

Selected papers presented at the 15th Symposium of Magnetic Measurements and Modelling SMMM'2025

A Short Review of the Magnetocaloric Effect and Selected Magnetocaloric Materials

P. GEĄBARA*

Department of Physics, Czestochowa University of Technology, Armii Krajowej 19, 42-200 Czestochowa, Poland

Doi: [10.12693/APhysPolA.149.S112](https://doi.org/10.12693/APhysPolA.149.S112)

*e-mail: piotr.gebara@pcz.pl

The present paper provides a short review of the magnetocaloric effect and selected magnetocaloric materials, such as Gd-based alloys, MnCoGe alloys, and La(Fe, Si)₁₃-type alloys. The magnetocaloric effect is a fundamental environmentally friendly technique for lowering temperature, which is nowadays highly developed due to its potential application in domestic refrigerators or heat pumps. This article delivers information on the theory of the magnetocaloric effect. Moreover, it reviews the structure and thermomagnetic properties of selected materials suitable for active magnetic regenerators working at close to room temperature.

topics: magnetocaloric effect (MCE), Gd/Gd-alloys, MnCoGe-alloys, La(Fe, Si)₁₃ alloys

1. Introduction

Degradation of the ozone layer was first noticed in the 1970s. This effect is extremely dangerous due to the protective role the ozone layer plays for the Earth. Nowadays, it is commonly referred to as the ozone hole. The research carried out in order to explain its causes revealed that substances such as sulfur and nitrogen oxides are destroying the ozone layer. Twenty years later, at the beginning of the 1990s, further investigations proved the destructive role of freon compounds used in the production and exploitation of aerosol diffusers and various kinds of refrigerators [1, 2]. After the publication of the Montreal Protocol, the production of freons was drastically limited and substitute compounds were discovered; yet, some of the freons are still irreplaceable in conventional cooling devices. Moreover, the directives of the European Union and energy-saving policies encourage the scientific community to seek alternative and energy-saving cooling techniques. Magnetic cooling based on the magnetocaloric effect (MCE) is a method of lowering temperature with the highest efficiency, which reaches even $\sim 60\%$ [3]. The MCE was discovered by Warburg [4] in the 1880s during the studies on the behavior of iron in an external magnetic field. Debye [5] and Giauque [6], independently, proposed the use of MCE to achieve ultralow temperatures lower than liquid helium. Currently, the first

magnetic cooling devices are relatively more expensive than the cooling techniques used in traditional domestic refrigerators (the costs are, respectively, several thousand or several hundred euros).

The discovery of the giant magnetocaloric effect (GMCE) in the Gd₅Si₂Ge₂ alloy [7] at near-room temperature by Pecharsky and Gschneidner Jr. (1997) started the next chapter in the development of magnetocaloric materials (MCM). Since the publication of their paper, an exponential increase in research on this topic has been observed.

This paper focuses on the physical fundamentals of the magnetocaloric effect and on selected groups of materials in which this phenomenon occurs close to room temperature.

2. Theoretical description of magnetocaloric effect

The presence of the magnetocaloric effect in a magnetic material enables heating and cooling processes of the samples in the presence of an external magnetic field. The phenomenon discovered by Warburg in 1881 during the experiment on the behavior of pure iron in a magnetic field [5] remained unexplained for over four decades. However, in the 1920s, Debye [6] and Giauque [7] came up with the idea of using this effect to achieve temperatures below that of liquid helium, which at the time was the

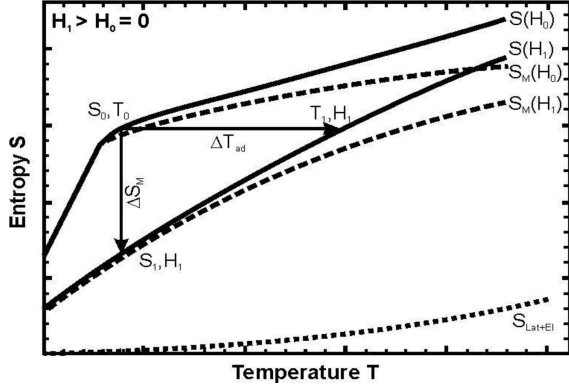


Fig. 1. Plot illustrating the change in entropy S for a solid having magnetic properties with respect to temperature T . Solid lines represent total entropy, and dashed lines represent magnetic entropy in magnetic fields $H_0 = 0$ and $H_1 > 0$; dotted line shows temperature dependence of nonmagnetic entropy coming from lattice and electron element; S_0 and T_0 denote entropy and temperature in $H = 0$, respectively; S_1 and T_1 represent entropy and temperature in $H_1 > 0$ [11].

