



## Caloric effects of quantum materials: An outlook

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### ABSTRACT

Solid-state cooling is an emerging technology embracing cryogenic and near room temperature devices. For further developments of this machinery, prototypes and caloric materials must be optimized in order to obtain a better final result than the well-known competitors based on gas compression technology. Thus, researches on materials and prototype optimization have been intensively carried out; and the present *mini-review* will focus on materials, specifically on quantum materials. We comprehensively describe their ability to produce heat, such as the magneto- and barocaloric effects on graphene, as well as the enhanced caloric properties of graphene-based nanocomposite. Quantum dots and frustrated magnets are also reviewed, linked with their potential to produce heat under an external perturbation, such as magnetic field (magnetocaloric effect) or mechanical pressure (barocaloric effect). This work shows that quantum materials are special materials, with advanced and emerging features that can be explored for application in devices for solid-state cooling.

### 1. Introduction

Standard refrigeration technology, based on vapor compression cycle, has failed to meet the requirements of high energy efficiency and sustainability due to its three major flaws: (i) refrigerants are flammable and, in addition, leaking gases damage the ozone layer, enhancing the greenhouse effect; (ii) gas compressors vibrate, produce noise and have short life due to mechanical moving parts; and (iii) low cooling efficiency and large energy consumption worsen the energy shortage. Therefore, the development of environmental-friendly, energy-saving and efficient new refrigeration technology has become one of the effective solutions. The solid-state multicaloric (e.g. baro-, elasto-, magneto-, electro- and toroido-caloric) effects [1–6] are topics of current interest due to the potential improvement of energy efficiency of cooling and temperature control, in combination with other environmental benefits associated to the technology.

Solid-state cooling is therefore an emerging refrigeration technology and has been proposed to be used for national defense, academic science, medical health care, industry and, mainly, household devices. This technology spans from air conditioners to cryocoolers, such as liquefaction of special gases (helium, nitrogen, hydrogen, oxygen, and neon). The liquid helium and liquid nitrogen can be used as refrigerant for physical

properties measurement and superconducting applications, into the enormous medical health care market. In addition, liquid hydrogen and liquid oxygen can be used as fuels for aerospace, military defense, and industrial production. Thus, the market for cryogenic and room temperature refrigeration, based on this advanced and emerging technologies, is enormous. There are good works describing in depth the caloric energy conversion of prototypes [7–10], as well as the remarkable relevance of the material [1,11] for the final prototype efficiency.

Quantum materials, strikingly different from conventional compounds (specially those used for solid-state refrigeration, such as intermetallics and oxides), have two main characteristics related to entanglement and topology. As a consequence, quantum ordering emerges, with the corresponding phase transitions [12–14]. This feature makes the community focus on the following two generic aspects when studying quantum materials: (i) the Coulomb interactions between electrons, promoting entanglement beyond the Fermi statistics, e.g. Majorana fermions as emergent quasi-particles excitation, and (ii) the topological properties of a single-electron Bloch wavefunctions in solids, e.g. quantized vortices in superconductors. We can cite: Dirac materials, topological insulators and semi-metals, Weyl semi-metals, frustrated magnets and so forth. Many of their properties arise from the confinement of electrons and holes at reduced dimensionality, e.g. 0D quantum

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dots, 1D quantum wires and 2D planar layers. These materials present an interesting aspect, named ‘emergence’ - unexpected cooperative physical behavior impossible to be predicted from a few elements of the system, such as magnetic monopoles [15], fractional quantum Hall effect on graphene [16,17], and spin liquids [18]. Thus, phenomena on quantum materials range from dissipationless transport to novel quasi-particle excitation; and such variety of features, in fact, empowers a new era in which quantum materials are broadly harnessed for device applications [13,14].

In this direction, caloric effects and their applications are also attributes of quantum materials, and this subject has attracted the attention of the community along the last years, as discussed herein. We comprehensively present the physical concepts, achievements from the literature and our viewpoint and perspective for several different quantum materials, namely Dirac materials (including graphene), quantum dots and frustrated magnets. Another class of quantum materials, intensively studied by the community, deserves a special review; and it has been published recently [19], discussing the caloric properties of molecular complexes.

