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Multicalorics — new materials for energy and straintronics (Review)

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The terms „multicaloric effect" and „multicaloric" are relatively new concepts and combine the phenomena and materials associated with the coexistence of conventional caloric effects under the action of external forces of various nature (magnetic field, electric field, mechanical action). Nowadays, caloric materials remain in the focus of attention of researchers, and approaches based on the use of the multicaloric effect are considered as one of the ways to improve the efficiency of conventional solid-state cooling systems. Of particular interest from a fundamental point of view are the cross effects observed under the combined external stimulus, as well as the nature of the relationship between magnetic, electrical, thermophysical properties and structure under such actions.

In this review, the theoretical foundations of the multicaloric effect are considered and an attempt is made to systematize multicaloric materials. Applied aspects of multicalorics are considered separately, and various experimental approaches to the study of their properties are presented. The presented review will be of interest to a wide range of specialists involved in the study of materials with caloric effects (magnetocaloric, electrocaloric, mechanocaloric), as well as those who are searching for new functional materials.

Keywords: magnetocaloric effect, electrocaloric effect, elastocaloric effect, barocaloric effect, multicaloric effect, multiferroics, multicalorics, magnetoelectric composites.

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Contents

1. Introduction

At present one of the topical problems of the cooling technology is the development and study of new alternative systems with an increased energy efficiency and ecological safety. The growing ecological problems (carbon dioxide emission, global warming, destruction of the ozone layer etc.) require immediate solving and make topical the search for new materials — coolants for „green" energy.

In recent years there is a growing interest to the search and study of materials where various giant caloric effects (CE) are observed, due to the possibility of their practical use in alternative, energy-efficient and environmentally friendly cooling systems based on solid-state compounds [1,2] (Fig. 1). Magnetocaloric (MCE), electrocaloric (ECE), mechanocaloric (MechCE) (particular cases, barocaloric (BCE) and elastocaloric (ElCE)) effects are known; their origin is conditioned by changes of temperature (entropy) at a change in the values of the corresponding external magnetic, electric or elastic fields [3–5]. One of the modern areas, actively studied in recent years in the condensed matter physics, is the approach based on the use of paired CEs. The approach to study of materials–thermodynamic properties, based on observation of at least two of the known CEs, has a uniting

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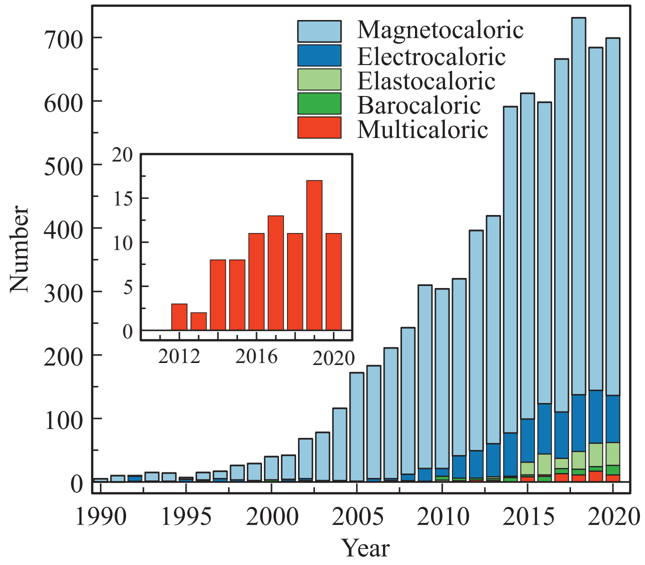

Figure 1. Number of publications, by keywords, „magnetocaloric“, „electrocaloric“, „barocaloric“, „elastocaloric“, „multicaloric“, obtained from search requests in the international Web of Science database.

term „*multicaloric*“ and is considered as a promising basis for improving the efficiency of energy systems based on single calorific effects [6–8].

The present review considers the modern aspects of multicaloric materials: from theoretical foundations to practical applications. Special attention is paid to their systemization, both according to the nature of external impacts and according to methods of making. We performed a detailed analysis both of natural multicaloric materials — single-phase systems demonstrating paired caloric effects under external forces of a different nature, and composites — artificially created systems consisting of a magnetic phase and a ferroelectric phase. Composite multicalorics of different cohesion degrees are considered and prospects of their application for specific practical tasks are described. The described approaches will help predicting and making new structures with high values of multicaloric effects for applications in energy-efficient technologies, straintronics and other promising technical fields.

2. Multicaloric effect: definition and thermodynamic relationships

The multicaloric effect (MultiCE) is a phenomenon which consisting in a reversible change of substance temperature (entropy) under the action of two or more external fields (magnetic, electric, mechanical stress) in adiabatic (isothermal) conditions (Fig. 2). Materials that demonstrate multicaloric effects are called *multicalorics*.

Among the first to discuss the possibility of multicaloric effect were A.M. Tishin and Yu.I Spichkin in whose monograph it was considered as a sum of the magnetocaloric and elastocaloric effects under simultaneous application of magnetic field and pressure [3]. Then an idea of giant caloric effects in the region of a first-order phase transition was put forth in 2010 by L. Mañosa and coauthors who found a giant barocaloric effect in the magnetocaloric Heusler alloy Ni$-$Mn$-$In [9]. This group later described the multicaloric effect thermodynamics and experimentally studied the multicaloric effect by the example of the intermetallic Fe$-$Rh alloy [10,11]. The term „multicaloric effect“ was used by M.M. Vopson when describing caloric effects in multiferroics [12], which was subsequently considered and studied in detail by Russian authors [13,14]. It is generally known that multiferroics include materials which demonstrate the coexistence of at least two of the known ferro-ordering kinds (magnetic, ferroelectric, mechanical) [15–17]. This gives grounds to consider multiferroics as potential candidates for observation of multicaloric effects. Theoretic and experimental papers of recent years show the feasibility of this idea and confirm the conjectures of possible observation of several CEs in multiferroics [13,14,18,19].

It is known that the main parameters which characterize caloric effects are the isothermal entropy change ΔS and adiabatic temperature change ΔT_{AD}, which can be represented by general formulas

$$\Delta S = \int_{0}^{Y_i} \left(\frac{\partial X_i}{\partial T}\right)_{Y_i} dY_i, \tag{1}$$

$$\Delta T_{AD} = -\int_{0}^{Y_i} \frac{T}{C_Y} \left(\frac{\partial X_i}{\partial T}\right)_{Y_i} dY_i, \tag{2}$$

where Y_i — the corresponding external field (E, $\mu_0 H$, σ or p), X_i — order parameter associated with the corresponding external impact (polarization P, magnetization M, linear or volume deformation ε), C_{Y_i} — heat capacity in the corresponding field Y_i.

Each subsystem (magnetic, electric and mechanical) is characterized by a certain kind of the caloric effect with the

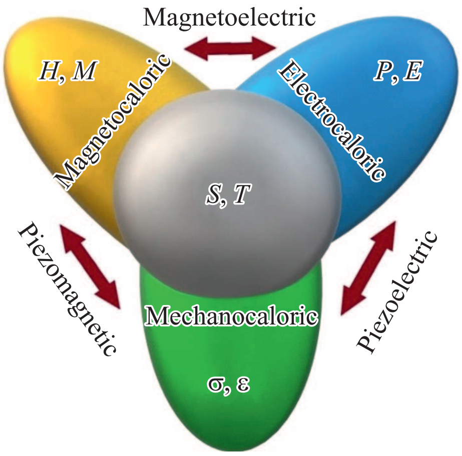

Figure 2. Schematic image of the multicaloric effect.

Interrelation of external field (Y_i) and order parameter (X_i) with caloric effect for each subsystem type

№	Subsystem	Y_i	X_i	Caloric effect
1	Magnetic	Magnetic field ($\mu_0 H$)	Magnetization (M)	Magnetocaloric effect (MCE)
2	Electric	Electric field (E)	Polarization (P)	Electrocaloric effect (ECE)
3	Mechanical	Mechanical action (σ or p) Isostatic compression Uniaxial compression	Deformation (ε)	Mechanocaloric effect (MechCE) Barocaloric (BCE) Elastocaloric (ElCE)

corresponding external field and order parameter (table). In this case caloric effects are single, while multicaloric effects are observed if two or more external fields are applied.

Let us consider the multicaloric effect in an isotropic system under the action of two external fields Y_1 and Y_2 based on the thermodynamic theory of caloric effects for multiferroics presented in [10]. The total entropy change caused by application of both external fields Y_1 and Y_2 in isothermal conditions can be written as follows:

$$\Delta S[T,(0,0)\to(Y_1,Y_2)] = \Delta S[T,(0,0)\to(Y_1,0)] + \Delta S[T,(Y_1,0)\to(Y_1,Y_2)], \quad (3)$$

where the first term of equality (3) is the isothermal entropy change for the caloric effect, associated with the order parameter X_1.

$$\Delta S[T,(0,0)\to(Y_1,0)] = \int\limits_0^{Y_1} \left(\frac{\partial X_1}{\partial T}\right)_{Y_1,Y_2=0} dY_1. \quad (4)$$

The second term of relationship (3) can be presented as

$$\Delta S[T,(Y_1,0)\to(Y_1,Y_2)] = \Delta S[T,(0,0)\to(0,Y_2)] + \int\limits_0^{Y_1} \frac{\partial}{\partial Y_1'}\left[\Delta S[T,(Y_1',0)\to(Y_1',Y_2)]\right] dY_1'$$

$$= \int\limits_0^{Y_2} \left(\frac{\partial X_2}{\partial T}\right)_{Y_2,Y_1=0} dY_2^2 + \int\limits_0^{Y_1} \frac{\partial}{\partial Y_1'}\left[\int\limits_0^{Y_2}\left(\frac{\partial X_2}{\partial T}\right)_{Y_1',Y_2=0} dY_2\right] dY_1'$$

$$= \int\limits_0^{Y_2} \left(\frac{\partial X_2}{\partial T}\right)_{Y_1,Y_2=0} dY_2^2 + \int\limits_0^{Y_1}\int\limits_0^{Y_2} \frac{\partial X_{12}}{\partial T} dY_1 dY_2. \quad (5)$$

Thus, equality (3) taking into account expression (5) can be presented as

$$\Delta S[T,(0,0)\to(Y_1,Y_2)] = \Delta S[T,(0,0)\to(Y_1,0)] + \Delta S[T,(0,0)\to(0,Y_2)] + \int\limits_0^{Y_1}\int\limits_0^{Y_2} \frac{\partial \chi_{12}}{\partial T} dY_1 dY_2. \quad (6)$$

As seen from expression (6), entropy change due to the action of two external fields Y_1 and Y_2 is not a sum of the contributions of order parameters X_1 and X_2 corresponding to these fields, depends on interaction between each of the subsystems and is determined by the third term of equation (6). The contribution associated with the interaction of these subsystems depends on quantity $\frac{\partial \chi_{12}}{\partial T}$, where χ_{12} is cross-susceptibility, which characterizes the degree of interrelation of order parameters. If Y_1 and Y_2 are a magnetic and an electric field, coefficient χ_{12} is called magnetoelectric (ME) susceptibility and characterizes the degree of electric polarization change under magnetic field application. It follows from expression (6) that the maximum contribution by the third term occurs when quantity $\frac{\partial \chi_{12}}{\partial T}$ takes on the maximum value. It means that the greatest contribution from cross effects will be observed in the region of phase transition temperature. It should be noted that, on the whole, expressions similar to those for isothermal entropy changes can be also easily obtained for the adiabatic temperature change. Thus, multiCE is not a sum of single caloric effects, but is associated with interaction between the magnetic, electrical subsystems and the material structure, which makes the corresponding contribution to the total effect.

