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Special issue on caloric materials

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Editorial

Special issue on caloric materials

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Caloric effects rely on the reversible component of the thermal response of a given material to an externally applied field [1, 2]. In general, these effects are small but in the vicinity of a phase transition certain solids might feature a large or even giant thermal response. From a technological perspective, materials exhibiting a large enough caloric response are interesting as a solid-state alternative to current gas compression cooling technologies.

Caloric effects induced by mechanical, electric and magnetic fields have been known for a very long time. For instance, in the mid nineteenth century, Joule already investigated the thermo-elastic properties of solids and he was able to measure small temperature changes during compression or expansion of springs immersed in a liquid [3]. The word magnetocaloric was first proposed one hundred years ago by Weiss and Picard [4] who observed small variations of temperature in Ni under application or removal of a magnetic field, close to its Curie point. For many years, the magnetocaloric effect in paramagnetic salts has been the only subject of significant research in the topic of calorics since this effect was successfully used to reach near absolute zero temperatures by means of the adiabatic demagnetization method [5]. Magnetocaloric effects gained increased attention in the seventies when Brown showed that magnetic cooling was possible about room temperature using Gd [6]. The discovery one decade later of a giant magnetocaloric effect in Gd–Si–Ge [7] boosted both basic and applied interest for the development of new materials with enhanced room-temperature magnetocaloric responses [8]. Later, ferroelectric [9] and ferroelastic/shape-memory materials [10, 11] showing, respectively, giant electrocaloric and mechanocaloric effects (induced by uniaxial stress and hydrostatic pressure) added to the family of giant caloric materials.

At present, it is acknowledged that solid-state refrigeration technologies based on these caloric effects will be given priority with the aim of (i) reducing wasting energy for home refrigeration and, perhaps more importantly, (ii) contributing to the necessary minimization of ozone depleting and greenhouse chemicals that seem unavoidable in present vapor-compression technologies. This is indeed one of the main objectives of the recent global climate Paris agreement.

This Special Issue is expected to bring out the state of the art of the present understanding and potential applications in the field of caloric materials. It consists of a collection of sixteen papers written by renowned authors in the field. From these contributions, about half of the papers are devoted to the magnetocaloric effect, which is still the most active topic of investigation. This predominance is clearly evidenced in figure 1 of the paper by Zarkevich *et al* [12], which gives the number of publications per year as a function of the publication year for magneto-, electro- and mechanocaloric effects. From the other half of the papers, only two contributions are about electrocaloric and six on mechanocaloric effects, from which only one is on the barocaloric effect.

A general viewpoint of the field of caloric materials is presented in the paper by Zarkevich *et al* [12], which summarizes the aims of the CaloriCool approach¹. The main objective of this consortium is the design of new caloric materials with improved properties. The paper essentially focuses on the case of magnetic materials and provides materials selection criteria that make use of known materials properties and appropriate algorithms for the discovery of the best performing materials.

In the block of magnetocalorics, the first group of papers deals with the development and characterization of new magnetocaloric materials. It begins with a paper by Boeije *et al* [13],



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¹ Information related to the CaloriCool consortium can be found at <https://caloricool.org>

where the study of the structural and electronic properties of $(\text{Fe,Mn})_2(\text{P,Si,B})$ compounds showing mixed magnetism is reported. This family of materials undergoes a magneto-elastic transition with either first or second-order character with very promising magnetocaloric properties. The authors show that the mechanism behind the phase transition in Fe_2P -based materials is the same isostructural mechanism for both first- and second-order transitions. This result suggests that close to the boundary between first and second order transitions, magnetocaloric materials with still high entropy content but low hysteresis might be designed. With a similar point of view, Franco *et al* [14] have studied a series of composition-related La-Fe-Si compounds with the aim of predicting the tricritical composition at which the transition changes from first to second order. This family of compounds, which is among the best magnetocaloric compounds developed so far, has also been reported in the paper by Lovell *et al* [15]. These authors have studied nucleation and dynamics in the vicinity of the metamagnetic first-order transition in $\text{La}(\text{Fe,Mn,Si})_{13}$. They conclude that the energy barriers for magnetization and demagnetization processes are of different magnitudes and, more importantly, that they can be tailored by controlling temperature and hydrostatic pressure.

The effect of doping with H, B, C and N in LaSiFe_{12} is investigated in the paper by Gercsi *et al* [18] by means of electronic first principle calculations. The results of this paper confirm that H provides the only chemical pressure on the lattice that avoids significant changes of the electronic structure and thus enables a fine tuning of the transition region, preserving the properties of the metamagnetic transition.

A numerical analysis of a generalized Bean–Rodbell model aimed at studying hysteresis properties of inhomogeneous magnetocaloric materials is proposed by Nielsen *et al* [16]. The results are significant in order to clarify the historical dependence effects in $\text{La}(\text{Fe,Si,Mn})_{13}\text{H}$, which are relevant in order to understand the reproducibility of magnetocaloric properties along cycling in practical applications.

