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A multicaloric cooling cycle that exploits thermal hysteresis

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The giant magnetocaloric effect, where large thermal changes are induced in a material upon application of a magnetic field, can be used for refrigeration applications such as cooling of systems from small to relatively large scale. However, commercial uptake has been limited. We propose an approach to magnetic cooling that rejects the conventional idea that the hysteresis inherent in magnetostructural phase-change materials must be minimised in order to maximise the reversible magnetocaloric effect. Instead, we introduce a second stimulus, uniaxial stress, so that we can exploit the hysteresis. This allows us to lock-in the ferromagnetic phase as the magnetising field is removed, drastically removing the volume of the magnetic field source and so reducing the amount of expensive Nd-Fe-B permanent magnets needed for a magnetic refrigerator. In addition, the mass ratio between the magnetocaloric material and the permanent magnet can be increased allowing scaling of the cooling power of a device simply by increasing the refrigerant body. The technical feasibility of this hysteresis-positive approach is demonstrated using Ni-Mn-In Heusler alloys. Our study could lead to enhanced usage of the giant magnetocaloric effect in commercial applications.

AN ALTERNATIVE TO CONVENTIONAL SOLID-STATE REFRIGERATION

Although there have been improvements in efficiency, the working principle for conventional cooling – vapour-compression – has remained largely unchanged for more than 100 years[1]. However, with the world's increasingly affluent population demanding more comfortable living and working conditions, it is vital that we address the development of much more efficient cooling technologies as an urgent priority[2,3]. Most research is focused on solid-state refrigeration and one of the caloric effects – electrocaloric[4,5], magnetocaloric[6,7], barocaloric[8,9] or elastocaloric[10,11]– where the material's entropy is forced to change under the application of an electrical, magnetic or mechanical field. The MCE, the most studied of the three, manifests itself as a change in the material's temperature as it is exposed to a magnetic field. This remarkable effect makes it possible to set up a magnetic cooling cycle[12].

Even though dozens of MCE demonstrators have been constructed[13], no commercially competitive magnetic refrigerator has ever been produced[14]. The problem is that in a field produced by permanent magnets (in the range of 1 T) the MCE of existing materials is too small, leading to small operating ranges. It is possible to increase the temperature range of a MCE device by employing what is called an active magnetic regeneration (AMR) cycle[15], but then only a small percentage of the MCE material contributes to the cooling[16]. The design of such an AMR machine is sketched in Fig. 1(a) with the magnetic field being varied by rotating either the MCE material or the magnet. Conventionally, the rare-earth element (REE) gadolinium[17] is used as the MCE material, but there are also demonstrators operating with La-Fe-Si or Fe_2P-type compounds[18]. Since the MCE in these materials is completely, or at least mostly, reversible, the magnetic field needs to be maintained during the whole heat-exchange process. Consequently, the quantity of REE-based Nd-Fe-B permanent magnets needed is at least four times the amount of MCE material and even larger when Halbach arrangements are used, making the system expensive and overly dependent on critical raw materials[19,20].

We present an alternative solid-state cooling cycle that exploits the thermal hysteresis that is inherent in MCE materials undergoing a first-order transition. After the phase transformation is driven by the magnetic field, removing the field leaves the material "locked" in the phase with high magnetisation because of the hysteresis, and so the magnetic field is only required for a very short time in order to tap the cold of the material. This concept drastically reduces the costs of the magnetic-field source because in this case the volume over which the magnetic field needs to be generated and maintained is very small[21]. At the same time, focusing the magnetic field means we can double the magnetic field strength up to 2 T. Since the MCE scales with the change in magnetic field, this can expand the temperature range of the refrigeration cycle. However, it requires an additional external stimulus, i.e., a mechanical stress, in order to "unlock" the MCE material and return it to its original state[22]. Consequently, a material with susceptibility to multiple external stimuli is a prerequisite in order to exploit the

