Prediction of large barocaloric effects in thermoelectric superionic materials

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We predict the existence of large barocaloric effects above room temperature in the thermoelectric fast-ion conductor Cu₂Se by using classical molecular dynamics simulations and first-principles computational methods. A hydrostatic pressure of 1 GPa induces large isothermal entropy changes of $|\Delta S| \sim 15-45 \text{ J kg}^{-1} \text{ K}^{-1}$ and adiabatic temperature shifts of $|\Delta T| \sim 10 \text{ K}$ in the temperature interval $400 \leq T \leq 700 \text{ K}$. Structural phase transitions are absent in the analysed thermodynamic range. The causes of such large barocaloric effects are significant $P$-induced variations on the ionic conductivity of Cu₂Se and the inherently high anharmonicity of the material. Uniaxial stresses of the same magnitude, either compressive or tensile, produce comparatively much smaller barocaloric effects, namely, $|\Delta S| \sim 1 \text{ J kg}^{-1} \text{ K}^{-1}$ and $|\Delta T| \sim 0.1 \text{ K}$, due to practically null influence on the ionic diffusivity of Cu₂Se. Our simulation work shows that thermoelectric compounds presenting high ionic disorder, like copper and silver-based chalcogenides, may render large mechanoicaloric effects and thus are promising materials for engineering solid-state cooling applications that do not require the application of electric fields.

I. INTRODUCTION

Conventional cooling technologies are based on compression cycles of greenhouse gases (e.g., hydrofluorocarbons), which pose serious threats to the environment. One kilogram of a typical refrigerant gas is, in terms of greenhouse impact, equivalent to two tonnes of carbon dioxide, which equals the total emissions produced by a car running uninterruptedly during six months [1]. Current cooling technologies, in addition, present two other important limitations, namely, the energy efficiency of the refrigeration cycles are relatively low ($<60\%$) [2], and they cannot be scaled down to small sizes (e.g., microchip dimensions).

Solid-state cooling is an emergent refrigeration technology that exploits thermal effects in materials, and which could solve most of the problems associated with traditional vapour-compression refrigeration. For instance, solid-state cooling systems do not represent any environmental threat in terms of greenhouse gas emissions and in principle can be reduced in size to fit within portable devices. The absence of moving parts and silent operation represent additional advantages over traditional refrigeration technologies. Two broad families of materials that are employed in solid-state cooling applications are caloric [2] and thermoelectric [3] compounds.

Caloric materials react thermally to external coercive fields like electric and magnetic bias [2] [4] [6] and mechanical stresses [7] [9]. Caloric effects result from field-induced transformations that involve large changes in entropy ($\sim 10–100 \text{ J kg}^{-1} \text{ K}^{-1}$). One typical example of caloric materials are shape-memory alloys (e.g., near equiatomic Ni-Ti alloys), which exhibit superb elastic properties and a martensite to austenite phase transition with a large latent heat that can be triggered by external fields [7] [9]. Solid-state cooling energy efficiencies of $\sim 75\%$ have been demonstrated for some caloric materials and further improvements appear to be within reach [2] [10].

Meanwhile, thermoelectric materials create an electric potential when subjected to a temperature gradient and vice versa, that is, they generate a temperature gradient when subjected to an electric bias. Thermoelectric refrigerators exploit the latter effect, known as the Peltier effect, and thus cooling is achieved via the application of electric fields [3] [11]. The efficiency of thermoelectric materials is measured by a dimensionless parameter called “thermoelectric figure of merit”, which typically adopts values of $\sim 1$ for good specimens [12]. Unfortunately, the energy efficiency of current thermoelectric refrigerators are relatively low as compared to that of conventional vapour compression systems [13]. Actually, much higher thermoelectric figures of merit than $\sim 1$ are necessary for thermoelectric coolers to become commercially viable [13].

Copper selenide, Cu₂Se, is an inorganic compound for which recently huge thermoelectric figures of merit of $\sim 2$ have been reported experimentally at high temperatures ($\sim 1,000 \text{ K}$) [14]. Above room temperature, the copper ions in Cu₂Se become highly mobile and the system enters a “superionic” state [15] [16] that is characterised by a very low lattice thermal conductivity ($\sim 1 \text{ W m}^{-1} \text{ K}^{-1}$) [14] [17]. The resulting “liquid-like” behaviour of the Cu ions appears to be the main cause for the huge thermodynamic figure of merit observed in this material. Likewise, large thermoelectric figures of merit have been reported for analogous superionic Cu- and Ag-based chalcogenides like Cu₄S, Cu₂Te, Ag₂Se, Ag₃S, Ag₃Te, and Cu₂−xAgₓX (X = S, Se and Te) alloys [18] [20]. Nevertheless, most of such thermoelectric fast-ion conductors exhibit low thermodynamic stability when subjected to strong electric fields owing to undesired electromigration [21] [22]. Consequently, these materials are not suitable for engineering practical solid-state cooling applications based on the Peltier effect due to limiting degradation issues [22].