The paper by Taubel *et al* [17] deals with structural and thermomechanic properties of the magnetocaloric Mn-Ni-Ge based $\text{MM}'\text{X}$ compounds. Starting with the MnNiGe compound, they show that by judicious simultaneous substitution of Fe for Mn and Si for Ge, it is possible to minimize antiferromagnetic coupling of Mn atoms and design a material undergoing a magnetostructural phase transition about room temperature, which displays a significant magnetization change, providing excellent magnetocaloric properties that can be controlled by both magnetic field and pressure.

The last paper in the group of magnetic materials by Loving *et al* [19] provides a complete characterization of Fe-Rh thin films and proves the possibility of strain-tuning magnetocaloric properties in these magnetocaloric films.

The block of papers on mechanocaloric effects covers a rather broad spectrum which spans the study of the physical properties of giant mechanocaloric materials towards specific materials and device engineering for laboratory demonstrators. All papers on elastocaloric effects report on martensitic alloys. These alloys are the most suited materials for elastocaloric purposes due to the strong sensitivity of the martensitic transition to uniaxial stresses. Among this group of papers, Fukuda and Kakeshita have unveiled the physical mechanisms leading to the elastocaloric effect in weakly first order martensitic transitions in a partially ordered Fe-Pt alloy [20]. They show that the leading contribution to the adiabatic temperature change is due to a pronounced softening of the Young modulus in these materials. The use of magnetic shape memory alloys in elastocaloric devices is challenging, owing to the intrinsic brittleness of these magnetic alloys. In his contribution, Sun *et al* [21] have used a directional solidification technique to produce strongly textured Ni-Mn-Sn rods. By using infrared thermography they have evidenced a significant cooling on releasing of a moderate stress. An important step towards the design of elastocaloric materials with arbitrary shapes is provided by the work of Hou *et al* [22]. They have been able to fabricate TiNi shape memory alloys by the additive manufacturing technique. These additive manufactured materials exhibit a superelastic behaviour with a narrow hysteresis. The combination of a relative large adiabatic temperature change and such a narrow hysteresis yields a large coefficient of performance for these materials, which makes them good candidates for the design of cooling devices. The last two papers on the group of elastocaloric effects report on cooling prototypes at two different length-scales. In the paper by Bruederlin *et al* [23], they use TiNi foils to build a miniature scale elastocaloric cooling device. The coefficient of performance of the overall device approaches 10% of Carnot efficiency. Although this value is still

too low for industrial applications, it largely outperforms the values reported for thermoelectric coolers, and provides great hope for the development of highest efficiency devices. At a much larger scale, Engelbrecht *et al* [24] report on regenerative elastocaloric devices made of TiNi parallel plates. A significant temperature span around 20° was achieved and there is still room for improvement because the regenerators did not work up to full transformation of TiNi plates. Improvement in the fatigue lifetime of TiNi shape memory alloys is still a challenge before cooling devices can be technologically competitive.

The last paper from the mechanocaloric block reports on the barocaloric effect. In their work, Gorev *et al* [25] explore the impact of successive structural phase transitions on the temperature and entropy changes of giant barocaloric fluorides and oxyfluorides. They show that on specific regions of the phase diagram, the magnitude of the barocaloric effect can be enhanced due to the overlap of caloric effects arising from successive phase transitions. This result will enable tailoring materials with optimal performances for barocaloric purposes.

The Special Issue is completed by two papers on electrocaloric materials. Both refer to multilayer capacitors, which are currently being used as working bodies in prototype cooling devices. In the first paper, Usui *et al* [26] analyse the effect of the ratio between electrically active and total volumes into the measured adiabatic temperature changes in these capacitors. They show that reliable adiabatic temperature changes can be measured for a large enough active volume. The values measured in their capacitors are promising to be exploited in prototype electrocaloric coolers and they point to the need of understanding heat flows in these multilayer capacitors. This aspect is addressed by Faye *et al* [27] in their contribution. They used infrared thermography to measure the temperature change of multilayer capacitors in different heat exchange configurations. Their study provides some guiding rules for the design of prototype coolers. Depending on the configuration, Newtonian and non-Newtonian heat exchange occurs, both cases with very large heat transfer coefficients which reach the needs for designing efficient cooling prototypes.

The collection of papers published in this Special Issue illustrate that the field of caloric materials is a mature field of research with a deep understanding of the basic mechanisms giving rise to large thermal reversible responses, responsible for the caloric effects. There are well established methods that permit the design of materials with optimal properties, well adapted to the needs of high efficiency cooling devices, and several laboratory prototypes have already been developed which show the prospects of these materials. There is, however, a long way to go before coolers based on caloric materials can realistically impact the refrigeration market. We hope that this Special Issue will represent a step forward in this exciting path.

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