At present there is generally accepted classification of multicalorics. We have tried to systematize multicaloric materials according to the bases, used for multiferroics, due to the affinity of these materials. Thus, materials where multicaloric effects can be observed are subdivided into

– „natural“ multicalorics — single-phase compounds the nature of whose caloric and multicaloric effects is associated with magnetic, electric ordering and their interrelation with the structure, as well as with ME interaction;

– „artificial“ multicalorics — composite structures of different cohesion type, in which caloric and multicaloric effects are a product of the properties of each component, as well as a result of their phase interaction.

Fig. 3. schematically shows the possible approaches for observation of multicaloric effects by the example of „natural“ and „artificial“ multicalorics. It can be seen that multicaloric effects can be observed using both the approach involving the direct application of external fields to a „natural“ multicaloric (Fig. 3, a) [20], and using the „composite“ method (Fig. 3, b) by the making of magnetoelectric composites for control of phase transition temperature and hysteresis of the composite's magnetic component, through mechanical action of the piezoelectric component by supplying electric voltage to it [21,22].

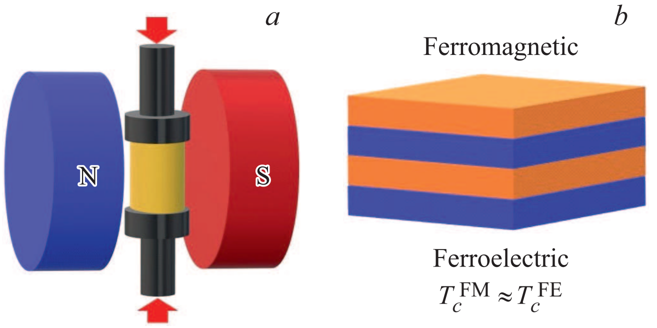

Figure 3. Schematic examples of experimental observation of the multicaloric effect in single-phase (*a*) and composite (*b*) multicalorics.

3. Multicaloric effects in natural multiferroics

3.1. Oxide ferroics

The main group of oxide ferroics pertains to multiferroics where caloric effects can be observed due to the coexistence of magnetic and electric ordering. Caloric effects in oxide ferroics have been poorly studied experimentally, while magnitudes of observed effects are low for possible practical applications. The experimental works in search for oxide ferroics with combined magnetocaloric and electrocaloric effects failed to achieve significant progress. Such compounds chiefly demonstrate a weak ME-effect, while caloric and multicaloric effect are observed mainly in the low temperature region, which complicates their practical application. Thus, for instance, magnetocaloric effect (~ 0.26 K in the magnetic field of 7 T at 5 K) and electrocaloric effect (~ 0.25 K in the electric field of 60 kV/cm at 180 K) were experimentally found in a polycrystalline sample based on lead ferroniobate $0.8Pb(Fe_{1/2}Nb_{1/2})O_3{-}0.2Pb(Mg_{1/2}W_{1/2})O_3$ [23].

MCE is the most well-studied one in multiferroics. Examples of papers dedicated to the study of MCE in multiferroics include the studies of orthorhombic frustrated systems of RMnO$_3$ ($R =$ Yb, Gd, Tb and Dy) and RMn$_2$O$_5$ [24], hexagonal manganites on the basis of YbMnO$_3$ [25], double perovskites La$_2$MnNiO$_6$ [26] and spinels MnCr$_2$O$_4$ [27]. However, these materials have a complex crystalline structure, hindering their synthesis and interpretation of experimental data. Their making is expensive, while the observed MCE maxima are localized at low temperatures, which prevents from considering such substances as materials used for solid-state cooling in the region of room temperatures.

The possible materials for CE implementation are multiferroics that combine spin-charge ordered structures, which may include the most well-studied compounds based on bismuth ferrite R_xBi$_{1-x}$FeO$_3$ (RBFO), obtained upon partial substitution of bismuth cations in BiFeO$_3$ (BFO) with isovalent cations of rare earth elements $R =$ La$-$Lu [19,28,29]. Such compounds crystallize into perovskite-like structures, are relatively simple to make, have a low electrical conductivity and high temperatures of magnetic and ferroelectric ordering. Direct measurements of CE in RBFO entails certain difficulties related both to high transition temperatures and to small absolute magnitudes of effects, experimental research capabilities for which are limited by sensitivity of measuring units in the high temperature region.

Another problem related to the obtaining of stable compounds is the complicated accounting of the impact of impurity iron-containing phases on the physical properties; the concentration and composition of such phases may vary even during measurements at high temperatures, often causing both enhancement and irreversible degradation of magnetic and dielectric properties. There is relatively little available information on estimation of CE in compounds synthesized on the basis of bismuth ferrite [19,30–32]. For instance, according to the results in [31], the maximum of magnetic entropy change in BiFeO$_3$ reaches the magnitude $\Delta S_{\max} = 8.4$ J/kg $\cdot$ K ($H = 8$ T) at $T = 18$ K, while the observed ECE in a solid solu-

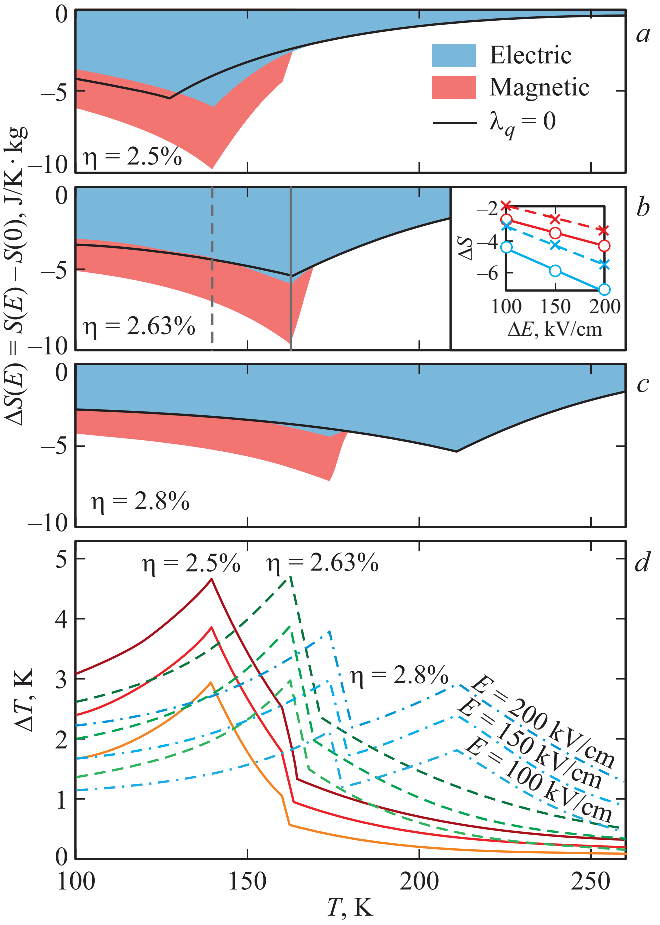

Figure 4. ECE in the electric field of 150 kV/cm at different volume change values (2.5, 2.63 and 2.8%) due to a change in the magnetic order parameter: temperature dependences of isothermal entropy change (*a*–*c*) and adiabatic temperature change (*d*). The blue and red colors show the electric and magnetic contributions to the total entropy respectively [33].

tion of $0.85(0.94Bi_{0.5}Na_{0.5}TiO_3-0.06BaTiO_3)-0.15BiFeO_3$ was $\Delta T_{\max} = -0.25\,K$ ($E = 60\,kV/cm$) in the region of $T = 400\,K$ [32]. It is seen that great changes of magnetic entropy in $BiFeO_3$ are observed at low temperatures, while the value of $\Delta S_{\max} = 1.9\,J/kg \cdot K$, obtained at 223 K, is considerably smaller than $\Delta S_{\max} = 9\,J/kg \cdot K$, achieved at 300 K in the conventional caloric materials. A giant enhancement of the calorific effect due to cross ME interactions in the $SrMnO_3$ multiferroic was predicted in [33]. A strong magnetoelectric coupling in the region of the phase transition temperature leads to cross caloric effects associated with the magnetic subsystem's contribution to ECE, which eventually increases the total caloric effect by approximately 60% (Fig. 4).

3.2. Fe−Rh alloys

Fe−Rh alloys are „natural" multicalorics and demonstrate significant values of caloric effects as compared to oxide ferroics. $Fe_{1-x}Rh_x$ (Fe−Rh) alloys with concentration x close to the equiatomic one have a $B2$ crystalline structure with a body-centered cubic lattice BCC (type CsCl) and demonstrate a metamagnetic transition from the low-temperature AFM-phase to the high-temperature FM-phase, under which the crystal lattice isotropically expands by $\Delta V/V \sim 1\%$ without changing its type [34]. The family of Fe−Rh alloys is the most convenient model object for studying the caloric and multicaloric effects, thanks to their simple crystalline structure, phase transition temperatures close to room temperatures and high values of the detected magnetocaloric [35,36], barocaloric [37] and elastocaloric effects [38]. Application of an external magnetic field shifts the magnetic phase transition towards low temperatures, while hydrostatic pressure exerts the reverse effect [11,37,39]. The authors of [38] studied a reverse elastocaloric effect for the $Fe_{49}Rh_{51}$ alloy by the direct method, and the adiabatic temperature change was $\Delta T = -5.17\,K$ under uniaxial tension with the mechanical load of 529 MPa. It should be noted than uniaxial tension exerts the same effect on the transition as the magnetic field, shifting the magnetic transition towards low temperatures. Thus, Fe−Rh alloys demonstrate the reverse magnetocaloric and elastocaloric, as well as the direct barocaloric effects. The multicaloric approach, based on a combination of magnetocaloric and barocaloric effects using an external magnetic field and hydrostatic pressure was experimentally applied in the papers of Prof. Manosa's team for the $Fe_{49}Rh_{51}$ alloy [11,37]. Paper [11] presents the experimental results of the studies of magnetic phase transition, caloric and multicaloric effects obtained via measurements of temperature dependences of magnetization under external magnetic field H and hydrostatic pressure p. Fig. 5 shows that a simultaneous action of magnetic field and pressure causes a competing effect — such behavior agrees with the scenario according to which H stabilizes the FM-phase with a high magnetization, while p stabilizes the AFM-phase with a small volume.

The experimental data on $M(T, H, p)$ using the thermodynamic relationships for the multicaloric effect was used to calculate the values for an isothermal entropy change under single and paired actions of magnetic field and hydrostatic pressure (Fig. 6).