## 2. Caloric effects: a brief survey

The magnetocaloric effect (MCE) was experimentally observed by P. Weiss and A. Piccard in 1917 [20]. Later, Debye [21] and Giauque [22] derived the conclusion that the adiabatic demagnetization can be used for refrigeration and thus proposed the idea that by using the adiabatic temperature change of a paramagnetic salt under a magnetic field, they could achieve ultra-low temperature. Based on this idea, Giauque and Mac Dougall [23] successfully reached temperatures of the order of 250 mK with paramagnetic salts, exceeding down, for the first time in the history, the 1 K barrier. For more than four decades, magnetic refrigeration technology never turns toward domestic use, due to the low working temperature range of the magnetocaloric materials.

Luckily, in 1976, Brown found that gadolinium could be used to build a magnetic cooler as refrigerant at room temperature [24]. The research almost stagnated for nearly two decades until the development of advanced magnetocaloric materials, with enhanced properties near room temperature, as the case of  $Gd_5(Si_xGe_{1-x})_4$  [25],  $La[Fe(SiAl)]_{13}$  [26], and Ni-Mn-Sn alloys [27]. In parallel with the research optimizing materials for room temperature devices, significant application in gas liquefaction and adiabatic demagnetization refrigerators below mK [28] still attract attention of the community, exploring intermetallic compounds [29], multiferroic materials [30], and molecular magnets [19,31,32].

Looking for new materials, with enhanced caloric properties, the investigations have been recently extended to new quantum materials, e.g. quantum dots [2,33,34], materials with quantum critical point [35,36], Dirac materials (as graphene) [37–40], Weyl semi-metals [41], molecular magnets [19], and etc. The caloric concept has been expanded and, nowadays, other caloric effects are intensively studied, such as the electrocaloric [6,37,42–44], elastocaloric [45], barocaloric [3,4], and toroidocaloric effects [46]. The case of multiple caloric effects in a single material is named as multicaloric effect [5]; and the research about this subject is quite significant, since it is able to enrich our abilities to develop efficient cooling devices and applications.

Recent reviews have been published, describing the caloric effect of materials in depth [1,47], but none of these included a comprehensive outlook for the caloric effect of quantum materials, except for the recent contribution of one of us [19], which presented a collection of results of magneto- and barocaloric effects for molecular magnets.

## 3. Dirac materials

### 3.1. Physical concepts behind Dirac materials

Materials described by the Dirac equation [48,49] present an energy spectrum with the valence and conduction bands meeting each other

close to the six Dirac points. See Fig. 1-left. The limit of  $m \rightarrow 0$  vanishes the gap and the dispersion relation becomes linear, different from the parabolic dispersion relation for metals - these are the so-called Dirac cones (see Fig. 1-right); and, as a consequence, electrons behave as relativistic massless particles. This main feature characterizes the Dirac materials (DM). Examples are graphene [50], Weyl semi-metals [51], and topological insulators [52], just to name a few. Further examples can be found in books [49] and reviews [48].

From these materials mentioned above, some are 3D Dirac materials, where the mass-dependent term of the Hamiltonian is usually made zero. For this case, the equation is known as Weyl equation and, consequently, those materials are named as Weyl semi-metals. If the valence and conduction band present a Dirac point, those materials, on the other hand, are named as 3D Dirac semi-metals.

In spite of these materials be quite different in nature, they have some features in common, mainly those characteristics directly derived from the energy spectra [50]. For instance, the temperature dependence for the specific heat and some transport properties (like suppressed back-scattering) - just to cite a few. Focusing on graphene, there are several important characteristics [53]: (i) low density, close to 0.77 mg/m<sup>2</sup>; (ii) transparency, absorbing 2.3% of the light intensity; (iii) breaking strength of 42 N/m, i.e., 100 times stronger than a hypothetical steel film of the same thickness; (iv) thermal conductivity close to 5000 W/mK, i.e., 10 times better than copper; (v) electrons into this material can cover micrometer distances without scattering, even at room temperature - it means that graphene has an excellent electrical conductivity. For a description of possible applications of graphene, see Refs. [54].

