor devices operating at cryogenic temperatures. The efficiency of traditional liquefaction methods is rather low at temperatures below 150 K, however, there is a fundamentally different approach to liquefy gases as the energy carrier of the future — magnetic refrigeration. Taking into account the recent progress in the development of superconducting magnets with magnetic fields of up to 15-22 T, this type of cooling at cryogenic temperatures could revolutionize gas-liquefaction technology. A review of recent scientific publications reveals a wide variety of different magnetic materials exhibiting significant magnetocaloric effect (MCE) in the temperature range of interest from 15 to 150 K (Fig. 1). This allows for efficient liquefaction of almost any natural gas. Based on this, there is the need for extensive adaptation (both experimental and theoretical) of magnetic cooling technology to the liquefaction of natural gas and hydrogen utilizing the magnetocaloric effect in strong magnetic fields.

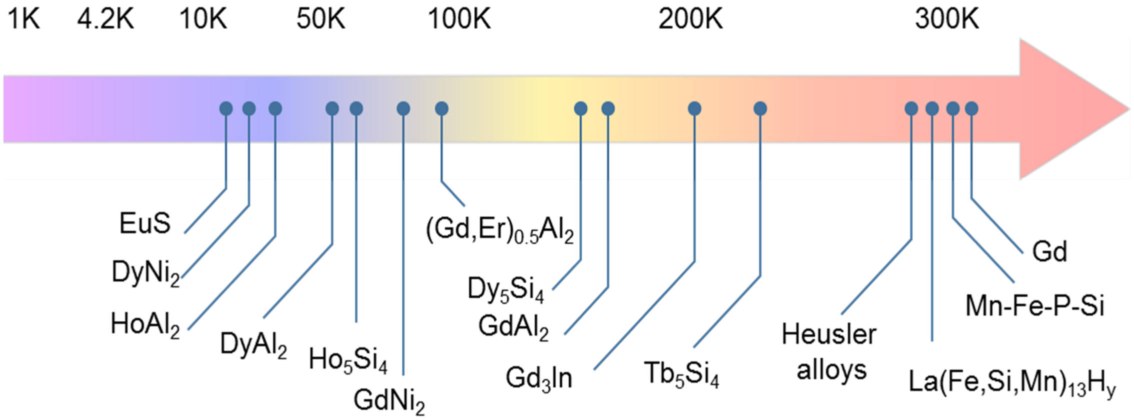

Fig. 1. Some perspective compounds for household and cryogenic magnetic cooling applications

In recent years, there has been a growing interest in Laves phases $RETm_2$ (RE — rare earth elements and Tm — transition metals) as potential candidates for magnetic cooling technology at cryogenic temperatures, in particular, as materials for liquefying natural gases [1] or other applications [2]. $REAl_2$ compounds are well-known intermetallic materials with interesting magnetic properties at low temperatures, as for instance reported in [3–6]. All lanthanides combine with aluminum to form the $REAl_2$ compound with the same crystal structure, which is the so-called C15 Laves cubic phase.

Thus, one of the most promising compounds, $DyAl_2$, has been thoroughly studied both theoretically and experimentally [7–13]. However, all studies have been performed in small magnetic fields only. This article is devoted to an additional study of the magnetic and magnetocaloric properties of the $DyAl_2$ compound in moderate magnetic fields with the aim of its possible application in magnetic cooling technology for natural gas liquefaction.

Samples preparation and Measurements

The investigated polycrystalline sample of $DyAl_2$ was synthesized by arc melting using a non-consumable tungsten electrode in protective argon atmosphere from the initial high-purity chemical elements Dy and Al with a purity o 99.998 at.%. To achieve homogeneity, the synthesized sample was remelted three times in the melting chamber of a Centorr Vacuum Industries 5SA furnace.

X-ray structural and phase analysis was carried out at room temperature with a Rigaku Ultima IV X-ray diffractometer using Cu-K_α radiation, and then all the data obtained were processed according to the modified Rietveld algorithm [14]. The elemental composition of the synthesized $DyAl_2$ alloy was studied on an ARL QUANT'X energy dispersive X-ray fluorescence spectrometer and scanning electron microscope JEOL JSM-6510LA. Magnetic measurements were carried out using Quantum Design Versa Lab according to standard measurement procedures in the temperature range $T = 50$–350 K in magnetic fields up to 3 T.