A combination of the magnitudes of applied magnetic fields and hydrostatic compression has demonstrated the

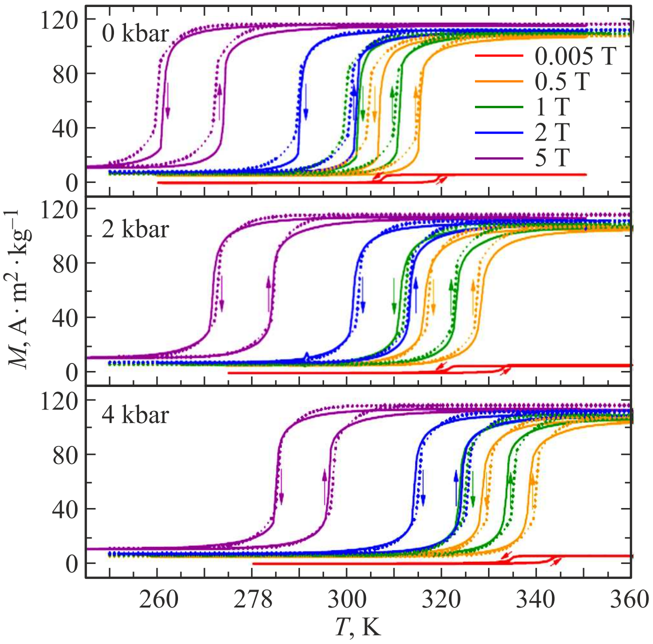

Figure 5. Temperature dependences of magnetization at different values of applied magnetic field and hydrostatic pressure for the $Fe_{49}Rh_{51}$ alloy [11].

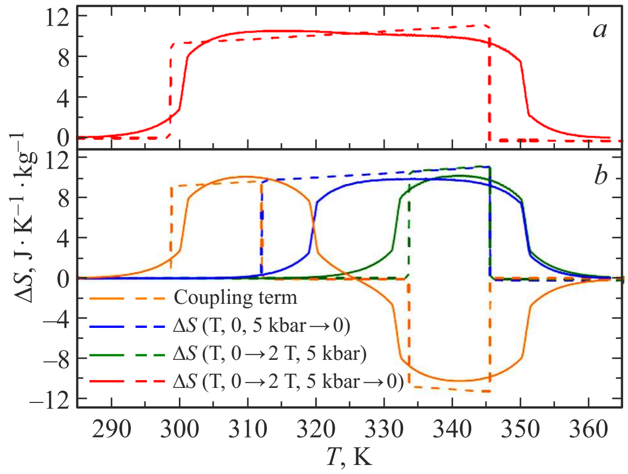

Figure 6. *a*) Temperature dependence of multicaloric entropy change for the $Fe_{49}Rh_{51}$ alloy corresponding to isothermal application of 2 T magnetic field and release of 5 kbar hydrostatic pressure. *b*) Temperature dependences of isothermal entropy change, corresponding to MCE (green), BCE (blue) and the resultant component of interaction between the magnetic subsystem and the structure (orange). The solid lines correspond to the experiment, the dashed ones — to the data obtained by numeric calculations based on the mean-field theory.

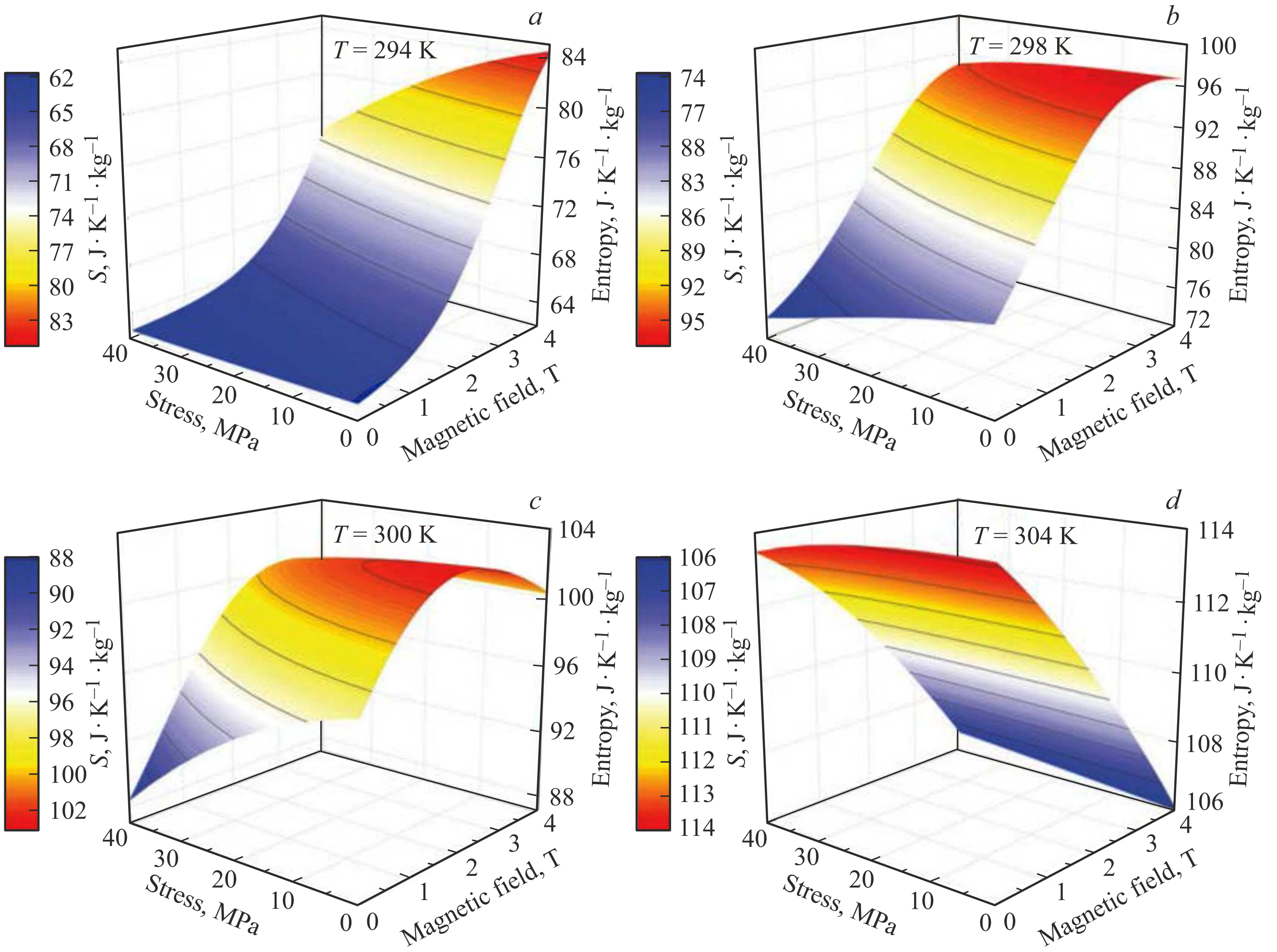

Figure 7. Isothermal entropy change as a function of magnetic field and mechanical load at different temperature values for the Ni–Mn–In alloy (*a–d*) [40].

possibility to control the transition temperatures and its width, as well as the possibility to change the sign ΔS from the direct to the reverse one.

3.3. Materials with structural phase transitions

The concept of using combinations of two or more external fields in natural multicalorics requires a search for materials with phase transitions sensitive to such actions. Such objects include materials with a magnetostructural first-order phase transition which demonstrate single magnetocaloric and mechanocaloric effects under application of external magnetic field and mechanical action respectively.

The most widespread class of such materials includes Heusler alloys (Ni–Mn–Ga, Ni–Mn–In), where the magnetocaloric and mechanocaloric effects are observed, a martensite phase transition at which results in a change of cell magnetization and cell [40–42].

An integrated research of the multicaloric effect in the Ni–Mn–In Heusler alloy was conducted using a specially developed calorimeter for determining the isothermal entropy and adiabatic temperature changes caused by a combined action of magnetic field and uniaxial compression. These results make it possible to conclude that a combined action of several external fields allows for observing caloric effects that exceeding the values in the case of single fields (Fig. 7). Other promising „natural“ multicalorics with I order phase transitions are alloys based on La–Fe–Si with a „giant“ MCE. Thus, for instance, an alloy of hydrogenated La–Fe–Si with „giant“ values of BCE and MCE was suggested for the multicaloric cooling concept [43]. The multicaloric approach can be also implemented using ferroelectric materials with a „giant“ ECE in the region of a structural phase transition. The calorimetry methods were used to study a conventional electrocaloric material — barium titanate $BaTiO_3$ under the hydrostatic pressure action [44]. A reverse BCE, the magnitude of which is comparable to the ECE values observed in this material, was found in the region of structural phase transitions at ~ 400 K (cubic–tetragonal) and ~ 280 K (tetragonal–orthorhombic). Sign difference occur due to a decrease of unit cell volume when heated through the transitions, while magnitude differences occur due to a large volumetric thermal expansion from both transition sides. ECE enhancement was found in a ferroelectric crystal of $\mathrm{Pb(Mn_{1/3}Nb_{2/3})O_3{-}32PbTiO_3}$ under uniaxial compression. It was found that enhancement of ECE $\Delta T_{\mathrm{ECE}} = 0.62\,\mathrm{K}$ can be achieved under uniaxial compression by 28 MPa, while single ECE at no load was approximately $\Delta T_{\mathrm{ECE}} = 0.27\,\mathrm{K}$ [45].

The main requirements for search of promising „natural" multicalorics are high values of caloric effects in the region of room temperatures. If a magnetic field and mechanical stress are used as an external action on the system, the required parameters differ from those for conventional magnetocaloric materials. Nevertheless, the basic requirements remain the same:

– a first-order phase transition in the region of room temperatures with an abrupt change of magnetization in a narrow temperature range;

– a high sensitivity of transition temperature to magnetic field for control of hysteresis effects.

The additional important requirements from the viewpoint of practical applications include good thermal conductivity, a simple process cycle of making and availability of initial elements. However, an important critical parameter in the case of multicalorics using a combined action of magnetic field and mechanical stress is the hysteresis width of the magnetic phase transitions. As distinct from the conventional magnetocaloric approach, hysteresis width shall be such that after magnetic field withdrawal the sample remains inside the hysteresis region for subsequent mechanical action. Then phase transition temperature is controlled by application (withdrawal) of mechanical load, consequently, the parameter dT/dp, which characterizes system sensitivity to mechanical actions shall be sufficiently large. The technical parameter in this case is stability of material properties under cyclic external actions. Mechanical microdefects caused by a multiple impact both of pressure and in case of lattice volume change due to a phase transition, eventually lead to a deterioration of the mechanical properties and degradation of caloric effects, which must be taken into account when searching for new multicaloric materials. One of the main disadvantages of the multicaloric approach using mechanical pressure is heat losses leading to a disruption of the system adiabaticity conditions. Since mechanical pressure, as distinct from magnetic field, cannot be applied to a sample without a contact, thermal conductivity of the contact material, through which pressure is applied, must be low.