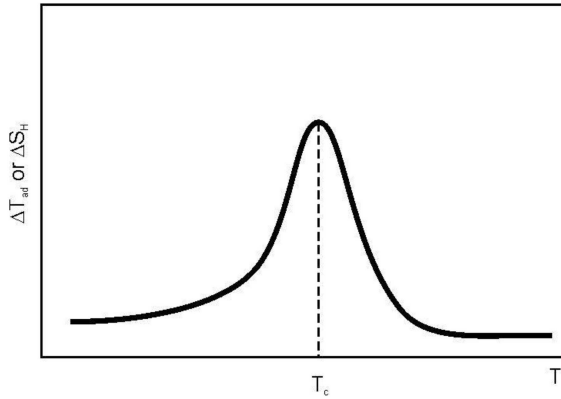


Fig. 2. Plot representing the correlation between the temperature and entropy changes, which are a measure of the magnetocaloric effect near the Curie temperature of the material [11].

lowest temperature that could be experimentally achieved. Although research on the magnetocaloric effect lasted for over a century, this investment is worthwhile in every respect now. Conventional cooling devices are said to be replaced in the near future with refrigerators or heat pumps based on the magnetocaloric effect. Magnetic heating or cooling processes are environment-friendly and offer low energy consumption [2, 8, 9]. In fact, the sheer volume of possible savings in oil resources, as the International Energy Agency announced in its report on the crises from 1973 and 1978, is calculated to be over 600 million tons per year by 2020, 80% of which would come from switching to heat pumps. Current scientific and technical achievements made in the area of magnetocaloric heat pumps make

us suppose that in the next 10–15 years they will become one of the most considerable heat sources used in the European Community countries, including Poland. Potential owners of single-family dwellings will surely appreciate magnetocaloric heat pumps as a more cost-effective alternative [10] and ecological reasons. Currently, the most important issue is the development of materials exhibiting a considerable magnetocaloric effect at temperatures close to room temperature. This effect occurs in all magnetic materials, and its intensity depends on the properties of the particular material. The presence of the effect is explained by the magnetic sublattice interactions with the applied external magnetic field, which leads to a magnetic change in the entropy of solids. Isothermal magnetization of materials such as paramagnets or weak ferromagnets decreases their entropy because of the arrangement of most spins. In the demagnetization process, the magnetic entropy value of the structure is regained, but since the adiabatic transformation occurs, the temperature of the material drops. The entropy of solids, being the temperature and magnetic field, is the sum of the magnetic part (as a temperature and magnetic function), electron, and crystalline part, which are only functions of temperature [11]. This can be written as follows

$$S(T, H) = S_M(T, H) + S_L(T) + S_E(T). \quad (1)$$

Figure 1 presents the dependence of particular entropy for ferromagnetic material placed in different magnetic fields.

The measure of the effect is assumed to be an adiabatic change in temperature or a magnetic entropy change. The magnitudes ΔT_{ad} and ΔS_M are related to the magnetization M of the sample. The magnetic field H and the temperature T are described by the Maxwell equation [11, 12]

$$\left(\frac{\delta S(T, H)}{\delta H}\right)_T = \left(\frac{\delta M(T, H)}{\delta T}\right)_H \quad (2)$$

and the equation describing the heat exchange [13]

$$\left(\frac{\delta T}{\delta H}\right)_S = -\left(\frac{\delta S}{\delta H}\right)_H \left(\frac{\delta T}{\delta S}\right)_H. \quad (3)$$

With the help of mathematical tools, we are able to define the dependence of the adiabatic temperature change [13]

$$\Delta T_{ad}(T, \Delta H) = -\int_{H_1}^{H_2} dH \left(\frac{T}{C(T, H)}\right)_H \left(\frac{\delta M(T, H)}{\delta T}\right)_H \quad (4)$$

and the relation of the magnetic entropy change [11] (see Fig. 2)

$$\Delta S_M(T, \Delta H) = \int_{H_1}^{H_2} dH \left(\frac{\delta M(T, H)}{\delta T}\right)_H, \quad (5)$$

where: T — temperature in absolute scale; $M(T, H)$ — magnetization; $C(T, H)$ — specific heat.

The above-given equations are fundamental to understanding and analyzing the magnetocaloric effect in solid states. Their analysis enables one to take new directions in the search for new materials featuring a considerable magnetocaloric effect.

3. Applications of MCE

Over four decades after the discovery of the magnetocaloric effect, Debye and Giauque presented a concept of achieving ultralow temperatures based on this phenomenon. Forty years later, in 1966, van Geuns [14] introduced a refrigerator working at temperatures above 1 K, which became really possible thanks to research on new materials. Nowadays, the magnetocaloric effect in ferromagnetic materials is used for magnetic cooling. The effect is an alternative to classical ways of lowering temperature, which are based on gas conversions and, as such, have a very negative impact on the natural environment. Hence, paramagnetic salts containing Gd or Ga, for which considerable magnetic entropy changes are observed at temperatures close to absolute zero, have been introduced in cooling methods. Using such materials, temperatures as low as 27 μK have been achieved, e.g., with the PrNi_5 compound [15].