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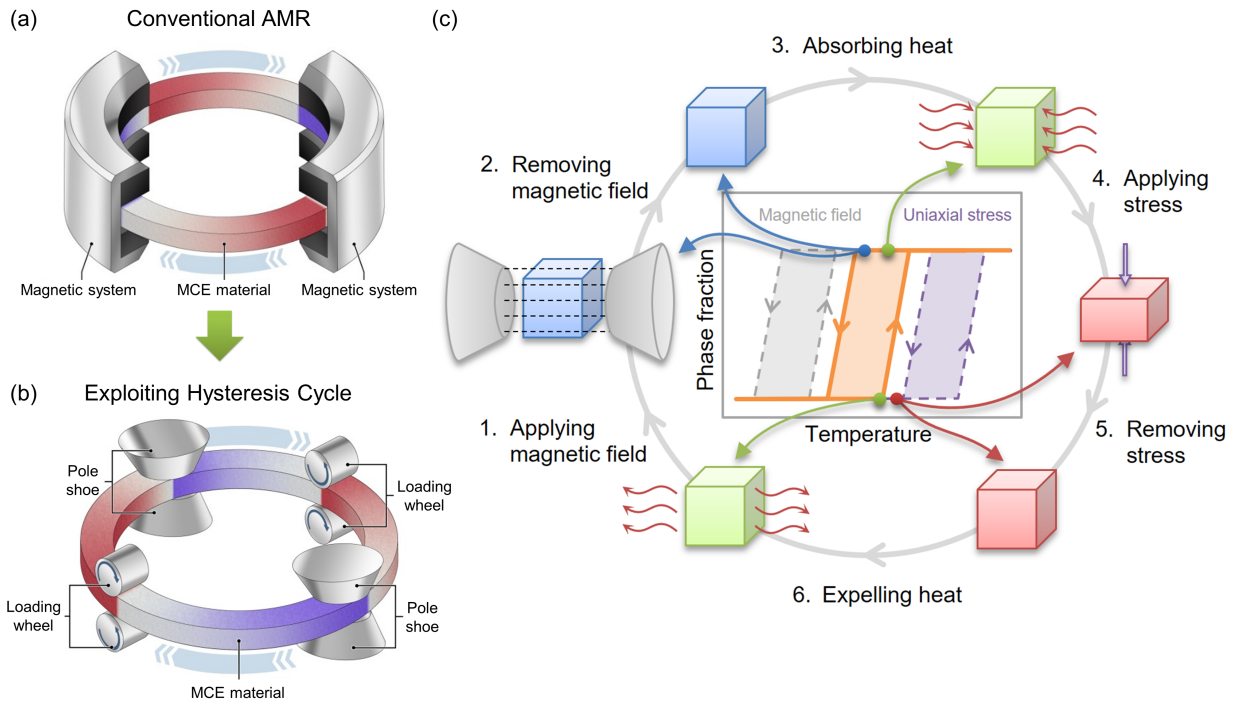

FIG. 1. Explanation of the exploiting hysteresis cycle in comparison to the conventional magnetocaloric cooling cycle. (a) Conventional active magnetic regenerator (AMR) where a large mass of permanent magnets is required. (b) Device that could utilise the thermal hysteresis of magnetocaloric materials. (c) Schematic of the six-step exploiting hysteresis cycle. The coloured boxes symbolise the multicaloric material whereas blue, green and red indicates low, ambient and high temperature. The diagram in the centre illustrates the hysteresis of the multicaloric transition by means of the phase fraction vs. temperature without external field (orange), in magnetic field (grey) and under the influence of uniaxial stress (purple).

thermal hysteresis.

The working principle of such a cycle as well as a scheme for the corresponding design of the machine is illustrated in Fig. 1(b) and (c). In general, any first-order magnetocaloric material with a tunable thermal hysteresis could be utilised in this cycle, even though, inverse magnetocaloric materials such as Heusler alloys are more favourable because they cool when the magnetic field is applied, thereby simplifying the heat exchange. In contrast, conventional compounds such as the La-Fe-Si type heat up when being magnetised and cool when applying the mechanical load[23]. The necessity for a direct contact between the loading unit and the cold heat exchanger makes the implementation of an efficient design more complicated.