4. Multicaloric effects in composite multiferroics

Composite multicalorics are artificial ME-compounds consisting of the corresponding magnetic and ferroelectric components. Since multicalorics can be classified as multiferroics, they can be described using the classification applied for ME-composites depending on cohesion type of their components [46]. It is known that the nature of magnetoelectric interaction in composite multiferroics is associated with interaction between the magnetic and ferroelectric components, while the ME-effect is absent in a separate component, which must be considered when dealing with caloric and multicaloric effects in ferroics of different nature. The possibilities to use composite technologies to design materials with multicaloric effects were discussed in [47], where the ME-interaction was considered as a way to control the caloric effects and enhance the total caloric effect. Based on the analysis of the available literature on this topic, two basic methodological approaches to design of promising materials with multicaloric effects can be distinguished:

– multicalorics with paired caloric effects;

– multicalorics with pronounced ME-interaction.

Multicalorics with paired caloric effects can include composites consisting of components having high values of caloric effects in each component of the studied object. To implement this approach, the components must be chosen so that their phase transition temperatures are close to each other. Thus, for instance, when considering a multicaloric composite consisting of magnetic and ferroelectric phases, the initial components must be materials with high MCE and ECE values with close temperatures of magnetic and ferroelectric phase transitions, in the region of which the maxima of caloric effects are observed. Unfortunately, this approach is not widely used in experimental studied of multiCE due to the difficulties related to experimental setup under simultaneous application of external fields, as well as the problem of search for composite components having close temperatures of magnetic and ferroelectric phase transitions. Thereat, the ratio of the magnetic and ferroelectric components of the composite, as well as the change rate of applied magnetic and electric field shall be selected with account of thermophysical properties (heat capacity, thermal conductivity) of each component for eventual observation of the synergistic effect. In this case, a contribution from ME-interaction is not considered as the main mechanism for enhancement of the total caloric effect, while the use of two or more external fields is considered as a way to increase energy efficiency and reduce expenses. A variant of this principle can be the use of the multicaloric approach as a way to optimize the „classical" technology of magnetocaloric cooling, by increasing the value of adiabatic temperature change by a unit of magnetic field intensity due to the contribution from ECE. An increase of magnetic component concentration leads to an increase of composite conductivity and leak currents, which may eventually cause a breakdown during ECE measurements. Paper [48] deals with the making and study of a multicaloric composite obtained by pressing and subsequent sintering of a mixture of magnetocaloric material powders — manganite $\mathrm{La_{0.85}Ag_{0.15}MnO_3}$ and a solid 0.67PNN−0.33PT solution having similar temperatures of magnetic and ferroelectric phase transitions. It was found that the ferroelectric 0.67PNN−0.33PT phase affects the magnetocaloric properties of manganite $\mathrm{La_{0.85}Ag_{0.15}MnO_3}$ as a result of mechanical pressure generated by the composite's ferroelectric component during a phase transition. Mixed multicaloric composites made by sintering of magnetic and ferroelectric powders with high values of caloric effects were studied in [14,49,50]. The mentioned papers studied single caloric (MCE and ECE), as well as the phases — mutual action on the corresponding kind of the caloric effect. As noted above, due to the experiment complexity and possible sample breakdown, measurements with simultaneous application of magnetic and electric fields were not carried out.

The second methodological approach to the making of composite multicalorics includes materials with high values of the direct or reverse ME-effects. An external field in this case is a mechanical action induced by an applied magnetic or electric field. Thus, for instance, for a ME-composite the magnetic component, when the magnetic field is activated, mechanically acts (as a result of due to magnetostriction) on the ferroelectric component and reduces polarization in it (the direct piezoelectric effect), which in its turn affects the electrocaloric properties of the composite's ferroelectric component. When an electric field is activated, the mechanical stress, induced in the ferroelectric component, due to the reverse piezoelectric effect leads to a change in the magnetization of the composite's magnetic component (the Villari effect). This eventually leads to a change in magnetic entropy ΔS_{magn}, one of the material's magnetocaloric parameters associated with magnetization of a magnetic material. The above-mentioned phenomena pertain to the direct and reverse ME-effects, are typical for composite multiferroics and have broad prospects for practical applications. Evidently, the final external action in the described cases is a mechanical action, as in the case of „natural" multicalorics. The difference is that the mechanical impact in case of composite multicalorics is indirect and is induced due to magnetostriction or a piezoelectric effect.

A review of papers on the study of caloric effects in composite multiferroics shows that the most popular sample types for design of new multicalorics with pronounced ME-effects are layered composites [46,51]. Both „thick" layered composites, obtained by gluing together of components of magnetocaloric and piezoelectric materials, and those obtained by deposition of magnetocaloric films onto piezoelectric substrates by means different techniques are used for these purposes. Papers [52–54] describe the studies of magnetic, magnetocaloric and magnetoelectric properties of two (three) layer multicaloric composites made by gluing together plates of magnetocaloric and piezoelectric material in different modes of electric field application.

The possibility to control MCE and temperature of magnetic transition through an electric field, applied to a piezoelectric composite layer was experimentally demonstrated in the paper using direct measurements of adiabatic temperature change [53].

The possibility to control magnetic properties of a magnetocaloric material, via a mechanical stress induced to an inverse piezoeffect by the example of „thick" two-layer Fe−Rh/PZT and three-layer PZT/Fe−Rh/PZT ME-components, made by gluing together, with comparable values of layer thickness was demonstrated in [52]. Thus, for instance, the application of a constant electric voltage to the PZT layer leads to a decrease of the temperature hysteresis width to 3 K in the two-layer Fe−Rh/PZT composite under application of the 25 V electric voltage and to 4 K in case of the three-layer PZT/Fe−Rh/PZT composite at 50 V. The authors explain the observed shift by a mechanical action of PZT piezoactive layers, which induces a deformation of the magnetocaloric Fe−Rh layer, leading to a change of its magnetic properties.

Another paper [54], where similar experiments were conducted on two- (three-) layer composites (Fe−Rh/PZT and PZT/Fe−Rh/PZT), demonstrated that the application of an electric with the magnitude of 8 kV/cm to a piezoelectric layer causes a relative degrease of magnetization of the Fe−Rh magnetic layer by 3.6% for two-layer composites (Fe−Rh/PZT) and by 5.4% for three-layer composites (PZT/Fe−Rh/PZT). The relative change of magnetization was estimated for the magnetization isotherms taken at 320 K — in the region of the temperature of a metamagnetic phase transition of the Fe−Rh layer, magnetic field value being 0.5 T. The calculations performed using the COMSOL Multiphysics software package using model parameters similar to the experiment have shown a nonuniform distribution of magnetization and mechanical stress across the magnetic layer volume in the mode of activated magnetic and electric field, while a comparison of the results of modeling on two- and three-layer composite layers has shown a more uniform distribution of mechanical stresses in case of a three-layer composite.

One of the main problems in studying multicaloric effects in glued together ME-composites is the loss of mechanical stresses on the interface. In case of „thick" composites with comparable values of layer thicknesses, a mechanical action induced by the piezoeffect is insufficient for controlling the magnetic transition temperature and hysteresis effects in the magnetocaloric layer. The resultant kind of deformation due to the applied magnetic and electric fields for a two-layer „thick" magnetoelectric composite is bending [55].

More encouraging, as compared to „thick" composites, results in control of the magnetic properties via an electric field were obtained for composites having small thicknesses of the magnetocaloric layer (band, film) [21,56–59]. This approach was implemented on a ME-composite made by gluing together a band of magnetocaloric Ni−Co−Mn−In alloy 22 mkm thick onto an oriented piezoelectric substrate of PMN−PT crystal [57]. It was demonstrated that the magnetic hysteresis can be reduced by 96% [21] for a film ME-composite Fe−Rh/BaTiO$_3$ with the Fe−Rh magnetic layer thickness of 50 nm by combining a magnetic field and a mechanical action (by supplying electric voltage to the piezoelectric BaTiO$_3$ substrate).

5. Applied aspects of multicaloric materials

The main applied aspect of materials with high values of caloric effects is the possibility of their use to create

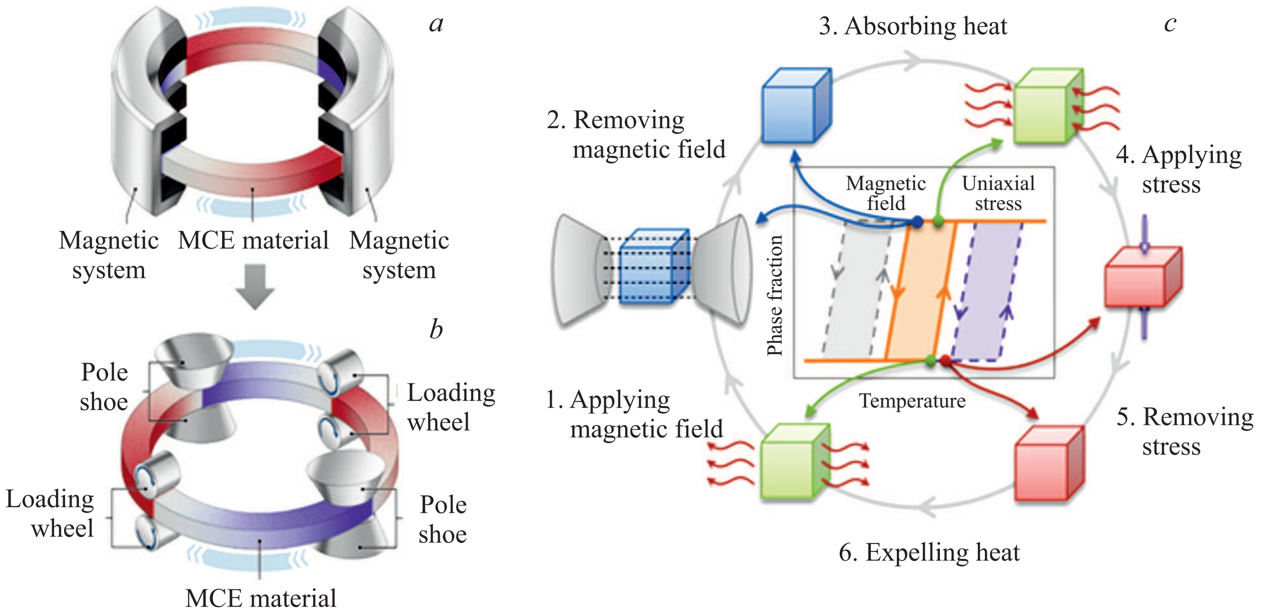

Figure 8. *a*) layout of an active magnetic regenerator for the conventional magnetic cooling system, *b*) layout of a multicaloric regenerator with the possibility of combined application of a magnetic field and a mechanical load, *c*) schematic image of a multicaloric cooling cycle with controlled temperature hysteresis.

alternative cooling systems and, therefore, the basic practical goa of multiCE study is research into the possibilities of its application to improve efficiency of the classical solid-state cooling concepts based on single caloric effects. However, the interesting effects and phenomena observed in multicalorics allow for extending their practical potential from sensorics to biomedicine.

The authors of [12] were among the first to consider a concept of multicaloric cooling, interest to which later became topical as an alternative approach for efficiency improvement of solid-state cooling systems. The current trends in experimental studies of multicaloric effects are as follows:

– search, making and study of new multicaloric materials, including composites consisting of components with initial high values of caloric effects, magnetostriction and piezoelectric parameters in the region of room temperatures;

– development and improvement of experimental procedures for simultaneous application of constant and cyclic external fields (magnetic, electric and mechanical) in „natural“ multicalorics.