For this survey, it is convenient to summarize the effect of a magnetic field on a graphene sheet, considering that it is the main kind of external excitation for caloric effects. It is well-known that a non-relativistic electron gas, with a parabolic dispersion relation, changes its energy spectrum when submitted to a magnetic field, by creating Landau Levels (LLs). For this non-relativistic case, the LLs depend on a linear fashion with the magnetic field and quantum number [55]. The same occurs for Dirac materials, however, due to the relativistic dispersion relation, the LLs for graphene depend on the square root of the magnetic field and the quantum number. Consequently, in a different fashion as the non-relativistic metal, LLs are not equidistant and the largest gap is between the zero-th and the first Landau level; and, due to this fact, it was possible to observe the quantum Hall effect on graphene [56]. See Fig. 2 (a) for a comparison between the LLs for graphene (top), with a non-regular separation (depending on the square root of the magnetic field); and a 2D non-relativistic material (bottom), with a regular separation (depending linearly on the magnetic field).

As mentioned above, an external magnetic field is able to change the energy spectrum and create the Landau structure. It is expected therefore either steps or oscillations on the thermodynamic quantities due to the

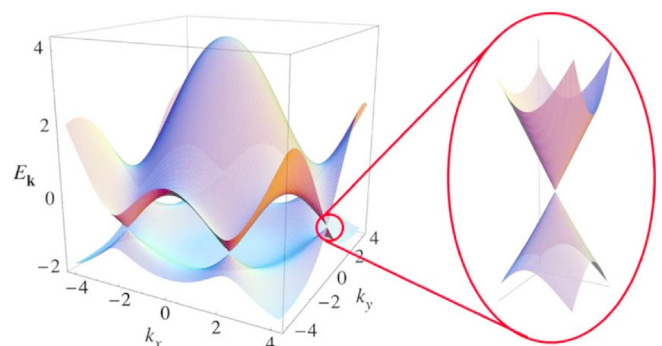
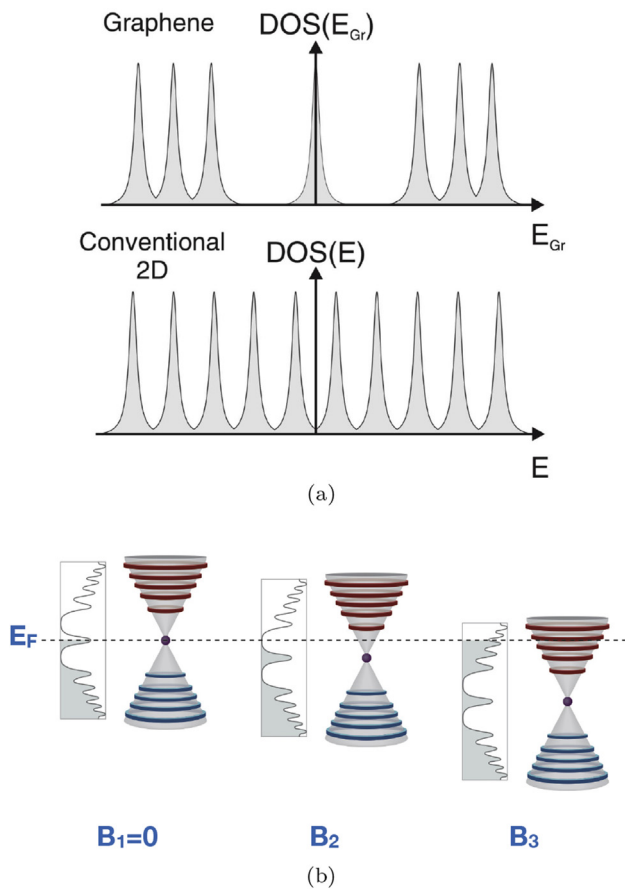


Fig. 1. Left: Energy spectrum for a graphene, obtained after the solution of the tight-binding Hamiltonian [50]. Right: highlight to the Dirac cone close to the Dirac point. This cone is a direct evidence of the linear dispersion relation for this material. Reprint from Refs. [50] with permission of the American Physical Society.