EXPERIMENTAL PROOF OF CONCEPT

In this study we focus on Ni-Mn-In Heusler alloys with metamagnetic martensitic transition showing an inverse magnetocaloric effect, which means a decrease in temperature when they are adiabatically magnetised (step 1 in Fig. 1(c)), and a tunable thermal hysteresis[24]. Besides other extrinsic and intrinsic effects, the hysteresis width is dominantly determined by the lattice mismatch between the cubic austenite and the tetragonally distorted martensite phase which can be adjusted by varying the chemical composition[25,26]. The high elastic energy barriers that separate parent and martensitic phases ensure, to a very good approximation, the athermal character of the transition. Consequently, the transformed fraction will not change while keeping temperature, stress and magnetic field constant[27]. In our hysteresis-positive approach, the magnetic field needs to be sufficiently high to completely transform the material. Then, due to the appropriately tuned thermal hysteresis, the reverse transition does not take place during demagnetisation, as sketched in step 2. This is the fundamental difference compared to the conventional AMR cooling cycle. In this way we turn the thermal hysteresis from being a problem for magnetocalorics into an advantage for multi-stimuli caloric materials. The irreversibility of the magnetostructural transition allows us to reduce the magnetised volume to a minimum, which means that we can abandon the large, expensive REE magnets that are required to produce a magnetic field over a large volume.

After locking the material in the ferromagnetic phase in step 3, the heat can be extracted from the cooling compartment in the absence of a magnetic field. In order to return the material to its original state, a loading unit is required, as illustrated by the wheel system in Fig. 1(b). In the case of Ni-Mn-In, the application of a mechanical load shifts the hysteresis curve to higher temperatures

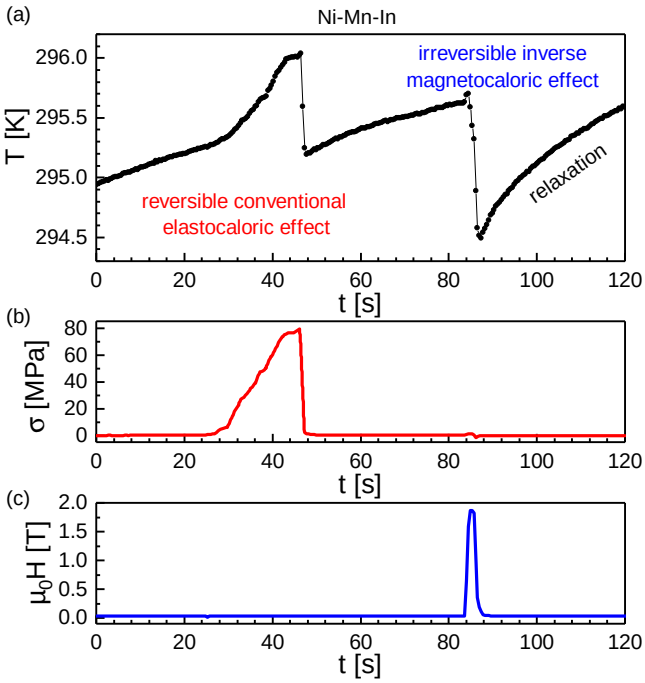

FIG. 2. Experimental demonstration of the exploiting hysteresis cycle. The sample temperature is shown in (a) as a function of time. While applying the stress (b) the temperature is increasing, but this is reversed when the material is unloaded. A short magnetic field pulse up to 1.8 T (c) then results in an irreversible cooling effect. After the pulse, the material slowly relaxes back to the temperature of the surroundings. In contrast, the temperature of a material with a reversible MCE would simply follow the magnetic field profile.

and consequently the material transforms back into the low-temperature phase. This process is accompanied by a large heating effect since the reverse transformation is induced (step 4 and 5). The excess heat can then be expelled to the surroundings in the final step 6. It is worth noting that part of the excess heat from the multicaloric material could also flow into the loading unit due to the direct contact. Therefore, the wheel system should either be thermally insulated or kept at the temperature of the hot reservoir. Like for the magnetisation step, the high stress field is only required over a very small volume. Further information on the six-step hysteresis-positive cycle can be found in the supplementary information (see Fig. S1).