Results and Discussion

Fig. 2 shows the X-ray diffraction pattern of $DyAl_2$ obtained at room temperature. Narrow peaks in the X-ray pattern indicate a well-crystallized sample. The crystal structure of the compound under study corresponds to the cubic Laves phase with the lattice parameter $a = 0.78365$ nm. Small intensity peaks located near the peaks of the main phase (shown in Fig. 2) in the diffraction pattern indicate the co-existence of impurity phases, including Dy_2O_3, cubic type DyN (DyO, DyC, Dy_3AlO) and another 1–3% phase, which could not be identified. As seen from Fig. 3, the presence of an impurity phase is confirmed by the SEM image, where the main phase $DyAl_2$ is shown in gray, and the impurity phases Dy_2O_3 and DyN are shown in dark gray and white colors. At low magnifications, a multiphase oxidized structure with some dendrites can be seen. Based on the SEM image (Fig. 3), the amount of impurity phases can be estimated to about 7–10%.

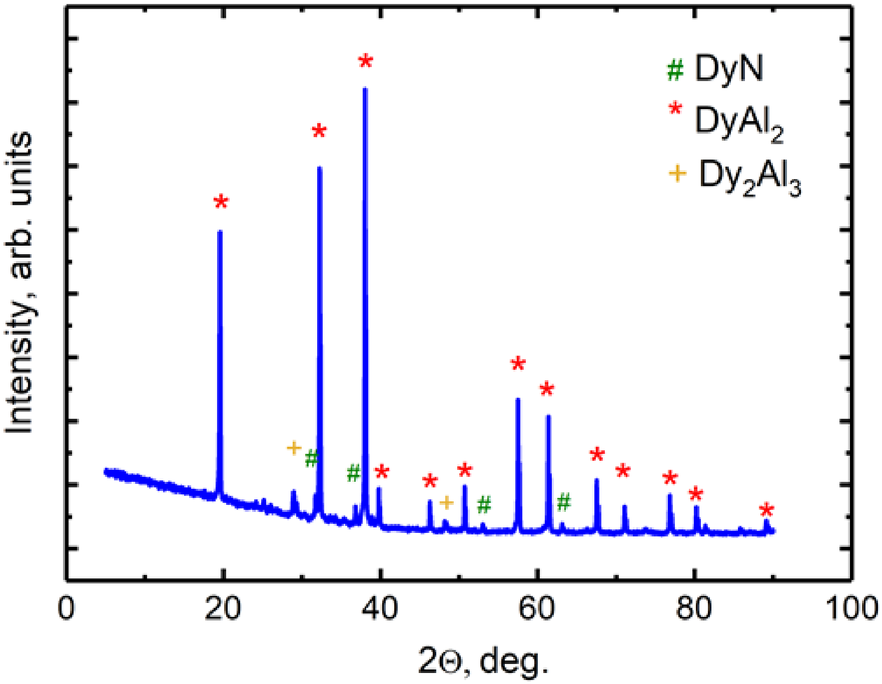

Fig. 2. X-ray pattern taken from $DyAl_2$ measured at room temperature

The field dependences of the magnetization of $DyAl_2$ which are measured in external magnetic fields up to 3 T in the temperature range 50–300 K with a step of 5 K are shown in Fig. 4. As can be seen from the hysteresis loop (see Fig. 5) measured at $T = 50$ K, the $DyAl_2$ compound is a soft ferromagnet with a low coercive field