In this study, we present theoretical evidence showing that thermoelectric superionic materials typified by Cu₂Se may exhibit large barocaloric effects when subjected to hydrostatic pressure (that is, barocaloric effects). In particular, an isotropic compression of $\sim 1 \text{ GPa}$ in the temperature interval $400 \leq T \leq 700 \text{ K}$ induces a sig-
nificant decrease in the ionic diffusivity of Cu$_2$Se, which translates into a large decrease in lattice entropy and overall enhancement in the thermodynamic stability of the system. Anharmonicity, which is inherently high in superionic materials [23],[25], also plays an important role on the estimated large entropy variations. The adiabatic temperature shifts accompanying the barocaloric effects amount to $\sim 10$ K, which are reasonably large as compared to those reported for other known barocaloric materials. Caloric effects produced by moderate uniaxial stresses (that is, elastocaloric effects), on the contrary, are quite small ($\sim 0.1$ K) due to practically negligible influence on the ionic diffusivity of Cu$_2$Se. Our study suggests that thermoelectric materials presenting high ionic disorder could be used for engineering solid-state cooling applications that do not require the application of electric fields, thus getting rid of potential thermodynamic instability issues.

II. COMPUTATIONAL METHODS

Molecular dynamics (MD) ($N$, $P$, $T$) simulations were performed with the LAMMPS code [26]. The pressure and temperature in the system were kept fluctuating around a set-point value by using thermostatting and barostatting techniques in which some dynamic variables are coupled to the particle velocities and simulation box dimensions. The interactions between atoms were modeled with the Morse potential reported by Namsani et al. in work [27]. This potential reproduces within a few percent the structural and elastic properties of Cu$_2$Se at high temperatures as reported from experiments and first-principles calculations [27]. The Coulombic interactions between ions, however, were neglected in this study in order to reproduce correctly the superionic behavior of Cu$_2$Se at high temperatures (Sec III).

We employed large simulation boxes, typically containing 14,000 atoms, and applied periodic boundary conditions along the three Cartesian directions. Off-stoichiometric Cu$_2$Se configurations were generated by removing a specific number of cations and anions randomly from the simulation cell (in order to fulfill the condition of charge neutrality). Newton’s equations of motion were integrated using the customary Verlet’s algorithm and a time-step length of $10^{-3}$ ps. Γ-point sampling for integration within the first Brillouin zone was employed in all the AIMD simulations. The total duration of each AIMD run was $\sim 200$ ps.

Ionic diffusion coefficients, $D_{Cu}$ and $D_{Se}$, were calculated with the formula [24]:

$$ D_i = \lim_{t \to \infty} \frac{\langle |R_i(t + t_0) - R_i(t_0)|^2 \rangle}{6t}, $$

(1)

where $R_i(t)$ is the position of the migrating ion labelled as $i$ at time $t$, $t_0$ an arbitrary time origin, and $\langle \cdots \rangle$ denotes average over time and particles. The mean squared displacement of each ionic species is defined as $\langle \Delta R_i^2(t) \rangle = \langle |R_i(t + t_0) - R_i(t_0)|^2 \rangle$.

Isothermal entropy changes associated to the barocaloric effect were estimated as [2]:

$$ \Delta S(P_{\text{max}}, T) = -\int_{P_0}^{P_{\text{max}}} \left( \frac{\partial V}{\partial T} \right)_P dP, $$

(2)

where $P_{\text{max}}$ represents the maximum applied hydrostatic pressure, and $V$ the volume of the system. In the case of elastocaloric effects, the same quantity is calculated as [2]:

$$ \Delta S(\sigma_{\text{max}}, T) = V_0 \int_{0}^{\sigma_{\text{max}}} \left( \frac{\partial \epsilon}{\partial \sigma} \right)_\sigma d\sigma, $$

(3)

where $\sigma_{\text{max}}$ represents the maximum uniaxial stress applied along an arbitrary Cartesian direction (denoted here as $z$), $\epsilon$ the strain deformation that the system undergoes along the same direction (i.e., $\epsilon(\sigma, T) = \frac{L_z(z, T) - L_z(0, T)}{L_z(0, T)}$, where $L_z$ corresponds to the length of the simulation box along the Cartesian $z$ direction), and $V_0$ the equilibrium volume of the system. Finally, the resulting adiabatic temperature shifts were estimated with the formula:

$$ \Delta T(\sigma_f, T) = -\int_{0}^{\sigma_f} \frac{T}{C_\sigma(T)} \cdot dS, $$