**Fig. 2.** (a) Landau levels for graphene (top), with a non-regular separation (depending on the square root of the magnetic field); and a 2D non-relativistic material (bottom), with a regular separation (depending linearly on the magnetic field). Reprint from Refs. [59] with permission of the *IOP Publishing*. (b) Dirac cones under zero gate voltage and increasing values of magnetic field ( $B_1 < B_2 < B_3$ ). Note the crossing of the Landau levels (represented on the Dirac cone), with the Fermi level. Reprint from Refs. [60] with permission of the *American Physical Society* - adapted.

crossing of the Landau levels with the Fermi level, as depicted on Fig. 2(b). This phenomenon is not exclusive of these quantum materials, and has been observed, for instance, on non-relativistic diamagnetic materials. Examples are the de Haas-van Alphen [57] and the Shubnikov-de Haas [58] effects, observed as oscillations on the magnetization and electrical conductivity, respectively. Based on this knowledge, we are now able to discuss the findings from the literature, and discuss the caloric effects of graphene.

Finally, there are good reviews about Dirac material [48,49], and we can cite, specifically, some reviews about graphene [50], Weyl semimetals [51], and topological insulators [52].

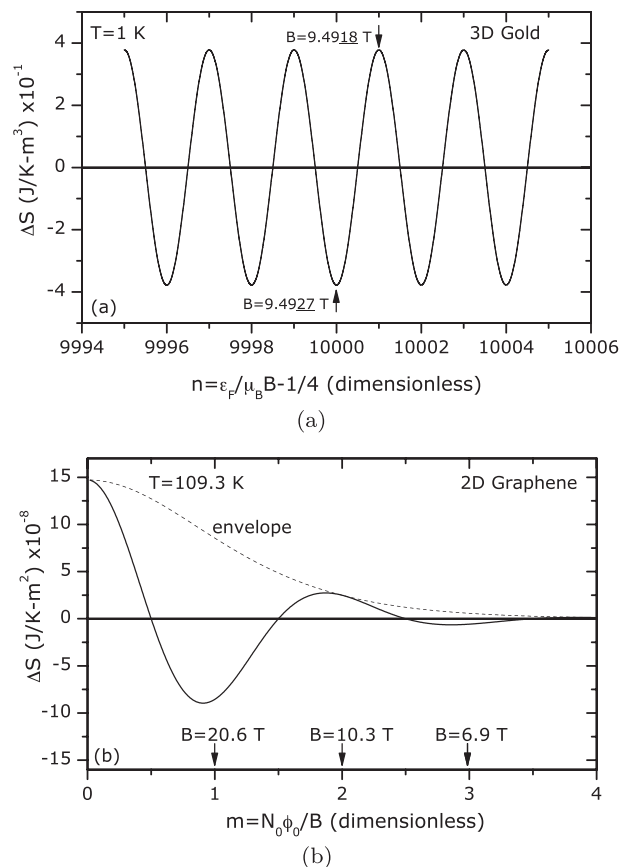
### 3.2. Achievements and recent advances

Dirac materials are, for most of the cases, diamagnetic materials, like graphene. Diamagnetic materials have a small magnetic moment, without order-disorder phase transition and, consequently, in principle, these do not attract the attention for magnetocaloric applications. However, these materials present the unique thermodynamic oscillations, based on the crossing of the Landau levels with the Fermi level, as depicted on Fig. 2(b). Considering this phenomenon, M. Reis [40] explored the MCE of graphene and, in fact, found oscillations on the caloric properties, in a complete analogy with the de Haas-van Alphen effect [57]. It has been previously described that a non-relativistic material (Gold) would present similar effect close to 1 K, with 1 mT for the

period of oscillations [61]. For graphene, due to the relativistic dispersion relation and the high Fermi velocity, the MCE was found above 100 K, with an oscillatory period close to 10 T [40]. See Fig. 3.

After this initial assessment of the subject, several other works have been developed, such as the study of the influence of longitudinal electric field on the oscillating magnetocaloric effect (OMCE) [39] and the electrocaloric effect [43] on graphene. Deepening the understanding of the theme, the OMCE of more complex structures of graphene has been explored, as bilayer [37], multilayer [38], and comparison cases [63]. More recently, Y. Benhouria and co-workers have described the dynamic MCE of ferromagnetic multilayer graphene, using quantum Monte Carlo simulation [64] and found a dependence of the relative cooling power on the period of the magnetic field excitation. It is worth mentioning the Brayton cycle based on the oscillatory caloric properties of graphene; however, this proposal is still of academic nature [6].