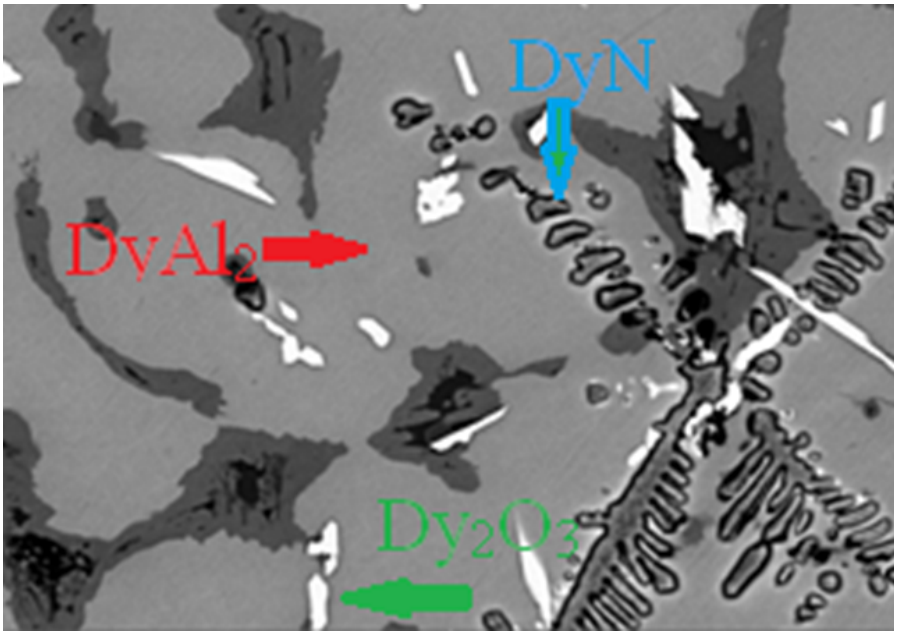

Fig. 3. SEM image of $DyAl_2$ (impurity phases are pointed by arrows)

$\mu_0 H_C \sim 6$ mT. The Belov — Arrott curves (Fig. 6) allow us to accurately determine the Curie temperature T_C, excluding the influence of undesirable effects arising from an external magnetic field [15]. Based on this data, the Curie temperature T_C of $DyAl_2$ is identified to be 55 K, which is slightly lower than reported by the group of researchers led by P.J. von Ranke [12], for which $T_C = 64.5$ K upon magnetization along the easy magnetization axis [100].

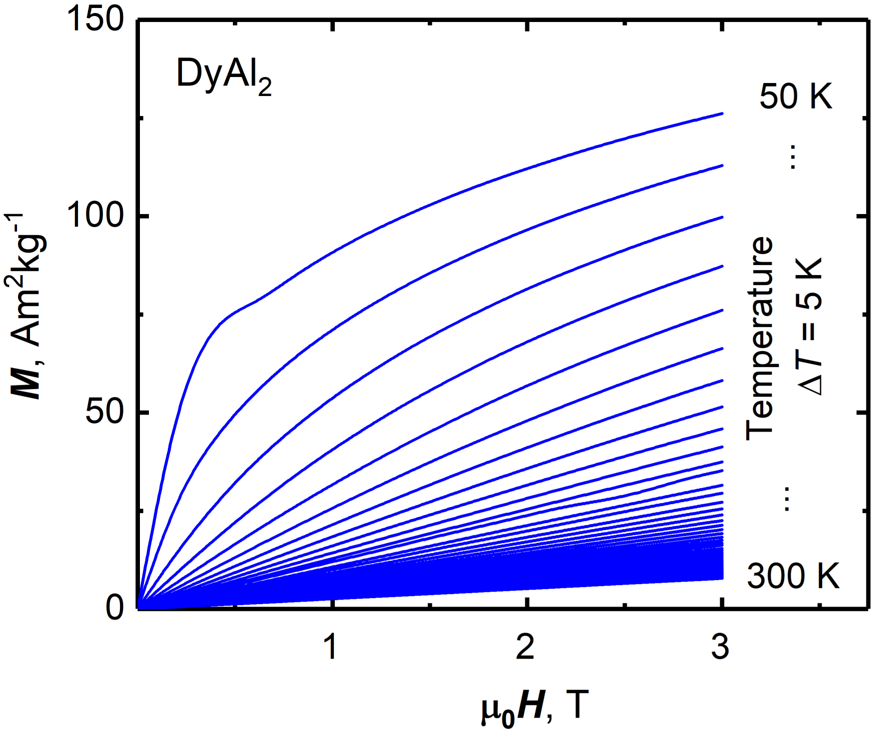

Fig. 4. Magnetic-field dependencies of magnetization of $DyAl_2$

For second-order magnetic phase transitions, the change in the isothermal magnetic entropy ΔS_m and the adiabatic change in temperature ΔT_{AD} can be easily calculated using Maxwell's relations [16]

$$\left(\frac{\partial S_M}{\partial H}\right)_{T,P} = \left(\frac{\partial M}{\partial T}\right)_{P,H},$$

$$\Delta S_M(T,H) = S_M(T,H) - S_M(T,0) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_{P,H} dH,$$