(4)

where $C_\sigma(T) = \left( \frac{dU}{dT} \right)_\sigma$ is the heat capacity of the crystal, which has been calculated at each specific set of stress–temperature conditions.
Copper selenide exhibits two crystalline phases, a low-temperature phase (α) that is stable up to ~ 400 K and a high-temperature phase (β) that is superionic [31]. The exact structure of the α phase still remains under debate [32, 33] however recent works have proposed that is monoclinic with space group $P2_1/c$ [34, 35]. The β phase exhibits the well-known cubic fluorite structure found in many binary fast-ion conductors (e.g., CaF$_2$ and UO$_2$) [25, 36], in which the Se ions are arranged according to a face-centered cubic lattice (space group $Fmar{3}m$) (Fig. 1a). Copper ions in the β phase diffuse throughout the crystal by hopping between tetrahedral sites and off-centered octahedral interstitial positions [16, 37, 38] (Fig. 1b–c). The critical temperature of the $\alpha \rightarrow \beta$ phase transition can be modified in practice with alloying and hydrostatic pressure as well [31].

Figure 1 shows the Cu diffusion coefficients, $D_{Cu}$, measured recently by Voneshen et al. at different temperatures by using neutron spectroscopy techniques [39]. $D_{Cu}$ values of $\sim 10^{-7}-10^{-6}$ cm$^2$s$^{-1}$ have been reported within the temperature interval $500 \leq T \leq 900$ K. Our theoretical first-principles results obtained from $ab\text{ initio}$ molecular dynamics (AIMD) simulations systematically overestimate those experimental $D_{Cu}$ values by roughly one order of magnitude. For instance, at $T = 500$ K (900 K) Voneshen et al. report 5.5 · $10^{-7}$ (3.4 · $10^{-6}$) cm$^2$s$^{-1}$ whereas we obtain 3.8 · $10^{-6}$ (4.2 · $10^{-5}$) cm$^2$s$^{-1}$. It should be mentioned, however, that in a previous experimental quasi-elastic neutron scattering study by Danilkin et al. much larger $D_{Cu}$ values than found by Voneshen et al. were reported at temperatures close to the $\alpha \rightarrow \beta$ transition [16]. Specifically, a Cu diffusion coefficient of $6.1 \cdot 10^{-5}$ cm$^2$s$^{-1}$ was measured at $T = 430$ K [16], which is significantly higher than our estimations based on AIMD simulations. Hence, there seems to be a lack of quantitative agreement between the sets of experimental $D_{Cu}$ data reported to date for $\beta$–Cu$_2$Se, and thus probably additional experiments are necessary to resolve such discrepancies.

We performed molecular dynamics (MD) $(N,P,T)$ simulations with the Morse potential proposed by Nam-sani et al. for $\beta$–Cu$_2$Se [24], considering both stoichiometric and off-stoichiometric systems. Unexpectedly, we found that for all the analysed compositions the reproduced ionic diffusivities were practically null ($D_{Cu} < 10^{-9}$ cm$^2$s$^{-1}$) at temperatures as high as 1,000 K.

Incidentally, we realized that by reducing the value of the ionic charges the diffusion of the copper ions increased. Actually, the best agreement between our MD results (considering a realistic off-stoichiometry of 2%) and the sets of experimental and AIMD $D_{Cu}$ data was obtained for neutrally charged particles (Fig. 1d). In that particular case the Cu diffusion coefficients estimated with MD at $T = 500$ K and $900$ K, for instance, are $7.9 \cdot 10^{-9}$ and $1.3 \cdot 10^{-5}$ cm$^2$s$^{-1}$, respectively. In view of these outcomes, and of the importance of accounting for ionic disorder in the simulation of superionic Cu$_2$Se, we decided to perform the subsequent analysis of mechanocaloric effects by adopting null ionic charges. As it is explained below, we do not expect that such a modification of the original interatomic potential will introduce significant bias on the determination of realistic mechanocaloric effects in $\beta$–Cu$_2$Se.

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**FIG. 1.** General description of Cu$_2$Se. a Ball-stick representation of the high-$T$ cubic structure known as fluorite (space group $Fmar{3}m$); for clarity purposes, the Cu ions are represented orderly in a simple cubic lattice b Tetrahedra formed by Se ions on the vertices; the center of the tetrahedra are described by the pseudocubic Wyckoff position 8c ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$). c Octahedra formed by Cu ions on the vertices; the center of the octahedra are described by the pseudocubic Wyckoff position 4d ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$). d Ionic diffusion coefficients estimated at different temperatures from neutron spectroscopy experiments [39], first-principles calculations based on density functional theory (AIMD-DFT), and molecular dynamics simulations performed with the Morse potential reported in [27] considering null ionic charges (MD-FF).
FIG. 2. Barocaloric effects in bulk Cu$_{2-\delta}$Se at temperatures $400 \leq T \leq 700$ K. a Ionic diffusion coefficients calculated at zero pressure and b $P = 1$ GPa. c Isothermal entropy changes induced by a maximum hydrostatic pressure of 1 GPa. d Adiabatic temperature changes induced by a maximum hydrostatic pressure of 1 GPa.