Magnetic refrigerators work in several ranges of temperatures [14]:

- (i) 1.5–4.2 K — where the helium II phase, necessary to maintain the NbTi superconductor below 2 K, is present. In this range, magnetic refrigerators replaced Joule–Thomson loop, which requires very low gas pressure (about 1000 Pa) and large gas flow;
- (ii) 4.2–20 K — where the liquefaction of hydrogen and superconductor cooling processes take place;
- (iii) 20–77 K — where high-temperature superconductors are cooled, with a maximum temperature being 4.2 K, or 1.5 K in the case of refrigerators.

The ferromagnetic substances are usually used in two temperature ranges:

- (i) 10–80 K (instead of liquid helium or nitrogen);
- (ii) room temperature regimes (in air-conditioning prototypes, magnetic freezers, and heat pumps).

The Curie temperature indicates which criterion a material should be subjected to, because the magnetic transformation (order–disorder) is within a very narrow range of temperatures near to the Curie point. The transformation is connected to a high value of magnetic entropy change ΔS_M , which is necessary for its practical application. At room temperature, $\text{Pr}_2\text{Fe}_{17}$ [16, 17], $\text{La}(\text{Fe}, \text{Si})_{13}$ [18, 19], or FeZrCrNbCuSiB [20, 21] alloys are used; in the 10–80 K range, Pr, Nd, Er, and Tm are used, as

well as intermetallic compounds, the best-known of which are REAl_2 (RE = Er, Ho, Dy) [22, 23] and RENi_2 (where RE = Gd, Dy, Ho) [24, 25]. Pure Gd and its compounds are materials with good magnetocaloric properties. It is the first material originally used for cooling near room temperature because its Curie point is at 294 K [26–28]. The magnetocaloric effect is expressed in numbers via magnetic entropy change ΔS_M , and it is about 2 J/(kg K) within an external magnetic field change of $\Delta\mu_0 H = 5$ T. Although Gd has good properties, its high price is a serious drawback, so instead of Gd, relatively cheap compounds and alloys based on iron are successfully used [16–21]. In comparison with Gd, new $\text{La}(\text{Fe}, \text{Si})_{13}$ compounds perform better as far as lower price and magnetic entropy change of about 20 J/(kg K) are concerned [18, 19]. The successful development of the mentioned magnetocaloric materials, as well as many others, encourages scientists to look for further insightful ways of searching for metallic and intermetallic materials in the range of temperatures satisfying consumers' needs.

4. Magnetocaloric materials

Previous studies on materials exhibiting the magnetocaloric effect at room temperature allowed the formulation of several empirical conditions that should be satisfied in order to obtain materials with desirable properties [29]. The magnetocaloric material should have the following properties:

- a considerable magnetic entropy change $|\Delta S_M|$ and therefore a large adiabatic temperature change $|\Delta T_{ad}|$;
- Curie temperature T_C near the room temperature;
- small energy loss due to material magnetization;
- very small heat hysteresis loop;
- small specific heat value but good thermal conductivity, which defines temperature change and heat exchange rate;
- large electrical resistance.

4.1. Gadolinium and its alloys

Gadolinium exhibits natural magnetocaloric properties. It is a lanthanum group element, existing in Earth's crust in the form of minerals such as monazite and bastnezite. Research based on neutron diffraction spectroscopy, carried out by Cable and Wollan in 1968, revealed that pure gadolinium exhibits ferromagnetic properties below 294 K. In the past, the studies on the magnetocaloric effect in Gd set new standards, and now newly developed materials are often compared with them [3].

The Gd magnetocaloric effect expressed in the adiabatic temperature change units ΔT_{ad} equals 6, 12, 16, 20 K, respectively, for magnetic field changes of $\Delta\mu_0 H = 2, 5, 7, 10$ T.

The best known magnetocaloric material based on Gd is the $Gd_5Ge_2Si_2$ alloy discovered by Pecharsky and Gschneidner Jr. in 1997. The excellent magnetocaloric properties of the $Gd_5Ge_2Si_2$ alloy result from a magnetic phase transition at the Curie point, accompanied by a structural transformation from monoclinic to orthorhombic structure. The value of magnetocaloric effect for $Gd_5Ge_2Si_2$ alloy expressed by ΔS_M magnetic entropy change units is 18.5 J/(kg K) under magnetic field change $\Delta\mu_0 H = 5$ T and at Curie temperature $T_C \approx 276$ K.