As regards the development and improvement of experimental procedures for the study of multicaloric materials, different solutions have been suggested for measuring MCE under the action of isotropic or uniaxial compression [40,60,61].

A multicaloric cooling cycle based on a combination of applied magnetic field and mechanical load was suggested in [20] (Fig. 8). The used approach minimizes the temperature hysteresis and MCE degradation, which eventually makes it possible to increase magnetic regenerator efficiency. Paper [60] suggested an experimental setup for measuring the adiabatic temperature change under a simultaneous action of a pulsed magnetic field up to 10 T and uniaxial compression up to 80 MPa (Fig. 9, *a*–*b*). The possibility to control both the magnitude of adiabatic temperature change ΔT_{AD}, and hysteresis width by combining magnitudes of applied magnetic field and mechanical load has been demonstrated by the example of the Ni–Mn–Ti–Co Heusler alloy (Fig. 9, *c*–*d*). Caloric and multicaloric effects were measured by the direct method, while the use of a pulsed magnet field will allow for approximating.

An original test system for studying multicaloric effects under a magnetic field and mechanical action was suggested in [61]. The setup design allows for studying a change of multicaloric material temperature under a simultaneous or successive action of magnetic field up to 1 T and uniaxial (isotropic) compression up to 500 MPa.

The system for multicaloric material testing consisting of the following parts: a permanent magnet of linear movement, a load-carrying framework, an insert for pressure generation *1*, a thermally insulated chamber *2* and a control and data acquisition system (Fig. 10, *a*–*b*). A magnetic field was generated by a cylindrical permanent Halbach magnet *6*, with gap flux density of 1 T. The magnet was moved linearly along the cylinder axis by means of pneumatic drive that allow for sample entry (exit) to the magnetic field maximum (minimum) within less than 0.1 s. Mechanical stress was generated using a uniaxial servohydraulic mechanical testing machine, which makes it possible to simulate the sample both statically and cyclically with different load profile shapes. A special pressure insert was made for triaxial compression experiments (Fig. 10, *c*). The suggested test was used (with direct measurement of

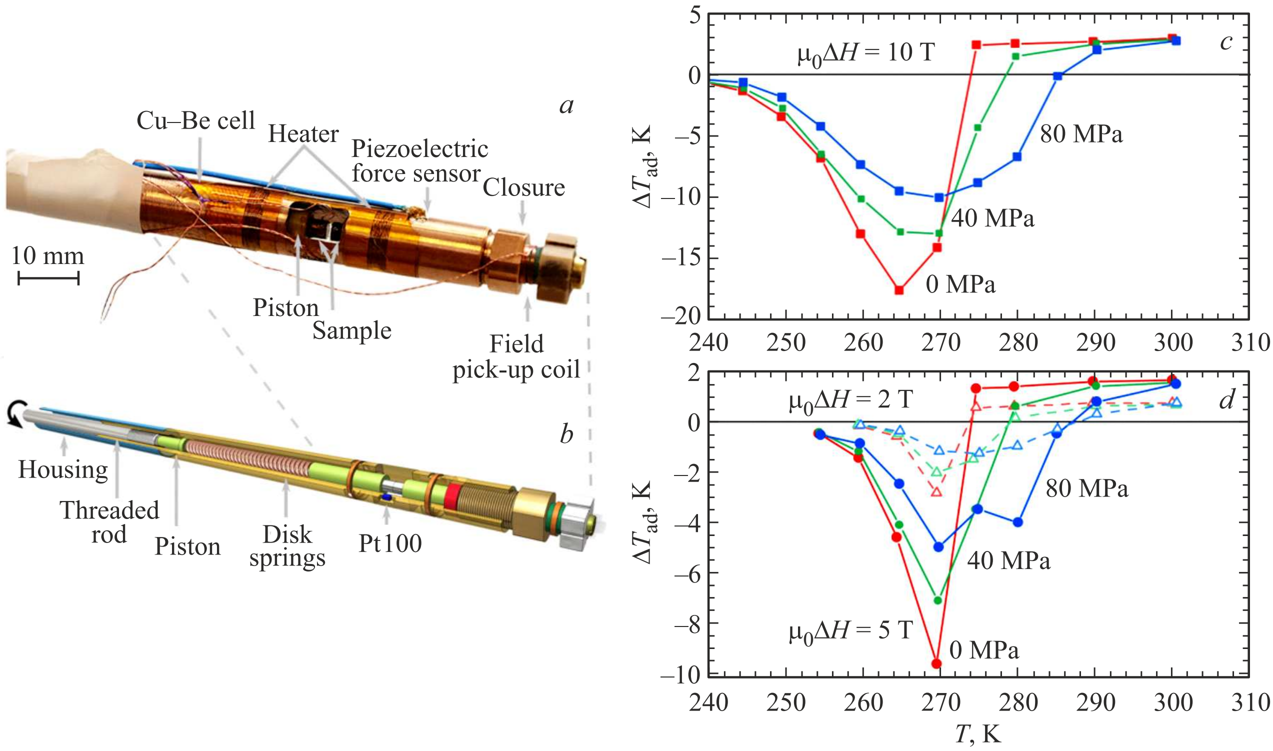

Figure 9. Real (a) and digital (b) image of a measuring insert for multicaloric studied in pulsed magnetic fields under uniaxial compression. Temperature dependences of adiabatic temperature change ΔT_{AD} in magnetic fields of 10 (a), 2 and 5 (b) T under uniaxial compression [60].

the magnetocaloric, barocaloric and multicaloric effects by the example of the Ni−Mn−In Heusler alloy) to show that a multi-action, which combines different external fields, helps achieve the specified result with a 75% decrease of the used magnetic field as compared to a single MCE and a 30% decrease of mechanical stress as compared to a single MechCE. The demonstrated approach can be used for upgrade of the prototypes of MCE-based solid-state cooling systems, to achieve the required values of cooling efficiency, but at a smaller magnetic field value. This will make the solid-state cooler cheaper due to a smaller weight, and , consequently, a decreased cost of the permanent NdFeB magnet.

An original concept based on a compact low-induction magnetic system for solid-state cooling systems was suggested in [62]. The studied material was a composite consisting of terfenol $\mathrm{Tb}_x\mathrm{Dy}_{1-x}\mathrm{Fe}_2$ ($x \sim 0.3$, Terfenol-D), material with a giant magnetostriction (up to 4000 ppm) capable of generating forces up to 4000 N and a shape memory alloy with high ElCE values ($\Delta T_{AD} \sim 12.8$ K) [63]. The final effect in this case if ElCE, while mechanical load is magnetically-induced and generated by terfenol magnetostriction. High values of $\Delta T_{AD} \sim 4$ K were obtained using a low-power magnetic field source of 0.16 T, so that the given system can be considered for compact solid-state cooling systems (Fig. 11).

The reviews of studies of the applied aspects of multicaloric materials show that the most interesting and up-to-date results were obtained for magnetic materials with a I order phase transition sensitive not only to magnetic field but also to mechanical action. The possibility to control magnetic properties via mechanical interaction made it possible to consider multicalorics as promising objects for straintronics — a new area in physics and engineering which uses control of solid bodies-properties by a controlled elastic deformation as a promising area for electronics and biomedicine [64,65].

The Fe−Rh alloy is the most appropriate one for these purposes in terms of transition temperature and magnetic transition parameters. Despite the observed record-breaking values of caloric effects, the family of these alloys it unsuitable for applications in the area of solid-state cooling due to expensiveness. Nevertheless, they can be applied in magnetic memory, magnetoelectronics, spintronics and magnionics, where large alloy volumes are not required, while geometry of thin films is quite compatible with the planar technology requirements [64,66,67]. Below is a review of some applications based on the unique magnetic properties of the multicaloric Fe−Rh material. It should be emphasized that the applications mentioned below do not use caloric and multicaloric effects, but are based on the peculiarities of their magnetic properties (a sharp AFM−FM-transition, narrow hysteresis, transition temperature in the region of room temperatures etc.).

A concept of an antiferromagnetic memristor based on the Fe−Rh/MgO film is presented in [68]. The Fe−Rh/MgO film an AFM−FM-transition in the region of 400 K and,