Fig. 2 shows a demonstration of the cycle on a laboratory scale. In this experiment, the Heusler material is loaded by a uniaxial stress of 75 MPa in order to turn it into the low-temperature martensite phase, resulting in significant heating. The mechanical load is created by a piston that is connected to a screw system. For technical reasons, the application of mechanical stress must be performed with care in order to prevent overshooting, whereas unloading the sample can happen instantaneously. After a certain waiting time, a short magnetic field pulse of 1.8 T with a duration of approximately 2 s is applied by an electromagnet and the Heusler sample cools down. The key point is that the magnetocaloric effect is not reversed when removing the magnetic field because of the thermal hysteresis. Since the sample is in thermal contact with the surroundings, its temperature relaxes back with time. This simulates the extraction of heat from the cooling compartment. Afterwards, the cycle can start over again.

For the cyclic tests, a Heusler alloy in bulk form with the composition $Ni_{49.6}Mn_{35.6}In_{14.8}$ was selected. Its martensitic transition with a thermal hysteresis of about 10 K occurs slightly below room temperature, as can be seen from Fig. 3(a). The magnetisation measurements in 0.2, 1 and 2 T are shown in the upper part. The magnetic field shifts the hysteresis curve towards lower temperatures as the austenitic high-magnetisation state is stabilised. In contrast, the application of uniaxial stress favours the low-temperature martensite phase and therefore the transition temperature is increased. In the lower part of Fig. 3(a), the compressive strain of the sample is plotted as a function of temperature under a constant uniaxial load up to 60 MPa. For those measurements, a mechanical testing machine was equipped with a heating and cooling chamber that allowed us to sweep the sample temperature. We observed that the magnetic field shifts the transition by approximately $-3.7\,\mathrm{K\,T^{-1}}$, whereas uniaxial stress increases the transformation temperature by about $+0.23\,\mathrm{K\,MPa^{-1}}$. These values are in agreement with data in the literature for similar samples[28]. In other words, a uniaxial load of 16 MPa is comparable to a magnetic field of 1 T, though the transition is shifted in the opposite direction.

The results of the cycling experiments under multiple stimuli are illustrated in Fig. 3(b). The magnetic field and the uniaxial stress were applied alternately at minute intervals. The whole measurement setup was heated in the background with a sweeping rate of $0.1\,\mathrm{K\,min^{-1}}$ in order to test the properties of the materials at different temperatures. Despite the simplicity of the setup and its poor thermal insulation, the feasibility of the hysteresis-exploiting concept is demonstrated in a sequence of cycles. The basic idea of obtaining an irreversible magnetocaloric effect in a cyclic manner was demonstrated, even though it accounts for little more than 1 K. In this example the sample was loaded with about 75 MPa. However, the application of such a large uniaxial stress is a harsh process that can lead to fatigue and even to the magnetocaloric material being destroyed. In tests on similar arc-melted Heusler alloys, several samples failed. One reason for this is that the grain sizes in those compounds are in the range of millimetres[29]. Therefore, cracks can propagate easily. One possibility for enhancing the mechanical stability of the material is to refine the microstructure by suction casting the materials.

Figure 4 summarises the results for the suction-cast material with a similar chemical composition to the bulk material. In Fig. 4(a) both the magnetisation and the