Several years later, the concept of biphasic Gd-based alloys was proposed in order to produce materials with enhanced refrigeration capacity (RC). Law et al. [30] proposed the concept of biphasic material composed of Gd matrix with GdZn inclusions. Maximum magnetic entropy change reached 3.42 J/(kg K) when the change in external magnetic field was ~ 2 T. Similar results of magnetic entropy change were obtained for GdPb alloy (3.04 J/(kg K)), for which a biphasic structure was produced [31]. An addition of Pd enabled the production of a biphasic Gd-based alloy, and the highest magnetic entropy change achieved 5.25 J/(kg K) for the $Gd_{95}Pd_5$ alloy [32, 33]. Another alloying was proposed by Jayaraman et al. [34], who reported successful fabrication of biphasic GdMn alloys. Conducted magnetocaloric measurements revealed a value of magnetic entropy change of 4.8 J/(kg K).

The main problem with Gd-based alloys is their relatively high price, which prevents their widespread application as an active magnetic regenerator (AMR) in commercial cooling devices.

4.2. MnCoGe alloys

Another group of MCMs with excellent magnetocaloric properties is $MM'X$ alloys (where M and M' are transition metals and X is a metalloid such as Ge, Si, or Sn). Such good properties are the result of martensitic transformation in the vicinity of magnetic transformation. The best-known magnetocaloric alloy that belongs to this group is MnCoGe. It crystallizes in a low-temperature orthorhombic TiNiSi-type structure (space group $Pnma$) and a high-temperature hexagonal Ni_2Ti (space group $P6_3/mmc$) (Fig. 3, see also [35]). The value of ΔS_M reaches 6 J/(kg K) under the change in external magnetic field of ~ 5 T and at the Curie temperature of ~ 293 K [36]. Selective addition of boron induced an occurrence of giant MCE, which was manifested by high $\Delta S_M = 47$ J/(kg K) [37]. Such a high value was the result of a magnetostructural transition in

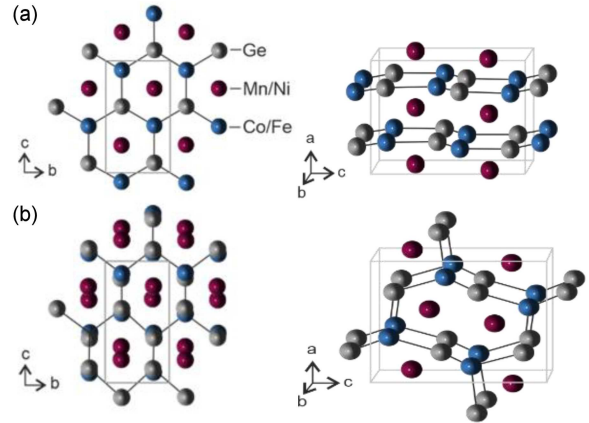


Fig. 3. Hexagonal (a) and orthorhombic structures (b) observed in the MnCoGe alloys [35].

the Curie temperature. Similar results were observed for the MnCoGe alloys modified by carbon ($MnCoGeC_{0.03}$) [37], nickel $Mn_{0.9}Ni_{0.1}CoGe$ [38], and gallium $MnCoGe_{0.95}Ga_{0.05}$ [39]. Moreover, interesting modifications influencing thermomagnetic properties were presented [36, 40, 41], where manganese was substituted by vanadium [40], chromium [41], palladium [36, 42], or zirconium [35, 36, 43]. Another interesting way for modification was the preparation of the MnCoGe alloys with off-stoichiometric composition [44, 45] or the introduction of vacancies into the crystalline structure [46].

4.3. La(Fe, Si)₁₃-type alloys

Gd- or MnCoGe-based materials are relatively expensive due to the high price of gadolinium or germanium. A cheaper alternative with promising magnetocaloric properties is the La(Fe, Si)₁₃-type alloys. They belong to the group of binary LaM₁₂ compounds, where M is Co, Fe, or Ni. The binary LaCo₁₃ compound is the only stable phase, whereas LaFe₁₃ or LaNi₁₃ do not exist. Such a situation is caused by the positive enthalpy of mixing. However, partial substitution of Fe by Si or Al decreases the total enthalpy of mixing, which leads to stabilization of the pseudobinary La(Fe, Si)₁₃-type structure. This type of alloys crystallizes in cubic pseudobinary NaZn₁₃-type structure. The La atoms occupy 8a positions (in Wyckoff notation), while Fe prefers two non-equivalent positions 8b and 96i (Fig. 4). The Curie temperature of the La(Fe, Si)₁₃ alloys depends strongly on Si content, but varies in the vicinity of 195 K. Such low values do not qualify them as an active magnetic regenerator in magnetic refrigerators working at room temperature. Due to this fact, for many years this type of alloy has been modified by introducing additives in order to change the Curie temperature and the magnetic entropy

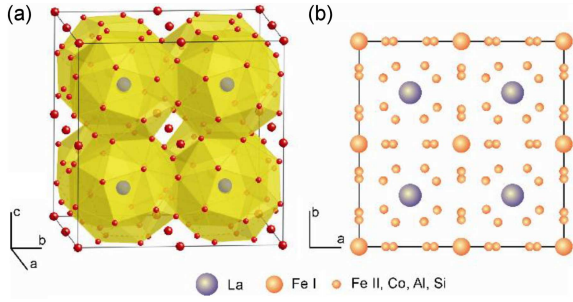


Fig. 4. Elementary cell of the NaZn₁₃-type [57].