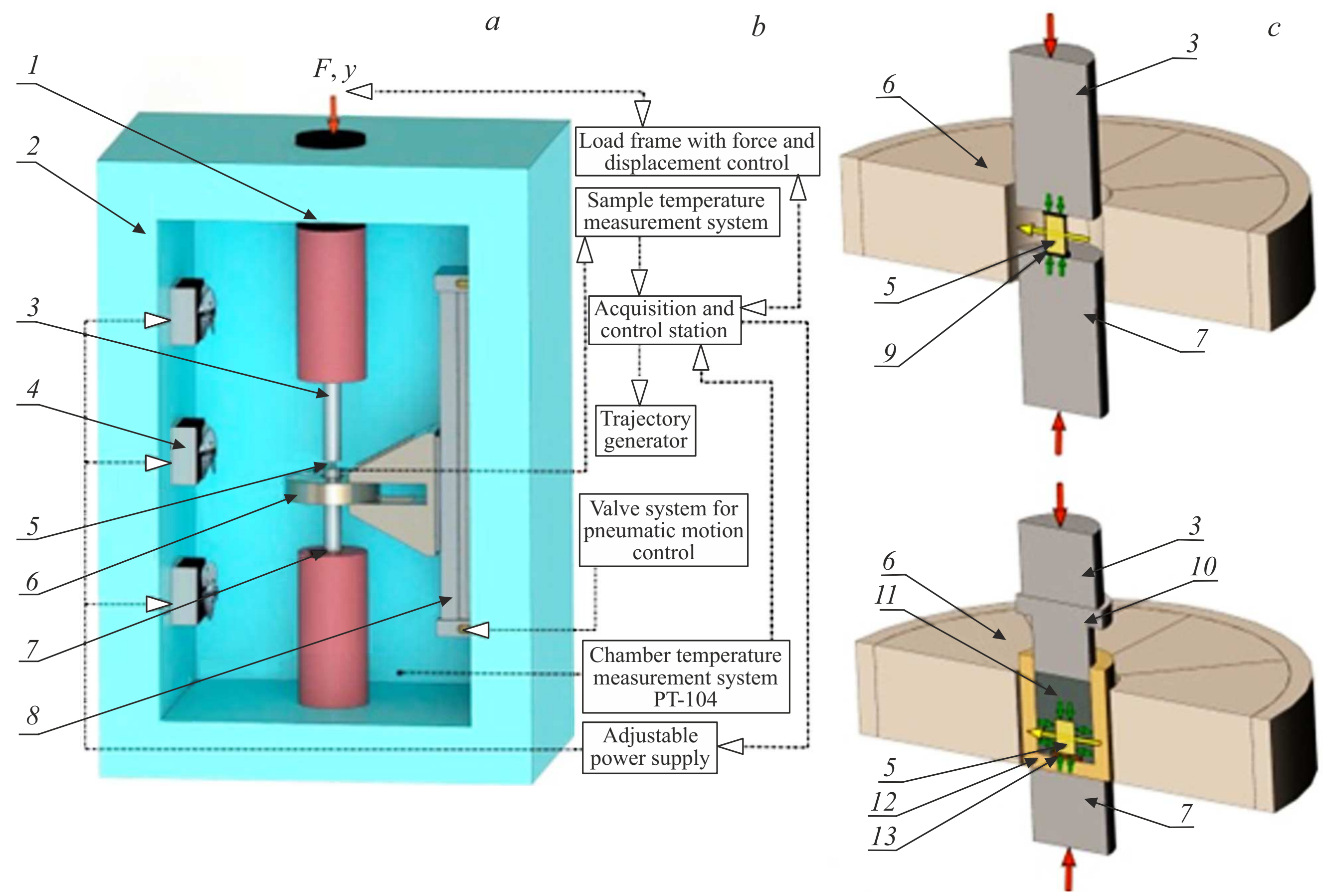

Figure 10. Model (*a*) and functional diagram (*b*) of a test setup for studying the multicaloric effect and the configuration of a loading system for uniaxial and triaxial mechanical stimulation (*c*): *1* — loading system, *2* — thermally insulated chamber, *3* — upper pin, *4* — chamber temperature stabilization system, *5* — sample, *6* — permanent Halbach magnet, *7* — lower movable shift, *8* — pneumatic system for linear movement of the Halbach magnet, *9* — sliding plates, *10* — piston pressure cell, *11* — medium for isotropic pressure propagation, *12* — pressure cell, *13* — plate made of composite epoxy material. The red lines correspond to an external mechanical load, the yellow ones — to a magnetic field, the green ones — to forces acting on the sample [61].

consequently, allows for setting different collective directions for Fe moments using the applied magnetic field. After cooling to the room temperature, an AFM-order is established with a moment direction predetermined by the applied magnetic field in the high-temperature FM-state (Fig. 12, *a*). An AFM-equivalent of anisotropic magnetoresistance is used for electrical sensing.

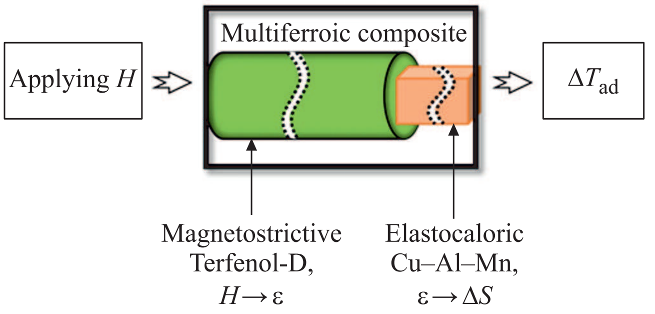

Figure 11. Layout of a compact device for multicaloric cooling based on the elastocaloric effect arising in the Cu–Al–Mn alloy due to mechanical interaction of the Terfenol-D magnetic material with giant magnetostriction as a result of magnetic field application [62].

A two-layer YIG/Fe–Rh structure (Fig. 12, *b*–*d*), consisting of a layer of yttrium-iron garnet (YIG) and Fe–Rh alloy as a functional element in planar magnon networks, performing spatial-frequency demultiplexing and the spin-wave mode filtration mode was suggested in [69,70]. This structure was demonstrated to be capable of controlling the propagation of spin-wave modes due to a sharp change in Fe–Rh magnetization in the region of the temperature of a magnetic phase transition close to room temperature. The same group of authors also demonstrated the possibility to control spin-wave transport via a inverse piezoeffect applied for control of multicalorics–magnetic properties [71]. Moreover, a spin-wave signal can be controlled by a slight change of temperature in the Fe–Rh plate caused by laser radiation.

Paper [72] suggested an element with an effect of tunnel anisotropic magnetoresistance based on the

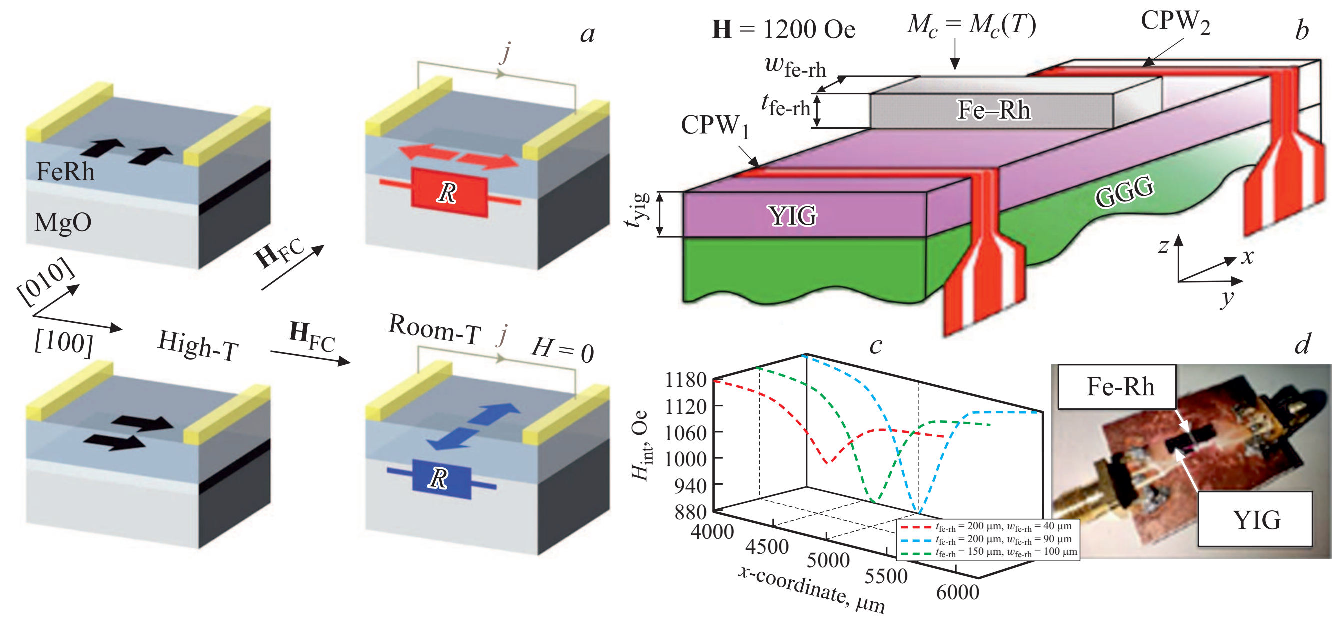

Figure 12. Schematic image of the operating principle of an antiferromagnetic memristor based on Fe−Rh/MgO films (*a*) [70]. Schematic image of YIG/Fe−Rh-structure of excitation and detection of controlled spin-wave transport (*b*). Profiles of the internal magnetic field $H_{\text{int}}(x)$ for different cases of geometric parameters of the $Fe_{48}Rh_{52}$ alloy (t_{ferh} and w_{ferh}) (*c*) and photo of the experimental YIG/Fe−Rh sample (*d*) [69].

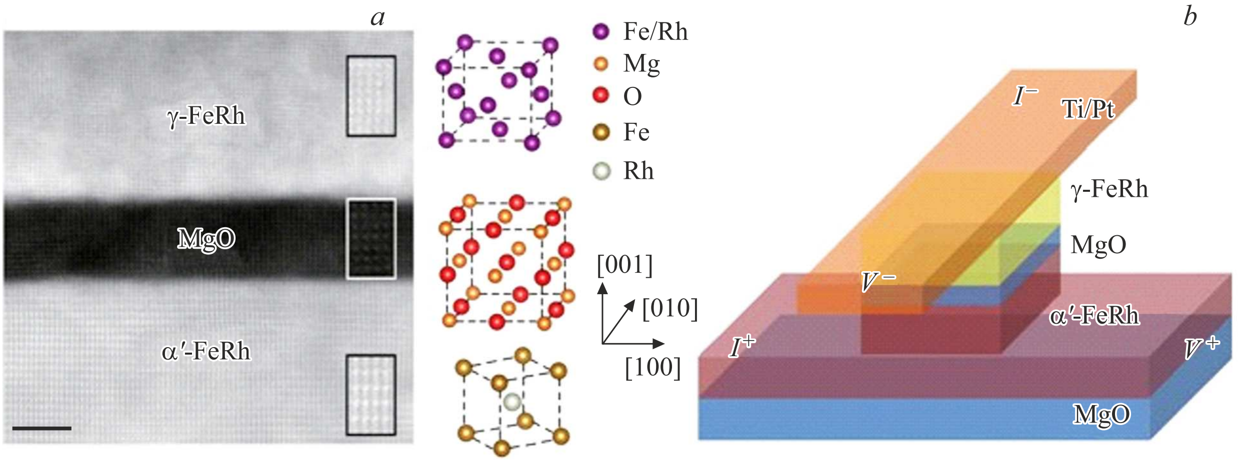

Figure 13. Microstructure and geometry of measurements of the α'-FeRh/MgO/γ-FeRh heterostructure. (*a*) Transverse TEM-image of the α'-FeRh/MgO/γ-FeRh heterostructure and layout of the crystal lattice of α'-FeRh, MgO and γ-FeRh. The scale length is 2 nm. (*b*) Layout of the sample and geometry of four-contact measurements [72].

α'-FeRh(30 nm)/MgO(2.7 nm)/γ-FeRh(10 nm) heterostructure deposited on a MgO(001) substrate (Fig. 13, *a*–*b*). The obtained value of tunnel magnetoresistance in this structure reaches 20% at room temperature.

As has been shown above, the prospects of practical application of multicaloric materials are associated with energy-efficient technologies for solid-state cooling and solutions for micro (nano) electronics. However, the unique properties of such materials are also considered as promising objects for biomedical applications.

Relatively recently, multicaloric materials were suggested [73,74] for biomedical purposes to solve various tasks — from „conventional" magnetic hyperthermia before release of medicines. The main idea of the suggested concept consists in the use of heat emitted or absorbed as a result of caloric effects to control the properties of promising thermally-sensitive polymers for biomedicine. An analysis of the available literature on biomedical applications of caloric and multicaloric materials has shown that the best magnetic materials for these purposes are those with I order phase transitions, classified as „natural" multicalorics. Thus, for instance, the authors of [75] suggested a medicine release method by way of MCE by making a composite of a thermally-sensitive polymer

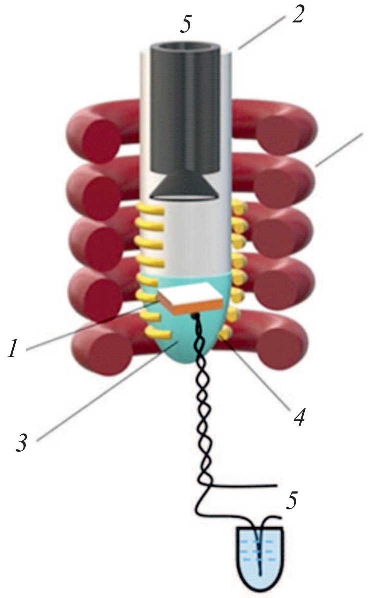

Figure 14. Layout of a setup for *in situ* studies of thermally-sensitive composites in a magnetic field (*1* — sample, *2* — thermally insulated tube, *3* — water, *4* — heater, *5* — thermocouple, *5* — video camera, *6* — magnetic field source [76].

and a material with a giant reverse magnetocaloric effect. The suggested thermally-sensitive polymer was poly-N-isopropylacrylamide (PNIPAM), which at a temperature close to the human body temperature (above 32°C) goes over from a swollen hydrated state to a „shrunken“state, displacing about 90 percent of the contained liquid, which potentially allows for its use for targeted transport of drugs and their controlled release.