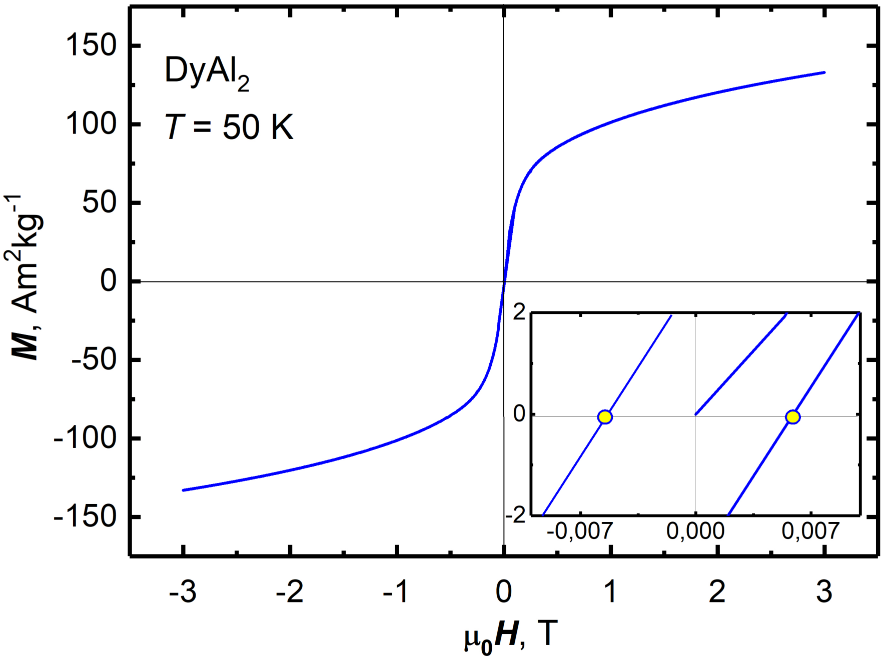

Fig. 5. Hysteresis loop of DyAl$_2$, measured at $T = 50$ K.
The inset shows the low-field area of hysteresis loop

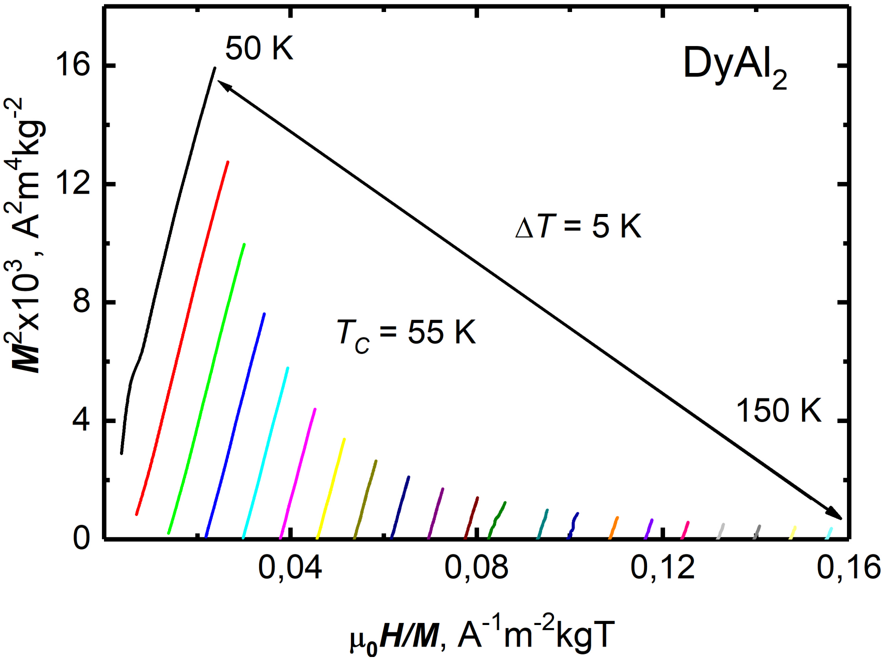

Fig. 6. Belov — Arrot plot of DyAl$_2$

that means, that the change of magnetic entropy in the field H will be equal to the difference between the entropies in the field $S(T,H)$ and without the field $S(T,0)$. On the other hand, as far as $dS = (C_P/T)\,dT$, then the infinitesimal adiabatic temperature for a reversible adiabatic-isobaric process is defined by:

$$dT = -\frac{T}{\Delta C_{P,H}}\left(\frac{\partial M}{\partial T}\right)_{P,H} dH, \quad \text{where } \Delta C_{P,H} = \frac{\partial(\Delta S_M)}{\partial T}. \tag{1}$$