change. These modifications can be summarized as follows:

- Co, when added to Fe (in La(Fe_{1-x-y}Co_xSi_y)₁₃ for a particular x and y range), causes an increase in the alloy's Curie temperature [47–49], while the magnetic entropy change decreases. Moreover, as it was shown in [50, 51], appropriate substitution of Fe by Co allowed for the production of a material with an extremely broad magnetic entropy change, for which a full width at half maximum (FWHM) of the $\Delta S_M(T)$ curve reaches even 100 K;
- H added during the annealing process under higher pressure or milling process in a hydrogen atmosphere causes a significant rise in Curie temperature, even by 100 K, slightly decreasing the value of magnetic entropy change ΔS_M at the same time [52–54];
- partial substitution of La by Nd in La(Fe_{1-x}Nd_x(Fe, Si)₁₃) substitutes La positions in the crystalline lattice, making it smaller and therefore shifting the Curie point up by a few degrees but also reducing the magnetocaloric effect [55, 56];
- Ce causes a decrease of T_C when, like Nd, it is added in a small fraction to La. It replaces La in the crystalline structure and shortens the lattice constant. However, the decrease in T_C in this case is caused by the magnetovolume effect. Ce addition also has a considerable influence on a better magnetocaloric effect due to the reinforcement of the metamagnetic transition [57–59];
- Pr also decreases the Curie temperature, reducing the losses of temperature and magnetic hysteresis. It improves magnetocaloric properties and magnetic entropy change. Moreover, an application of strong magnetic fields to samples doped by Pr induces a first-order metamagnetic phase transition [60–63];
- Gd (present in the crystalline structure) does not influence T_C but decreases significantly the ΔS_M value because of the change from a first-order to a second-order phase transition [64];

- Er, which is a very interesting metal from rare-earth (RE) elements, replaces La in the crystalline structure and therefore shortens the lattice constant, simultaneously increasing T_C . Exchange interactions between Er–Er and Er–Fe sublattices are also responsible for the growth in the T_C value. At a ratio of 1:10 of Er quantity to La quantity, we also observe a better magnetocaloric effect [65];
- N is introduced analogously to the hydrogenation process. Nitrogenation process changes the Curie temperature considerably, even up to 80 K, making elementary cells smaller by 10%. The process also improves the alloy's magnetization by up to 10% [66];
- Al stabilizes alloys' phase, also increasing T_C value. In LaFe_{11,0}Co_{0,8}(Si_{1-x}Al_x)_{1,2} alloy, T_C rises from 276 to 290 K when the Al:Si ratio is 6:10, but ΔS_M decreases from 18.5 to 8.8 J/(kg K) [67, 68];
- Mn addition causes a decrease in lattice constant and a reduction in the Curie temperature. Moreover, a small addition results in a decrease in magnetic entropy change, but the further increase in Mn content improves the ΔS_M value [69, 70];
- Dy causes an increase in the Curie temperature, due to RE–Fe interactions, while magnetic entropy changes slightly decreases [71];
- Ho decreases the Curie point and magnetic entropy change due to the enhancement of the second-order phase transition [62].

An interesting effect of the described substitutions was presented in [72]. An anomalous thermal expansion of α -Fe inclusions in the La(Fe, Si)₁₃-type matrix was studied. Such a phenomenon was the result of an interaction between the La(Fe, Si)₁₃-type phase and α -Fe, and it was independent of the order of phase transition. On the other hand, the intensity of this effect was higher for the sample doped with Ce, which manifested a first-order phase transition.

Figure 5 shows a graphical representation of ΔS_M vs T_C and areas of working range for the materials mentioned in the present paper. It is clearly visible that the potential application of the mentioned materials is very wide, and will depend on the specific conditions of use.

5. Perspectives for the development of magnetocaloric materials

As it was shown by Law et al. [73], a new trend in the development of MCMs will be the production of materials with both orders of phase transition. The first-order transition will provide relatively high magnetic entropy change, whereas the second-order phase transition will deliver a broader temperature

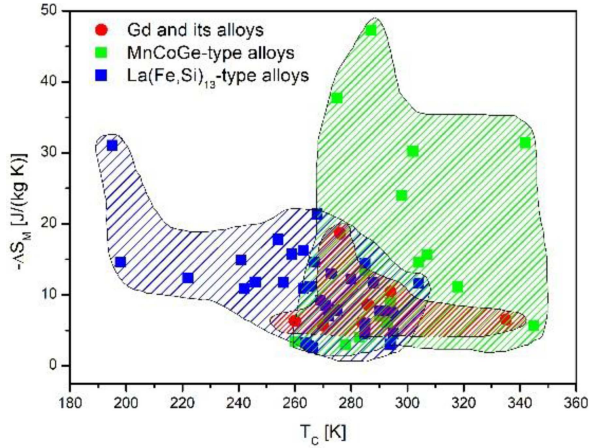


Fig. 5. Areas of working range of magnetocaloric materials described in the present paper.