Theoretical results describing the fundamentals of graphene proposed that mechanical strain creates a strong local gauge field [65], only because of its massless Dirac band structure. This local pseudo-magnetic field has been experimentally verified by N. Levy and co-workers [66] on a graphene nanobubbles submitted to strain. The local field was found to be greater than 300 T. These works opened the doors for a new area of research, named as ‘straintronics’ [67]. In what concerns the caloric properties, S. Lisenkov et al. used atomistic simulations to study the elastocaloric of graphene (and carbon nanotubes) [68], and found 3.6 K of adiabatic temperature change under an applied strain of 2.5 GPa for graphene. N. Ma and M. Reis [4] have also studied, theoretically, the barocaloric effect (BCE) of graphene, and found those characteristic



**Fig. 3.** Oscillating magnetocaloric effect as a function of a dimensionless quantity, proportional to the reciprocal magnetic field for (a) a non-relativistic diamagnetic material (Gold) and (b) a relativistic diamagnetic material (graphene). The electronic structure of these two materials is responsible for this difference. Reprint from Refs. [62] with permission of the *American Institute of Physics*.

oscillations due to the crossing of the Landau levels (due to the strain) with the Fermi level; with a match between the BCE and the MCE. Later [3], the same authors described the oscillating adiabatic temperature change. In few words, a graphene sheet is able to cool down or heat up depending on the value of the mechanical strain. The absolute value of adiabatic temperature change is of the order of 0.1 K for a base temperature of 100 K. See Fig. 4 for better understanding of this oscillating effect.

From the experimental side, H. Zhu and co-workers [69] provided a graphene-based superlattice with intercalated metal-oxide frameworks and graphene. The authors found the maximum value of magnetic entropy change of 0.4 J/kgK, at 240 K and 1.5 T of magnetic field change - a result remarkably larger than the parent compound  $\text{VO}_2$  [70]. Lu Yang et al. [71] verified that 1.0 wt% of incorporation of graphene nanofillers into electrocaloric polymer is able to enhance the electrocaloric effect (ECE), for low values of electric field: the authors obtained a magnetic entropy change of 24.8 J/kgK and an adiabatic temperature change of 5.2 K, under a low electric field of 40 MV/m. T. Prabhakaran and co-authors [72] prepared  $\text{Ni}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4$ /graphene nanocomposites and observed also an enhancement of the caloric properties due to the structural coupling of the parent compound with graphene. The authors claimed that the observed caloric properties were greater than the ferrites results reported so far. I. Kucuk et al. [73] prepared a composite of manganite and graphene nanoplates  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ :GNPs and found that the magnetic entropy change increases, in comparison to the parent compound, for 2% of GNP. Z. Han and co-workers [74] produced a graphene-based device with a giant electrocaloric effect, with an adiabatic temperature change close to 7 K at 383 K, under an electric field of 857 kV/cm. V. Korolev et al. [75] measured the magnetocaloric potentials of graphene oxide flakes for 1 T of magnetic field change. The most important result from this last work is the experimental challenge, measuring, for the first time, the caloric potential of graphene oxides using microcalorimeters around room temperature. From the best of our knowledge, these are the experimental contributions discussing the caloric effect of graphene-based materials.

Note, most of the contributions discussing the caloric effect on Dirac materials, up to now, is related to graphene. However, very recently, two works have discussed the MCE of other classes of DM. A. Ali and Y. Singh [41] explored the anisotropies of the ferromagnetic Weyl semi-metal  $\text{Co}_3\text{Sn}_2\text{S}_2$  to study the rotating magnetocaloric effect. A. Bestwick and co-workers [76] used the MCE of topological insulators for cooling the sample below the dilution refrigerator base temperature.

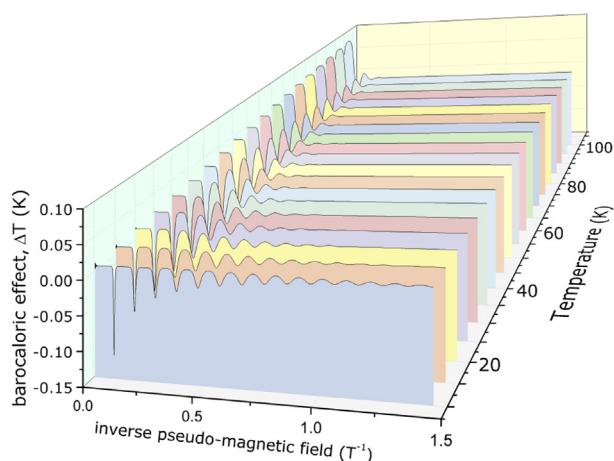


Fig. 4. Oscillating barocaloric effect for graphene, represented as the adiabatic temperature change, as a function of the inverse pseudo-magnetic field, proportional to the mechanical strain applied to the graphene sheet. The result is presented for several base temperatures. Reprint from Refs. [3], under the terms of the Creative Commons CC BY license.