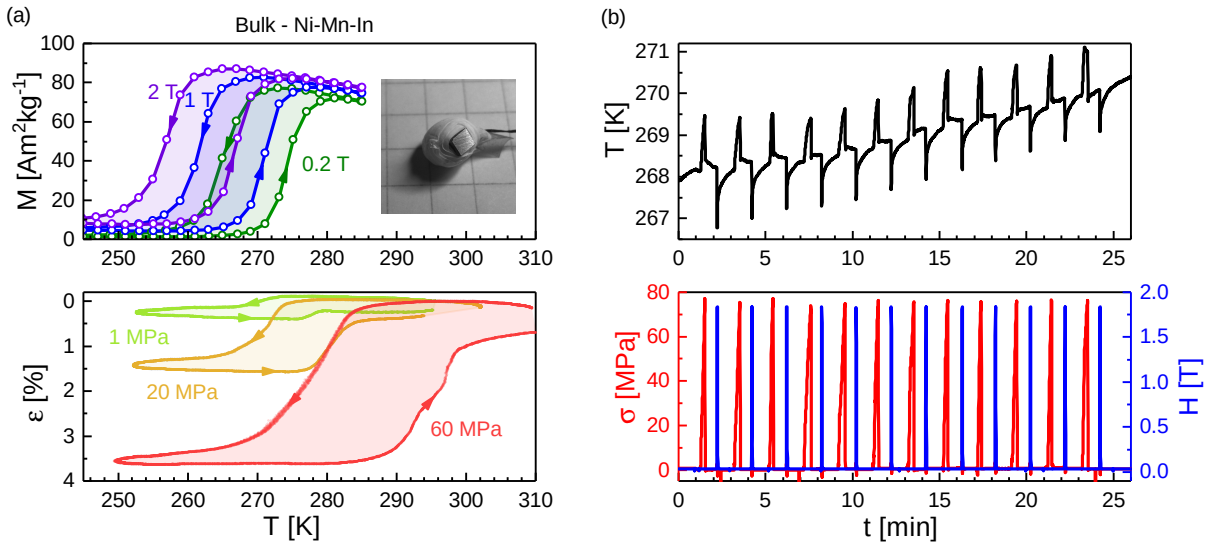

FIG. 3. Bulk Ni-Mn-In Heusler sample under the influence of a mangetic field and uniaxial stress. (a) Temperature dependence of magnetisation M and compressive strain ε in various magnetic and uniaxial stress fields. The image shows the cuboid sample connected with the thermocouple. (b) Cyclic thermal response of the Heusler alloy as it is alternately exposed to a mechanical load (heating signal) and a magnetic field pulse (cooling signal). The temperature of the surroundings was swept in the background.

compressive strain of the sample are plotted. When a magnetic field is applied, the transition shifts by about $-1\,\mathrm{K\,T^{-1}}$, whereas uniaxial stress increases the transition temperature T_t by approximately $0.1\,\mathrm{K\,MPa^{-1}}$. Compared to the bulk sample in Fig. 3, the $\frac{dT_t}{dH}$ and $\frac{dT_t}{d\sigma}$ values are significantly smaller because the transition of the suction-cast sample is close to the Curie temperature of the austenite phase. In comparative measurements of the adiabatic temperature change (see supplementary information) in cyclic magnetic fields of 1.9 T, we were able to demonstrate that the suction-cast material provides only a vanishingly small reversible magnetocaloric effect related to the first-order transition. As shown in Fig. S2 of the supplementary information, the irreversible ΔT_{ad} in this field change accounts for $-1.28\,\mathrm{K}$ in the first field application of a "fresh" material. By applying the multi-stimuli hysteresis cycle, it is possible to exploit almost the entire potential ΔT_{ad}. For the cyclic tests in Fig. 4(c) it is apparent that an irreversible temperature change of $-1.2\,\mathrm{K}$ can be achieved. Furthermore, the mechanical integrity of the specimen is much improved due to the fine microstructure. Figure 4(b) shows a light-microscopy image of sample in the martensite state with fine needle-like structures. However, the grain boundaries of the parent austenite phase that separate the different martensitic regions are still visible. During the suction casting of the melt, the grains grow in a radial direction towards the centre of the rod and have a typical width between 100 and 250 µm. This special microstructure can withstand much larger uniaxial stresses than conventionally arc-melted counterparts, even beyond 100 MPa.

Figure 4(c) shows the thermal response of the suction-cast material when a magnetic field pulse of about 1.8 T (even minutes) and mechanical load of 80 MPa (odd minutes) are alternately applied. The temperature of the holder was increased from 290 to 298 K with $0.25\,\mathrm{K\,min^{-1}}$ to study the response in different temperature regions of the martensitic transition. The diagonal curve represents the absolute temperature profile of the sample (right-hand axis). In order to illustrate the temperature profile of the material in a clearer form, the baseline heating curve was subtracted, as shown on the left-hand axis. It is possible to distinguish three different regions. Below approximately 292 K (minute 0–7) the magnetocaloric cooling effect is predominantly reversible and the sample temperature reverts instantly after the field pulse. At this low temperature, the material is mainly in the martensite state.