working range (δT_{FWHM}). Another possibility is further modification of chemical composition and microstructure, which will result in an improvement of magnetocaloric properties [74]. The preparation of multicaloric materials will enable more effective use of active regenerators in novel refrigerators [75]. Law et al. [73] focused on finding new techniques for characterizing magnetocaloric materials in order to better understand their properties and behavior. These include advanced imaging methods, high-resolution spectroscopy, and computational modeling, which help in designing materials with optimized performance.

Taking into account European Union directives concerning the reduction of carbon footprint, CO₂ emission, and energy saving, it will be extremely important to integrate magnetocaloric cooling systems with renewable energy sources such as wind or solar power.

6. Conclusions

It is almost impossible to present all information concerning the magnetocaloric effect and magnetocaloric materials; however, a small attempt was made in this paper. Although MCE is more than a hundred years old, it is still studied intensively. A short review of the most suitable MCMs working at room temperature was presented. As it was shown above, the main MCM is Gd and its alloys. Natural properties, such as the Curie temperature, low hysteresis, and relatively good magnetic entropy change, qualify it as a candidate for an active magnetic regenerator in magnetic refrigerators. However, its high costs are an obstacle.

Another good candidate are MnCoGe-type alloys. The magnetostructural transition results in high magnetic entropy change at near-room temperature. However, the high cost of Ge and low

structural stability are the main obstacles to practical application in domestic devices.

The last group of materials described in this article are the alloys of La(Fe, Si)₁₃-type. Relatively high content of Fe and good magnetic properties allowed us to consider these materials the most promising candidates for active magnetic regenerators in magnetic cooling devices. Ongoing studies on the modification of chemical composition, preparation techniques, and improvement of magnetocaloric properties will make it possible to use them in commercial refrigerators next to the Heusler alloys.

References

- [1] A.M. Tishin, Y.I. Spichkin, *The Magnetocaloric Effect and its Application*, 1st ed., CRC Press, Boca Raton 2003.
- [2] K.A. Gschneidner, Jr., V.K. Pecharsky, *J. Appl. Phys.* **85**, 5365 (1999).
- [3] C. Zimm, A. Jastrab, A. Sternberg, V. Pecharsky, K. Gschneidner, Jr., M. Osborne, I. Anderson, in: *Advances in Cryogenic Engineering*, Vol. 43, Springer, Boston (MA) 1998, p. 1795.
- [4] E. Warburg, *Ann. Phys.* **13**, 141 (1881).
- [5] P. Debye, *Ann. Phys.* **81**, 1154 (1926).
- [6] W.F. Giauque, *J. Am. Chem. Soc.* **49**, 1864 (1927).
- [7] V.K. Pecharsky, K.A. Gschneidner, Jr., *Phys. Rev. Lett.* **78**, 4494 (1997).
- [8] K.A. Gschneidner, Jr., V.K. Pecharsky, *Ann. Rev. Mater. Res.* **30**, 387 (2000).
- [9] V.K. Pecharsky, K.A. Gschneidner, Jr., *Appl. Phys. Lett.* **70**, 3299 (1997).
- [10] D. Vuarnoz, A. Kitanovski, M. Diebold, F. Gendre, P.W. Egolf, *Phys. Stat. Solidi C* **4**, 4552 (2007).
- [11] V.K. Pecharsky, K.A. Gschneidner, Jr., *J. Magn. Magn. Mater.* **200**, 44 (1999).
- [12] A.M. Morrish, *The Physical Principles of Magnetism*, John Wiley & Sons, 2001.
- [13] R.S. Ingarden, A. Jamiołkowski, R. Mru-gała, *Fizyka Statystyczna i Termodynamika*, PWN, Warszawa 1990 (in Polish).
- [14] J.R. van Geuns, *Philips Res. Rep. Suppl.* **6**, 1 (1966).
- [15] H. Ishimoto, N. Nishida, T. Furubayashi, M. Shinohara, Y. Takano, Y. Miura, K. Ôno, *J. Low Temp. Phys.* **55**, 17 (1984).
- [16] K. Mandal, A. Yan, P. Kersch, A. Handstein, O. Gutfleisch, K.-H. Müller *J. Phys. D* **37**, 2628 (2004).