#### 4. Quantum dots

Quantum dots (QDs), also named as ‘artificial atoms’, are man-made nanoscale crystals composed of periodic groups of IV, II-VI, IV-VI or III-V semiconductor materials such as Si, Ge, ZnS, CdS, CdSe, CdTe, ZnSe, PbS, PbSe, InP, InAs, and others. Their reduced size induces a shift of the electronic excitations to higher energy, concentrating the oscillator strength into just a few transitions, conferring unique quantum-confined photonic and electronic properties. With tunable core sizes, it is possible to attain a broad adsorption profile, narrow, size-dependent, and symmetric photoluminescence spectra, depending on the constituent materials. QDs show also strong resistance to photobleaching and chemical degradation, significant photostability and high quantum yields. These artificial semiconductor nanoparticles have many applications in composites, solar cells and fluorescent biological labels. Although physically larger than organic dyes and fluorescent proteins, their cumulative optical properties offer great biological utility. There are important reviews in the literature about this topic [77,78].

In what concerns the connection with caloric effects, there are few results in the literature about quantum dots, such as the one from O. Negrete and co-workers [34], who have detailed studied the magnetocaloric effect due to spin and spinless non-interacting electrons trapped into a semiconductor quantum dot. The authors observed that the addition of spin changes the character of the MCE, from normal to inverse. In addition, they also claimed that the characteristic frequency of the parabolic confinement potential of the dots is also able to tune the character of the MCE (either normal or inverse), with direct consequences on the applications of the material. The same group [33], in the same year of 2018, explored the MCE of a model combining a repulsive potential ( $U(r) \propto r^{-2}$ ) and an attractive one ( $U(r) \propto r^2$ ). The consequence is the confinement of the electron into a ring, with an antidot at the center of the nanostructure. The authors noticed that, changing the antidot radius (related to the chemical potential and parameters of the repulsive potential), it is also possible to change the character of the MCE, from normal to inverse. F. Peña et al. [79,80], based on the knowledge of the previous works, started discussing the semiconductor and graphene quantum dots into the scenario of quantum thermodynamics, comparing the classical and quantum approach for a magnetic Otto cycle. A description of quantum thermodynamics is beyond the scope of the present work, in spite to be in connection with the topic. We did not find any experimental result about the caloric performance of quantum dots.

We stress there are several kinds of QDs. Those created from external electrodes, doping, strain, impurities, as well as interface between two different semiconductor. These confinements will firstly affect the quantized energy spectrum of the dots and then their caloric properties, thereby leading to the possible multicaloric effects, including electro-, magneto- and baro-caloric effects. Theoretical and experimental research about multicaloric effects on QDs will certainly draw much attention in the future. The works above presented are of great importance, considering those have paved the way for further research.

#### 5. Frustrated magnets

Frustration can be caused by either competing interactions or geometric factors, such as triangular-packed spins with antiferromagnetic interactions. Real magnetic systems have some degree of frustration, due to the possible competition of several magnetic interactions; however, for this section, we will focus on the geometric frustrated magnetic system and their physical properties. One consequence of geometric magnetic frustration, for instance, is the quantum spin liquid (QSL), a state of matter where magnetic ordering is suppressed down to zero temperature due to strong quantum fluctuations. For a deep reading about frustrated magnets, see Ref. [81].