Above approximately 292 K (minute 7–23), increasing amounts of austenite are locked by the thermal hysteresis, preventing it from transforming back into martensite. For this reason the cooling effect becomes irreversible during the magnetic-field pulse with a maximum value of $-1.2\,\mathrm{K}$ obtained at 295.5 K (minute 22). Here, the temperature change of the material is maintained long after the magnetic-field pulse and it takes about 1 min to relax back to the background temperature. Furthermore, the heating of the sample is intensified during the stress application, which indicates that a larger amount of austenite is switched back into martensite. In contrast, above 296 K (minute 24–29) the transition turns into a conventional MCE, which is reversible. At these high temperatures, the austenite phase is dominant and since its Curie temperature, being approximately 305 K, is rather close, a temperature increase of 1.3 K is observed. However, the temperature change is immediately

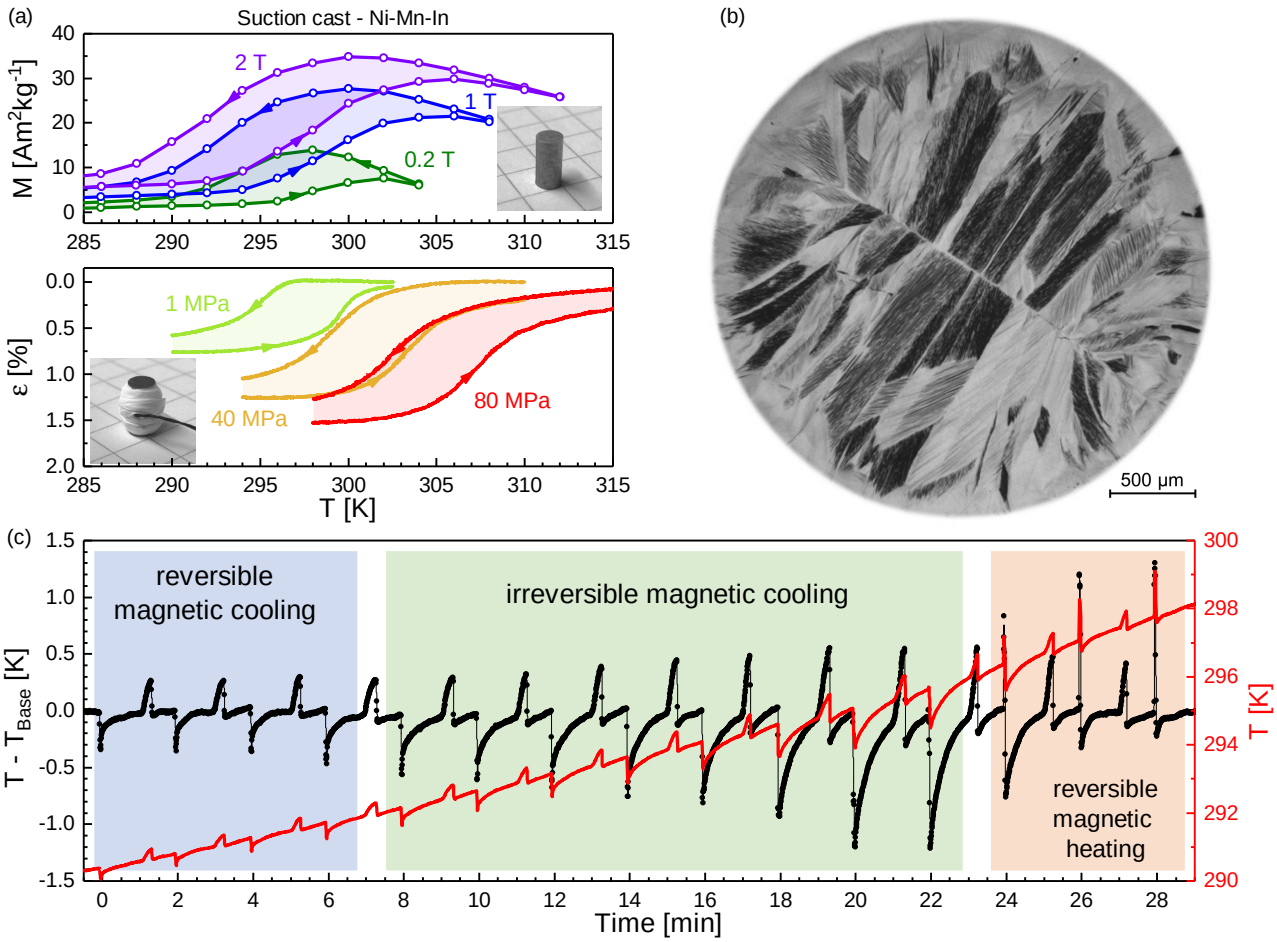

FIG. 4. Testing the multicaloric performance of suction-cast Ni-Mn-In under the influence of a magnetic field and uniaxial stress. (a) Temperature dependence of magnetisation M and compressive strain ε in various magnetic and uniaxial stress fields. The images show the sample with and without a thermocouple being connected. (b) Light microscopy of the suction-cast material in martensite state, illustrating the radial grain growth. (c) Cyclic thermal response of the Heusler alloy when it is alternately exposed to a uniaxial stress up to 80 MPa (heating signals) and a magnetic field pulse up to 1.8 T (cooling signals). The absolute temperature of the sample is given by the right-hand scale. The temperature of the surroundings was swept in background with 0.25 K min^{-1}. The baseline-subtracted temperature profile is plotted on the left-hand scale. A distinction is made between the three areas where the MCE is inverse, both reversible and irreversible, and conventional in nature.

reversed when the magnetic field decreases. A small irreversible part is also present at these temperatures, since a small amount of martensite could be formed by the applied stress application, but this is not significant.

ON THE POTENTIAL OF THE EXPLOITING HYSTERESIS CYCLE