When the magnetic field is activated, the composite cools down due to the reverse MCE and the thermally-sensitive polymer goes over to a swollen (gel-like) state in which the loaded medicine is released from the polymer. This effect is achieved by selecting types of magnetocaloric material and polymer, while magnitude of the anticipated useful effect (medicine release) is controlled by the amplitude of the applied magnetic field. The suggested method is based on application of a low-frequency high-amplitude magnetic field, is one of the promising non-invasive methods for action on the medicine carrier and is safer as compared to the method when a high-frequency alternating magnetic field is applied. Operability of this idea in the *in situ* mode was demonstrated in a magnetic field up to 8 T by the example of a smart composite consisting of thermally-sensitive PNIPAM polymer and the conventional magnetocaloric material Gd [76].

A special insert was assembled for this purpose, which allows for real-time observation of the control of the thermally-sensitive polymer composite's properties via a magnetic field. It should be noted than other caloric effects can also be used to control the properties — ECe, MechCE by choosing a material with a corresponding effect magnitude and transition temperature as a second component, but the advantage of MCE is that a magnetic field allows for non-contact control of the polymer properties, while the required temperature change is achieved by using commercial medical magnetic resonance imaging units.

Materials with a giant MCE in the region of physiological temperatures chiefly pertain to multicalorics with first-order phase transitions (Fe−Rh, Ni−Mn−In, La−Fe−Si) and demonstrate an abrupt direct or reverse magnetic structural transition. This property can be used for automatically controlled hyperthermia when high-frequency heating is stopped (that is, the effect is switched off) above a certain temperature (e.g., 40°C) due to material's transition to a paramagnetic state. The function of activation can be implemented similarly due to a reverse magnetic structural transition.

The possibility to use multicaloric materials for MRI diagnostics was demonstrated in [77,78]. Paper [77] for the first time suggested using the Fe−Rh alloy as a promising contrast agent for MRI with a function of „automatic switch-off“ due to an abrupt magnetic transition from the antiferromagnetic state to the ferromagnetic one in the range of physiological temperatures. The mechanism of „automatic activation“ for MRI applications was demonstrated by the example of a multicaloric La−Fe−Si alloy in powder form with a direct magnetic transition. Transition temperature in both cases (temperature of effect „on/off“) is regulated by an external magnetic field.

The most promising ones from among the known multicaloric materials for biomedical applications are Fe−Rh alloy-based compounds. This assumption is based on the following facts:

– a record-breaking value of the magnetocaloric effect (up to −4−6 K/T) in magnetic fields which are already used in medical practice (e.g., a magnetic resonance imaging unit);

– phase transition temperature is in the region of physiological temperatures (30−40°C);

– temperature and parameters can be controlled by heat treatment, chemically, by pressure, magnetic field; transition sensitivity is approximately — 8−9 K/T;

– lower toxicity [79].

The advantage of using multicaloric materials with a pronounced MCE is the possibility to implement activation of the effect of non-invasive medicine release, while implementation of the approach using ECE, ElCE or BCE can be only invasive, which requires electrical wires or a direct mechanical contact.

6. Conclusion

A review of the fundamental and applied aspects of multicaloric allows for making a conclusion on a great potential of these materials. Materials initially considered as objects for solid-state cooling, thanks due their unique properties, are applied in different regions — from straintronics to biomedicine. The most well-studied multicalorics at present are magnetic materials with a 1 order phase transition.

The contemporary aspects in the development of this area include both the search for promising multicaloric materials and the development of new experimental methods for their study.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] A. Kitanovski, J. Tušek, U. Tomc, U. Plaznik, M. Ožbolt, A. Poredoš. Magnetocaloric energy conversion — From theory to applications (2015). https://www.springer.com/gp/book/9783319087405.

[2] T. Gottschall, K.P. Skokov, M. Fries, A. Taubel, I. Radulov, F. Scheibel, D. Benke, S. Riegg, O. Gutfleisch. Adv. Energy Mater. **9**, 1970130 (2019). DOI: 10.1002/aenm.201970130.

[3] A.M. Tishin, Y.I. Spichkin. The magnetocaloric effect and its applications. CRC Press, Taylor andd Francis Group (2016). DOI: 10.1887/0750309229.

[4] A. Greco, C. Masselli. Magnetochemistry **6**, (2020). DOI: 10.3390/magnetochemistry6040067.

[5] C. Cazorla. Appl. Phys. Rev. **6**, 041316 (2019). DOI: 10.1063/1.5113620.

[6] E. Stern-Taulats, T. Castán, L. Mañosa, A. Planes, N.D. Mathur, X. Moya. MRS Bull. **43**, 295 (2018). DOI: 10.1557/mrs.2018.72.

[7] A.A. Amirov. Chelyabinsk Phys. Math. J. **6**, 78 (2021). DOI: 10.47475/2500-0101-2021-1610 6.

[8] M.M. Vopson. Phys. B: Condens. Matter. **513**, 103 (2017). DOI: 10.1016/j.physb.2017.02.034.

[9] L. Mañosa, D. González-Alonso, A. Planes, E. Bonnot, M. Barrio, J.-L. Tamarit, S. Aksoy, M. Acet. Nature Mater. **9**, 478 (2010). DOI: 10.1038/nmat2731.

[10] A. Planes, T. Castán, A. Saxena. Phil. Mag. **94**, 1893 (2014). DOI: 10.1080/14786435.2014.899438.

[11] E. Stern-Taulats, T. Castán, A. Planes, L.H. Lewis, R. Barua, S. Pramanick, S. Majumdar, L. Mañosa. Phys. Rev. B. **95**, 104424 (2017). DOI: 10.1103/PhysRevB.95.104424.

[12] M.M. Vopson. Solid State Commun. **152**, 2067 (2012). DOI: 10.1016/j.ssc.2012.08.016

[13] A.S. Starkov, I.A. Starkov. ZhETF **146**, 297 (2015) (in Russian). DOI: 10.7868/s0044451014080082.

[14] I.N. Flyorov, E.A. Mikhalyova, M.V. Gorev, A.V. Kartashev. FTT **53**, 421 (2015) (in Russian).

[15] A.P. Pyatakov, A.K. Zvezdin. Phys.-Usp. **55**, 557 (2012). DOI: 10.3367/ufne.0182.201206b.0593.

[16] A.K. Zvezdin, A.P. Pyatakov. Usp. Fiz. Nauk. **174**, 465 (2004). DOI: 10.3367/UFNr.0174.200404n.0465.

[17] N.A. Spaldin. MRS Bull. **42**, 385 (2017). DOI: 10.1557/mrs.2017.86.

[18] M.M. Vopson. J. Phys. D **46**, 345304 (2013). DOI: 10.1088/0022-3727/46/34/345304.

[19] A.A. Amirov, I.I. Makoed, D.M. Yusupov. Chelyabinsk Phys. Math. J. **5**, *2*, 140 (2020). DOI: 10.24411/2500-0101-2020-15201.

[20] T. Gottschall, A. Grácia-Condal, M. Fries, A. Taubel, L. Pfeuffer, L. Mañosa, A. Planes, K.P. Skokov, O. Gutfleisch. Nature Mater. **17**, 929 (2018). DOI: 10.1038/s41563-018-0166-6.

[21] Y. Liu, L.C. Phillips, R. Mattana, M. Bibes, A. Barthélémy, B. Dkhil. Nature Commun. **7**, (2016). DOI: 10.1038/ncomms11614.

[22] Q.B. Hu, J. Li, C.C. Wang, Z.J. Zhou, Q.Q. Cao, T.J. Zhou, D.H. Wang, Y.W. Du. Appl. Phys. Lett. **110** (2017). DOI: 10.1063/1.4984901.

[23] H. Ursic, V. Bobnar, B. Malic, C. Filipic, M. Vrabelj, S. Drnovsek, Y. Jo, M. Wencka, Z. Kutnjak. Sci. Rep. **6** (2016). DOI: 10.1038/srep26629.

[24] M. Balli, B. Roberge, P. Fournier, S. Jandl. Crystals **7** (2017). DOI: 10.3390/cryst7020044.

[25] B. Sattibabu, A.K. Bhatnagar, K. Vinod, A. Mani. Phys. B: Condens. Matter. **514**, 37 (2017). DOI: 10.1016/j.physb.2017.03.024.

[26] M. Balli, P. Fournier, S. Jandl, M.M. Gospodinov. J. Appl. Phys. **115**, 173904 (2014). DOI: 10.1063/1.4874943.

[27] K. Dey, A. Indra, S. Majumdar, S. Giri. J. Magn. Magn. Mater. **435**, 15 (2017). DOI: 10.1016/j.jmmm.2017.03.068.

[28] I.I. Makoed, A.A. Amirov, N.A. Liedienov, A.V. Pashchenko, K.I. Yanushkevich. Solid State Sci. **95**, 105920 (2019). DOI: 10.1016/j.solidstatesciences.2019.06.009.

[29] I.I. Makoed, A.A. Amirov, N.A. Liedienov, A.V. Pashchenko, K.I. Yanushkevich, D.V. Yakimchuk, E.Y. Kaniukov. J. Magn. Magn. Mater. **489**, 165379 (2019). DOI: 10.1016/j.jmmm.2019.165379.

[30] I.A. Starkov, A.S. Starkov. Int. J. Solids Struct. **100–101**, 187 (2016). DOI: 10.1016/j.ijsolstr.2016.08.015.

[31] B. Ramachandran, M.S.R. Rao. Appl. Phys. Lett. **95**, 142505 (2009). DOI: 10.1063/1.3242411.

[32] G.P. Zheng, S. Uddin, X. Zheng, J. Yang. J. Alloys Compd. **663**, 249 (2016). DOI: 10.1016/j.jallcom.2015.12.056.

[33] A. Edström, C. Ederer. Phys. Rev. Lett. **124**, 167201 (2020). DOI: 10.1103/PhysRevLett.124.167201.

[34] A. Zakharov. Fiz. Met. Metalloved. **24**, 84 (1967).

[35] A.M. Aliev, A.B. Batdalov, L.N. Khanov, A.P. Kamantsev, V.V. Koledov, A.V. Mashirov, V.G. Shavrov, R.M. Grechishkin, A.R. Kaul, V. Sampath. Appl. Phys. Lett. **109**, 202407 (2016). DOI: 10.1063/1.4968241.

[36] S.A. Nikitin, G. Myalikgulyev, A.M. Tishin, M.P. Annaorazov, K.A. Asatryan, A.L. Tyurin. Phys. Lett. A **148**, 363 (1990). DOI: 10.1016/0375-9601(90)90819-A.