Some authors have studied the influence of frustration on the caloric effects, as the case of J. Zemen and co-workers [82], who modeled a geometrically frustrated magnetic structure and then evaluated the

barocaloric effect, proposing then a barocaloric cooling cycle. This phenomenology was possible due to the strong spin-lattice coupling linked to the magnetic frustration. The authors suggested  $Mn_3AN$  ( $A = Rh, Pd, Ag, Co, Ni, Zn, Ga, In, Sn$ ) as a new class of barocaloric materials. Following the same idea, D. Matsunami et al. [83] examined how geometric frustration in antiferromagnetic compounds could enhance the barocaloric effect, studying the behavior of frustrated antiferromagnets  $Mn_3GaN$ . They found an entropy change of 22.3 J/kgK for 139 MPa of pressure change, near room temperature. Recently, D. Boldrin and co-workers [84] obtained, for the geometrically frustrated antiferromagnet  $Mn_3NiN$ , a large pressure-driven isothermal entropy change of 35 J/kgK, for 280 MPa of pressure change around the Néel temperature (close to 250 K). For the sake of comparison, the standard metal  $Gd_5Si_2Ge_2$  presents 13 J/kgK, for 300 MPa of pressure change and 265 K [85].

H. Hamilton et al. [86] studied a magnetic metal organic framework (MOF), as an example of 2D material with triangles-in-triangles or triangulated-Kagome-lattice. They found remarkable possibilities of materials design via chemical perturbations and, consequently, changes in the degree of magnetic frustration. These results had direct implications for the MCE applications, as suggested by the authors. R. Li et al. [87] presented the *Gaudefroyite*, a Kagome lattice with frustrated Mn ions and a quantum spin-liquid behavior below 9 K. The authors found a MCE of 15 J/kgK, at 14 K and 7 T of magnetic field change. This value of entropy change is related to geometric frustration, as also claimed by other authors [88,89]. More recently, T. Isono and co-workers [90], apart from MCE application, have used the MCE to show a decoupled spin-lattice ordering in the quantum spin-liquid state, for some organic spin-1/2 triangular-lattice with antiferromagnet spin ordering. These results make clear the possibility of using frustrated antiferromagnetic materials as solid-state coolant.

## 6. Perspectives and concluding remarks

Almost the totality of results discussing the caloric properties of Dirac materials for applications and academical purposes are related to graphene. Theoretical results are focused on the oscillatory behavior of the thermodynamic quantities of single, double and multilayer graphene; and, for a while, these results are limited to this phenomenon. The results are interesting from the academic point of view; however, those lack experimental validation for further studies. Considering the nature of this caloric effect (based on the Landau structure change), it is unrealistic a direct comparison with standard magnetic metals (in which have their caloric effect based on magnetic ordering change).

On the other hand, the experimental results are promising, from the caloric perspective and practical purpose. It is clear, from the review presented above, that all prepared graphene-based nanocomposites have their caloric properties enhanced. This is therefore an excellent strategy to follow in the future, producing new composites and heterostructures for caloric applications. Possibilities are: sol-gel based oxides and multiferroics composites [91] doped with graphene, for multicaloric purposes.

As could be noticed for graphene-based works, the experimental and theoretical results are completely detached from each other. There is no matching among the theoretical and experimental achievements in relation to sample kind, temperature range, external excitation, etc; and for future advances in the subject, theory and experiment must communicate.

Quantum dots were also reviewed along this work. The caloric properties of these materials (and antidots) can be set as either normal or inverse by managing their physical parameters, such as spin and confinement potential. Frustrated magnets have also been reviewed due to their enhanced barocaloric properties. As described along the corresponding section, frustration can be caused by either competing interactions or geometric factors and, consequently, induce quantum effects, such as quantum spin liquids. We have reviewed the literature and highlighted that, for some materials, specially the  $Mn_3AN$  ( $A = Rh,$

$Pd, Ag, Co, Ni, Zn, Ga, In, Sn$ ), a strong spin-lattice coupling takes place. The consequence is a large barocaloric effect, for a small value of applied pressure, across the Néel temperature of the system, usually near room temperature. For instance, for  $Mn_3NiN$ , the isothermal entropy change was found close to 35 J/kgK, for 280 MPa of pressure change, around the Néel temperature of 250 K. Another class of materials, the metal complexes, deserves special attention and gained a special review elsewhere [19].

We are convinced that quantum materials constitute a special class of materials, with a sort of advanced and emerging features that deserve to be explored.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## CRediT authorship contribution statement

**Mario S. Reis:** Conceptualization, Writing - original draft, Writing - review & editing. **Ning Ma:** Writing - original draft, Writing - review & editing.

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