In conclusion, our experiments have demonstrated that the hysteresis-exploiting cycle works on a laboratory scale. In particular, the suction-cast Ni-Mn-In Heusler alloy was a very promising innovation, due to its enhanced mechanical strength and reasonably large thermal hysteresis. These inverse magnetocaloric materials have the advantage that they cool during the field-application step, where no mechanical contact is required, which simplifies the heat transfer. However, most first-order MCE alloys could be used for such a cycle. The only requirements are a tuned thermal hysteresis, a sufficient magnetic field dependence of the transition temperature and an external stimulus that can transform the material back to its original state. This cycle represents a multicaloric approach to magnetic refrigeration that exploits the thermal hysteresis of a MCE material instead of attempting to avoid it. The advantage is that the full potential of the Heusler compound can now be utilised in a cyclic process, even if it shows no reversible ΔT_{ad} in conventional magnetic-field cycling. In the supplementary information, an approximation of the energy balance derived from experimental data can be found (see Figs. S3 - S5). In an exemplary six-step cooling cycle, the extra work associated with the deformation (per unit mass) due to the application of a uniaxial stress

can be approximated at the material level from Fig. 4(a) to $W_{\mathrm{ela}} \approx 17.6\,\mathrm{J\,kg^{-1}}$ (mass density $\rho = 7.0\,\mathrm{g\,cm^{-3}}$), which is about 60 % larger than the magnetisation work $W_{\mathrm{mag}} \approx 10.6\,\mathrm{J\,kg^{-1}}$. Instead, a conventional four-step magnetocaloric cooling cycle would require a magnetic field change of about 4 T in order to obtain a similar ΔT_{ad}. The corresponding magnetic work would then amount to about $22.2\,\mathrm{J\,kg^{-1}}$ which is less than the sum of W_{ela} and W_{mag} in the exploiting hysteresis cycle. However, it is important to remember that the magnetic field strength cannot be increased much beyond 2 T when using permanent magnets as the field source for the refrigerator. Fortunately, this impasse might be overcome by combining the magneto- and elastocaloric effects as described here.