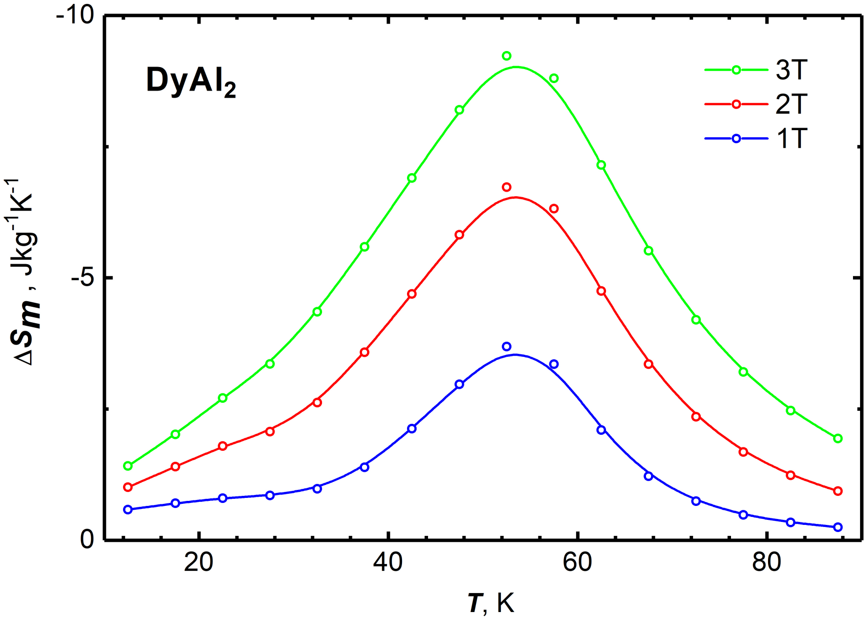

Fig. 7. Temperature dependences of magnetic entropy change ΔS_m of $DyAl_2$

Thus, the MCE is directly proportional to the absolute temperature, the derivative of the magnetization with respect to temperature at a constant field, the magnitude of the change of the magnetic field, and is inversely proportional to the heat capacity. After integrating equation (1), we obtain the MCE value in the following form

$$\Delta T_{AD}\left(T,\Delta H\right)=-\int_{H_1}^{H_2}\left(\frac{T}{C\left(T,H\right)}\right)_H\left(\frac{\partial M\left(T,H\right)}{\partial T}\right)_H dH. \tag{2}$$

The results of calculation ΔS_m for $DyAl_2$ are shown in Fig. 6. The change in magnetic entropy reaches its maximum value $\Delta S_m = -9.26$ J/(kg·K) in the vicinity of the Curie temperature $T_C = 55$ K when the magnetic field changes up to 3 T. Using equation (2) and the zero-field specific heat of $DyAl_2$ from [8], we can estimate the adiabatic temperature change of our compound to be approximately 3.7 K at T_C in a magnetic field change of 3 T. Thus, it is obvious that the $DyAl_2$ alloy, when the magnetic field changes up to 10 T (or higher), which can be easily generated by a superconducting magnet, can be used in a wide temperature range with a significant MCE.

Conclusions

Looking into the future of natural gas liquefaction technology, it can be assumed that magnetic cooling technology will be widely used for this purpose due to its energy efficiency and environmental friendliness. This assessment is based mainly on the fact that today there is a huge variety of readily available superconducting magnets operating in the cryogenic temperature range. The results of our experimental studies of the MCE in $DyAl_2$ clearly showed the great potential of this Laves phase compound to be utilized in magnetic fields created by superconducting magnets which could lead to the realization of natural gas liquefaction by magnetic cooling.

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МАГНИТОКАЛОРИЧЕСКИЙ ЭФФЕКТ В ПОЛИКРИСТАЛЛИЧЕСКОМ $DyAl_2$ ДЛЯ КРИОГЕННОГО СЖИЖЕНИЯ ГАЗА, ИССЛЕДОВАННЫЙ В МАГНИТНЫХ ПОЛЯХ ДО 3 Тл

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В последние годы природный газ приобретает всё большее геополитическое значение как источник энергии, транспортируемой на большие расстояния для потребления во многих различных секторах экономики. Однако современные технологии сжижения углеводородов очень сложны и дороги. С учётом значительного прогресса в области современных сверхпроводящих источников магнитного поля магнитное охлаждение становится альтернативой традиционному парогазовому охлаждению. В криогенном температурном диапазоне фазы Лавеса являются одними из наиболее эффективных материалов с магнитокалорическим эффектом. Данная статья посвящена исследованию магнитокалорического эффекта в магнитных полях до 3 Тл в $DyAl_2$. В таких магнитных полях изменение магнитной энтропии в этом интерметаллическом соединении составляет $\Delta S_m = -9.26$ Дж/(кг·К) и достигается вблизи температуры Кюри $T_C = 55\,$К.

Ключевые слова: *магнитокалорический эффект, магнитное охлаждение, фаза Лавеса, сжижение природного газа, ферромагнетики.*

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