- [17] K. Pawlik, I. Škorvánek, J. Kováč, P. Pawlik, J.J. Wysocki, O.I. Bodak, *J. Magn. Magn. Mater.* **304**, 510 (2006).
- [18] A. Yan, K.-H. Müller, O. Gutfleisch, *J. Alloy Compd.* **450**, 18 (2008).
- [19] J.D. Zou, B.G. Shen, J.R. Sun, *J. Phys. Condens. Matter* **19**, 196220 (2007).
- [20] N. Chau, P.Q. Thanh, N.Q. Hoa, N.D. The, *J. Magn. Magn. Mater.* **304**, 36 (2006).
- [21] A. Kolano-Burian, M. Kowalczyk, R. Kolano, R. Szymczak, H. Szymczak, M. Polak, *J. Alloys Compd.* **479**, 71 (2009).
- [22] T. Hashimoto, K. Matsumoto, T. Kurihara, T. Numazawa, A. Tomokiyo, H. Yayama, T. Goto, S. Todo, M. Sahashi, in: *Advances in Cryogenic Engineering Materials*, vol. 32, Springer, Boston (MA) 1986, p. 279.
- [23] T. Hashimoto, T. Kuzuhara, M. Sahashi, K. Inomata, A. Tomokiyo, H. Yayama, *J. Appl. Phys.* **62**, 3873 (1987).
- [24] C.B. Zimm, E.M. Ludeman, M.C. Severson, T.A. Henning, in: *Advances in Cryogenic Engineering*, Vol. 37, Springer, Boston (MA) 1992, p. 883.
- [25] A. Tomokiyo, H. Yayama, H. Wakabayashi, T. Kuzuhara, T. Hashimoto, M. Sahashi, K. Inomata, in: *Advances in Cryogenic Engineering Materials*, Vol. 32, Springer, Boston (MA) 1986, p. 295.
- [26] A.M. Tishin, K.A. Gschneider, Jr., V.K. Pecharsky, *Phys. Rev. B* **59**, 503 (1999).
- [27] G. Green, J. Chafe, J. Stevens, J. Humphrey, in: *Advances in Cryogenic Engineering*, Vol. 35, Springer, Boston (MA) 1990, p. 1165.
- [28] S.M. Benford, G.V. Brown, *J. Appl. Phys.* **52**, 2110 (1981).
- [29] M.-H. Phan, S.-C. Yu, *J. Magn. Magn. Mater* **308**, 325 (2007).
- [30] J.Y. Law, L.M. Moreno-Ramírez, J.S. Blázquez, V. Franco, A. Conde, *J. Alloys Compd.* **675**, 244 (2016).
- [31] P. Gębara, M. Hasiak, J. Kovac, M. Rajnak, *Materials* **15**, 7213 (2022).
- [32] P. Gębara, Á. Díaz-García, J.Y. Law, V. Franco, *J. Magn. Magn. Mater.* **500**, 166175 (2020).
- [33] Á. Díaz-García, J.Y. Law, P. Gębara, V. Franco, *JOM* **72**, 2845 (2020).
- [34] T.V. Jayaraman, L. Boone, J.E. Shield, *J. Magn. Magn. Mater.* **345**, 153 (2013).
- [35] F. Qian, Q. Zhu, X. Miao, J. Fan, G. Zhong, H. Yang, *J. Mater. Sci.* **56**, 1472 (2021).
- [36] P. Gębara, Z. Śniadecki, *J. Alloy Compd.* **796**, 153 (2019).
- [37] N.T. Trung, L. Zhang, L. Caron, K.H.J. Buschow, E. Brück, *Appl. Phys. Lett.* **96**, 172504 (2010).
- [38] C.L. Zhang, H.F. Shi, E.J. Ye, Y.G. Nie, Z.D. Han, D.H. Wang, *J. Alloys Compd.* **639**, 36 (2015).
- [39] D. Zhang, Z. Nie, Z. Wang, L. Huang, Q. Zhang, Y.-D. Wang, *J. Magn. Magn. Mater.* **387**, 107 (2015).
- [40] S.C. Ma, Y.X. Zheng, H.C. Xuan, L.J. Shen, Q.Q. Cao, D.H. Wang, Z.C. Zhong, Y.W. Du, *J. Magn. Magn. Mater.* **324**, 135 (2012).
- [41] N.T. Trung, V. Biharie, L. Zhang, L. Caron, K.H.J. Buschow, E. Brück, *Appl. Phys. Lett.* **96**, 162507 (2010).
- [42] K. Kutynia, A. Przybył, P. Gębara, *Materials* **16**, 5394 (2023).
- [43] K. Kutynia, P. Gębara, *Materials* **14**, 3129 (2021).
- [44] S.C. Ma, Q. Ge, Y.F. Hu et al., *Appl. Phys. Lett.* **111**, 192406 (2017).
- [45] Y. Li, H. Zhang, K. Tao, Y. Wang, M. Wu, Y. Long, *Mater. Des.* **114**, 410 (2017).
- [46] J. Liu, T. Gottschall, K.P. Skokov, J.D. Moore, O. Gutfleisch, *Nat. Mater.* **11**, 620 (2012).
- [47] A.T. Saito, T. Kobayashi, H. Tsuji, *J. Magn. Magn. Mater.* **310**, 2808 (2007).
- [48] X.B. Liu, Z. Altounian, *J. Magn. Magn. Mater.* **264**, 209 (2003).
- [49] E.C. Passamani, C. Larica, J.R. Provetti, A.Y. Takeuchi, A.M. Gomes, L. Ghivelder, *J. Magn. Magn. Mater.* **312**, 65 (2007).
- [50] M. Katter, V. Zellmann, G.W. Reppel, K. Uestuener, *IEEE Trans. Magn.* **44**, 3044 (2008).
- [51] P. Gębara, P. Pawlik, *J. Magn. Magn. Mater.* **442**, 145 (2017).
- [52] K. Mandal, O. Gutfleisch, A. Yan, A. Handstein, K.-H. Müller, *J. Magn. Magn. Mater.* **290**, 673 (2005).
- [53] L.G. de Medeiros, N.A. de Oliveira, *J. Alloys Compd.* **424**, 41 (2006).
- [54] S. Fujieda, Y. Hasegawa, A. Fujita, K. Fukamichi, *J. Magn. Magn. Mater.* **272**, 2365 (2004).
- [55] D.T. Kim Anh, N.P. Thuy, N.H. Duc, T.T. Nhien, N.V. Nong, *J. Magn. Magn. Mater.* **262**, 427 (2003).
- [56] Y. Zhu, K. Xie, X. Song, Z. Sun, W. Lv, *J. Alloys Compd.* **392**, 20 (2005).
- [57] A. Fujita, S. Fujieda, K. Fukamichi, *J. Magn. Magn. Mater.* **310**, e1006 (2007).