In the proof of concept we obtained a temperature change of −1.2 K. The largest irreversible temperature changes reported in a field of approximately 2 T amount to −8 K in Ni-Mn-In-Co[30] and as much as −9.2 K for the compound Fe-Rh[31]. The next step is to match these large temperature changes to the hysteresis-exploiting cycle with designed-for-purpose of materials. A simple refrigerator would only require two stages with tailored transition temperatures switched in series to build up a sufficiently large temperature span where 50 % of the magnetocaloric material is active in cooling compared to the few percent that is active in a conventional AMR cycle (further information on the heat flow management, on segmentation issues and on cascade devices with two and more stages can be found in Figs. S6 and S7).

Making use of the fact that the multicaloric material retains its temperature drop after the magnetisation and demagnetisation step, there is no necessity for a fast flow of the exchange fluid (see supplementary material for further information) as required in the classical AMR[12]. This claim originates from the restriction that the amount of the magnetocaloric material is more or less fixed for a given magnet arrangement. Therefore, an enhancement of the cooling power is obtainable solely by increasing the operating frequency of the AMR device. However, many technical problems such as the pressure drop of the fluid through the regenerator or the slowness of the valve system limit the frequency to typically 1 Hz[13]. In great contrast, in the hysteresis positive approach the ratio between the magnetocaloric and magnet material and therefore the cooling power is scalable by enlarging the heat exchanger body keeping the magnetic system, the loading unit and the operating frequency the same (see Fig. S8), being an essential advantage of the multi-stimuli approach. This concept will allow a drastic reduction in the amount of expensive and raw-material-critical Nd-Fe-B permanent magnets needed for a cooling machine and at the same time outperform magnetic refrigerators that use the AMR principle in terms of efficiency.

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AUTHOR CONTRIBUTIONS

T.G., M.F., A.T., L.P. and K.P.S. were responsible for the sample preparation. T.G., A.G., A.P. and L.M. designed and performed the tensile test and cycling experiments. A.T., M.F. and K.P.S. took care of the adiabatic temperature change measurements and microscopy. All authors discussed the results and developed the explanation of the experiments. T.G. wrote the manuscript supported by all co-authors. O.G. led the project.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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METHODS

Samples with the nominal composition $Ni_{50.0}Mn_{35.5}In_{14.5}$ were prepared by arc melting. The ingots were turned upside down and remelted several times in order to ensure chemical homogeneity. One batch was further treated using the suction-casting option of the arc melter in order to prepare rods with a diameter of 3 mm. Both specimens were subsequently annealed at 900 °C for 24 h, followed by water quenching. The bulk sample was cut and polished into a block with dimensions of $2 \times 2 \times 5.5\,\mathrm{mm}^3$. The suction-cast material was prepared with a length of 4.9 mm. The magnetic measurements were made on a commercial VSM using small fragments. Temperature-dependent dilatometry measurements involved a mechanical-testing machine operating in constant-load mode. The setup included a variable-temperature chamber in order to cool and heat the piston unit at a rate of $1\,\mathrm{K\,min^{-1}}$. The sample temperature and height were directly measured with a type-T thermocouple and a strain-gauge sensor attached to both pistons, respectively. For the experimental demonstration of the cooling cycle , an in-house-constructed setup was used in which uniaxial stress was applied mechanically by a screw. The load was determined via a force sensor installed in the piston axis. The temperature of the sample, measured directly by a type-T thermocouple, could be varied by a thermal bath connected to the base plate of the piston unit. For the application of the magnetic field pulse, a commercial electromagnet was used. A Hall probe situated near the sample detected the magnetic field strength. Comparative measurements of the adiabatic temperature change (in the absence of mechanical load) of the suction-cast material in a magnetic-field change of 1.9 T in continuous and discontinuous protocol have been performed in a purpose-built device using standard type-T thermocouples[24].

Data availability. The data that support the findings of this study are available from the corresponding authors upon reasonable request.