[37] E. Stern-Taulats, A. Planes, P. Lloveras, M. Barrio, J.-L. Tamarit, S. Pramanick, S. Majumdar, C. Frontera, L. Mañosa. Phys. Rev. B **89**, 214105 (2014). DOI: 10.1103/PhysRevB.89.214105.

[38] S. Nikitin, G. Myalikgulyev, M. Annaorazov, A.L. Tyurin, R.W. Myndyev, S.A. Akopyan. Phys. Lett. A **171**, 234 (1992). DOI: 10.1016/0375-9601(92)90432-L.

[39] A.A. Amirov, F. Cugini, A.P. Kamantsev, T. Gottschall, M. Solzi, A.M. Aliev, Y.I. Spichkin, V.V. Koledov, V.G. Shavrov. J. Appl. Phys. **127** (2020). DOI: 10.1063/5.0006355.

[40] A. Grácia-Condal, T. Gottschall, L. Pfeuffer, O. Gutfleisch, A. Planes, L. Mañosa. Appl. Phys. Rev. **7**, 041406 (2020). DOI: 10.1063/5.0020755.

[41] A. Chirkova, F. Bittner, K. Nenkov, N.V. Baranov, L. Schultz, K. Nielsch, T.G. Woodcock. Acta Mater. **131**, 31 (2017). DOI: 10.1016/j.actamat.2017.04.005.

[42] F. Albertini, J. Kamarád, Z. Arnold, L. Pareti, E. Villa, L. Righi. J. Magn. Magn. Mater. **316**, 364 (2007). DOI: 10.1016/j.jmmm.2007.03.020.

[43] E. Lovell, H.N. Bez, D.C. Boldrin, K.K. Nielsen, A. Smith, C.R.H. Bahl, L.F. Cohen. Phys. Status Solidi — Rapid Res. Lett. **11**, 1700143 (2017). DOI: 10.1002/pssr.201700143.

[44] E. Stern-Taulats, P. Lloveras, M. Barrio, E. Defay, M. Egilmez, A. Planes, J.L. Tamarit, L. Mañosa, N.D. Mathur, X. Moya. APL Mater. **4**, 091102 (2016). DOI: 10.1063/1.4961598.

[45] A. Chauhan, S. Patel, R. Vaish. Acta Mater. **89**, 384 (2015). DOI: 10.1016/j.actamat.2015.01.070.

[46] C.W. Nan, M.I. Bichurin, S. Dong, D. Viehland, G. Srinivasan. J. Appl. Phys. **103**, 031101 (2008). DOI: 10.1063/1.2836410.

[47] C. Binek, V. Burobina. Appl. Phys. Lett. **102**, 031915 (2013). DOI: 10.1063/1.4788690

[48] I. Starkov, A. Amirov, L. Khanov, A. Starkov. Ferroelectrics **569**, 222 (2020). DOI: 10.1080/00150193.2020.1822680.

[49] E. Mikhaleva, I. Flerov, A. Kartashev, M. Gorev, A. Cherepakhin, K. Sablina, N. Mikhashenok, N. Volkov, A. Shabanov. J. Mater. Res. **28**, 3322 (2013). DOI: 10.1557/jmr.2013.360.

[50] E. Mikhaleva, E. Eremin, I. Flerov, A. Kartashev, K. Sablina, N. Mikhashenok. J. Mater. Res. **30**, 278 (2014). DOI: 10.1557/jmr.2014.369.

[51] J. Ma, J. Hu, Z. Li, C.-W. Nan. Adv. Mater. **23**, 1062 (2011). DOI: 10.1002/adma.201003636.

[52] A.A. Amirov, A.S. Starkov, I.A. Starkov, A.P. Kamantsev, V.V. Rodionov. Lett. Mater. **8**, 353 (2018). DOI: 10.22226/2410-3535-2018-3-353-357.

[53] A.A. Amirov, V.V. Rodionov, I.A. Starkov, A.S. Starkov, A.M. Aliev. J. Magn. Magn. Mater. **470**, 77 (2019). DOI: 10.1016/j.jmmm.2018.02.064.

[54] A.A. Amirov, I.A. Baraban, A.A. Grachev, A.P. Kamantsev, V.V. Rodionov, D.M. Yusupov, V.V. Rodionova, A.V. Sadovnikov. AIP Adv. **10**, 025124 (2020). DOI: 10.1063/1.5130026.

[55] A.A. Amirov, T. Gottschall, A.M. Chirkova, A.M. Aliev, N.V. Baranov, K.P. Skokov, O. Gutfleisch. J. Phys. D **54** (2021). DOI: 10.1088/1361-6463/ac25ae.

[56] R. Zhao, H. Huang, W. He, H. Wang, H.M. Jafri, J. Wang, X. Ma. J. Alloys Compd. **806**, 1491 (2019). DOI: 10.1016/j.jallcom.2019.07.291.

[57] Y.Y. Gong, D.H. Wang, Q.Q. Cao, E.K. Liu, J. Liu, Y.W. Du. Adv. Mater. **27**, 801 (2015). DOI: 10.1002/adma.201404725.

[58] R.O. Cherifi, V. Ivanovskaya, L.C. Phillips, A. Zobelli, I.C. Infante, E. Jacquet, V. Garcia, S. Fusil, P.R. Briddon, N. Guiblin, A. Mougin, A.A. Ünal, F. Kronast, S. Valencia, B. Dkhil, A. Barthélémy, M. Bibes. Nature Mater. **13**, 345 (2014). DOI: 10.1038/nmat3870.

[59] Q.B. Hu, J. Li, C.C. Wang, Z.J. Zhou, Q.Q. Cao, T.J. Zhou, D.H. Wang, Y.W. Du. Appl. Phys. Lett. **110**, 222408 (2017). DOI: 10.1063/1.4984901.

[60] T. Gottschall, E. Bykov, A. Grácia-Condal, B. Beckmann, A. Taubel, L. Pfeuffer, O. Gutfleisch, L. Mañosa, A. Planes, Y. Skourski, J. Wosnitza. J. Appl. Phys. **127**, 185107 (2020). DOI: 10.1063/5.0006079.

[61] A. Czernuszewicz, J. Kaleta, D. Lewandowski. Energy Convers. Manag. **178**, 335 (2018). DOI: 10.1016/j.enconman.2018.10.025.

[62] H. Hou, P. Finkel, M. Staruch, J. Cui, I. Takeuchi. Nature Commun. **9**, 4075 (2018). DOI: 10.1038/s41467-018-06626-y.

[63] A.G. Olabi, A. Grunwald. Mater. Des. **29**, 469 (2008). DOI: 10.1016/j.matdes.2006.12.016.

[64] A.A. Bukharaev, A.K. Zvezdin, A.P. Pyatakov, Y.K. Fetisov. Usp. Fiz. Nauk **188**, 1288 (2018). DOI: 10.3367/ufnr.2018.01.038279.

[65] Yu.I. Golovin, A.O. Zhigachev, D.Yu. Golovin, S.L. Gribanovsky, A.V. Kabanov, N.L. Klyachko. Izv. RAN. Ser. fiz., **84**, 988 (2020) (in Russian). DOI: 10.31857/s0367676520070108.

[66] S.A. Nikitov, A.R. Safin, D.V. Kalyabin, A.V. Sadovnikov, E.N. Beginin, M. V. Logunov, M.A. Morozova, S.A. Odintsov, S.A. Osokin, A.Y. Sharaevskaya, Y.P. Sharaevsky. Usp. Fiz. Nauk **190** (2020). DOI: 10.3367/ufnr.2019.07.038609.

[67] A. Fert. Usp. Fiz. Nauk **178**, 1336 (2008). DOI: 10.3367/ufnr.0178.200812f.1336.

[68] X. Marti, I. Fina, C. Frontera, J. Liu, P. Wadley, Q. He, R.J. Paull, J.D. Clarkson, J. Kudrnovský, I. Turek, J. Kuneš, D. Yi, J.H. Chu, C.T. Nelson, L. You, E. Arenholz, S. Salahuddin, J. Fontcuberta, T. Jungwirth, R. Ramesh. Nature Mater. **13**, 367 (2014). DOI: 10.1038/nmat3861.

[69] S.A. Odintsov, A.A. Amirov, A.P. Kamantsev, A.A. Grachev, V.V. Rodionova, A.V. Sadovnikov. IEEE Trans. Magn. (2021). DOI: 10.1109/TMAG.2021.3085402.

[70] S.A. Odintsov, A.A. Amirov, A.A. Grachev, V.V. Rodionova, A.V. Sadovnikov. FTT **63**, 1317 (2021) (in Russian). DOI: 10.21883/ftt.2021.09.51307.24h.

[71] A.A. Grachev, O. V. Matveev, M. Mruczkiewicz, M.A. Morozova, E.N. Beginin, S.E. Sheshukova, A.V. Sadovnikov. Appl. Phys. Lett. **118**, 262405 (2021). DOI: 10.1063/5.0051429.

[72] X.Z. Chen, J.F. Feng, Z.C. Wang, J. Zhang, X.Y. Zhong, C. Song, L. Jin, B. Zhang, F. Li, M. Jiang, Y.Z. Tan, X.J. Zhou, G.Y. Shi, X.F. Zhou, X.D. Han, S.C. Mao, Y.H. Chen, X.F. Han, F. Pan. Nature Commun. **8** (2017). DOI: 10.1038/s41467-017-00290-4.

[73] V.I. Zverev, A.P. Pyatakov, A.A. Shtil, A.M. Tishin. J. Magn. Magn. Mater. **459**, 182 (2018). DOI: 10.1016/j.jmmm.2017.11.032.

[74] A.M. Tishin, Y.I. Spichkin, V.I. Zverev, P.W. Egolf. Int. J. Refrig. **68**, 177 (2016). DOI: 10.1016/j.ijrefrig.2016.04.020.

[75] A.M. Tishin, J.A. Rochev, A.V. Gorelov. US patent 9,017,713,B2, priority from 13.10.2006 (2015).

[76] A.A. Amirov, D.M. Yusupov, E.K. Murliev, C.A. Gritsenko, A.M. Aliev, A.M. Tishin. Mater. Lett. **304**, 130626 (2021) DOI: 10.1016/j.matlet.2021.130626.

[77] M. Barbic, S.J. Dodd, H.D. Morris, N. Dilley, B. Marcheschi, A. Huston, T.D. Harris, A.P. Koretsky. Magn. Res. Med. **81**, 2238 (2019). DOI: 10.1002/mrm.27615.

[78] M. Barbic, S.J. Dodd, H. ElBidweihy, N.R. Dilley, B. Marcheschi, A.L. Huston, H.D. Morris, A.P. Koretsky. Magn. Res. Med. **85**, 506 (2021). DOI: 10.1002/mrm.28400.

[79] Y. Cao, Y. Yuan, Y. Shang, V.I. Zverev, R.R. Gimaev, R. Barua, R.L. Hadimani, L. Mei, G. Guo, H. Fu. J. Mater. Sci. **55**, 13363 (2020). DOI: 10.1007/s10853-020-04921-y.