- [58] S. Fujieda, A. Fujita, K. Fukamichi, N. Hirano, S. Nagaya, *J. Alloys Compd.* **408**, 1165 (2006).
- [59] P. Gębara, J. Marcin, I. Skorvanek, *J. Electron. Mater.* **46**, 6518 (2017).
- [60] S. Fujieda, A. Fujita, K. Fukamichi, *J. Magn. Magn. Mater.* **310**, e1004 (2007).
- [61] S. Jun, Q.-Y. Dong, Y.-X. Li, J.-R. Sun, *J. Alloys Compd.* **458**, 115 (2008).
- [62] P. Gębara, J. Kovac, *Mater. Des.* **129**, 111 (2017).
- [63] A.M. Aliev, A.G. Gamzatov, N.Z. Abdulkadirova, P. Gębara, *Int. J. Refrig.* **151**, 146 (2023).
- [64] P. Kumar, N.K. Singh, K.G. Suresh, A.K. Nigam, *Physica B* **403**, 1015 (2008).
- [65] M. Balli, D. Fruchart, D. Gignoux, M. Rosca, S. Miraglia, *J. Magn. Magn. Mater.* **313**, 43 (2007).
- [66] A. Thayer, I. Hlova, Y. Mudryk, X. Liu, V.K. Pecharsky, *J. Alloys Compd.* **920**, 165927 (2022).
- [67] J. Shen, Y.-X. Li, B. Gao, J.-R. Sun, B.-G. Shen, *J. Magn. Mag. Mater.* **310**, 2823 (2007).
- [68] P. Gębara, P. Pawlik, I. Škorvánek, J. Bednarcik, J. Marcin, Š. Michalik, J. Donges, J.J. Wysocki, B. Michalski, *J. Magn. Magn. Mater.* **372**, 201 (2014).
- [69] P. Gębara, J. Marcin, *Acta Phys. Pol. A* **133**, 648 (2018).
- [70] N.Z. Abdulkadirova, A.G. Gamzatov, K.I. Kamilov, A.T. Kadirbardeev, A.M. Aliev, Y.F. Popov, G.P. Vorob'ev, P. Gębara, *J. Alloys Compd.* **929**, 167348 (2022).
- [71] P. Gębara, J. Kovac, *J. Magn. Magn. Mater.* **454**, 298 (2018).
- [72] P. Gębara, M. Cesnek, J. Bednarcik, *Curr. Appl. Phys.* **19**, 188 (2019).
- [73] J.Y. Law, V. Franco, L.M. Moreno-Ramírez, A. Conde, D.Y. Karpenkov, I. Radulov, K.P. Skokov, O. Gutfleisch, *Nat. Commun.* **9**, 2680 (2018).
- [74] V.V. Sokolovskiy, M.A. Zagrebin, V.D. Buchelnikov, V.V. Marchenkov, *Phys. Met. Metallogr.* **124**, 1069 (2023).
- [75] J.Y. Law, L.M. Moreno-Ramirez, A. Diaz-Garcia, V. Franco, *J. Appl. Phys.* **133**, 040903 (2023).