A. Barocaloric effects

The normal ($\alpha$) to superionic ($\beta$) phase transition in Cu$_2$Se is very promising from a barocaloric point of view since it involves a large change of entropy (that is, a latent heat of $|\Delta S| = 78.4$ J kg$^{-1}$ K$^{-1}$ [40]) and it is sensitive to hydrostatic pressure, $P$. In particular, the critical $\alpha \rightarrow \beta$ transition temperature decreases under compression according to the numerical relationship $T_{\alpha\rightarrow\beta} = 408 - 0.624 P - 0.012 P^2$ (where temperature is in units of K and pressure of kbar) [31]. A rough estimation of the potential barocaloric effects associated to such a first-order transition based on the experimentally reported values of the heat capacity ($C_P \approx 400$ J kg$^{-1}$ K$^{-1}$ [14]) and latent heat, that is, $|\Delta T| = -\frac{T}{|\Delta S|}$ [2], leads to a colossal adiabatic temperature change of $\sim 80$ K. This value is much larger than the $|\Delta T|$ measured in the archetypal fast-ion conductor AgI with differential scanning calorimetry techniques (36 K), in which an analogous order-disorder phase transformation occurs close to room temperature [41]. Nevertheless, the exact nature of the low-$T$ phase in Cu$_2$Se has not been determined yet unequivocally and consequently we cannot simulate that phase with reliability. Hence, we are not going to analyse here the barocaloric effects associated with the $\alpha \rightarrow \beta$ phase transition. Experimental investigations on such potentially colossal barocaloric effects are in fact highly desirable.

Meanwhile, large barocaloric effects have been recently predicted for the superionic conductor Li$_3$N near room temperature, in which no structural phase transition occurs when applying moderate hydrostatic pressures on it [42]. In particular, large isothermal entropy changes of about 25 J kg$^{-1}$ K$^{-1}$ have been estimated at $T = 300$ K and $P = 1$ GPa, which result from stress-induced variations on the volume an ion-transport properties of the material. Here, we investigate the possible existence of barocaloric effects in $\beta$–Cu$_2$Se at high temperatures, $400 \leq T \leq 700$ K, caused by similar atomistic mechanisms than in Li$_3$N.

Figures 2a-b show the influence of hydrostatic pressure on the diffusion coefficient of copper ions in $\beta$–Cu$_2$Se, for
FIG. 3. Thermodynamic properties of Cu$_{2-\delta}$Se at temperatures $400 \leq T \leq 700$ K. 

(a) $T$-derivative of the volume calculated at zero pressure and $P = 1$ GPa. Thermal expansion coefficients defined as $\alpha_T = \frac{1}{V} \left( \frac{dV}{dT} \right)_P$ are shown in the insets. 

(c) Heat capacity calculated at zero pressure and $P = 1$ GPa. 

which we have considered several representative compositions [31]. In all the cases, ionic transport is significantly depleted under an isotropic compression of 1 GPa. For instance, at $T = 700$ K and zero pressure we estimate $1.3 \cdot 10^{-6}$ and $1.8 \cdot 10^{-6}$ cm$^2$s$^{-1}$ for Cu$_2$Se and Cu$_{1.90}$Se, respectively, whereas at the same temperature and $P = 1$ GPa we obtain $3.1 \cdot 10^{-7}$ and $5.2 \cdot 10^{-7}$ cm$^2$s$^{-1}$. Such large reductions in $D_{Cu}$ suggest the presence of large entropy variations as induced by pressure; also, they indicate a potential enhancement in the overall thermodynamic stability of the material. Figure 2c reports the isothermal entropy changes that we have explicitly calculated in $\beta$-Cu$_2$Se by using Eq.(2) and considering a maximum pressure of 1 GPa. Such estimated entropy changes in fact turn out to be quite large. Specifically, we obtain negative values of $|\Delta S| \sim 15$–$45$ J kg$^{-1}$ K$^{-1}$ throughout the selected temperature interval, in which the largest entropy variations are attained at the highest considered $T$. 

Besides the large $D_{Cu}$ variations caused by pressure, the intrinsically high anharmonicity of $\beta$–Cu$_2$Se [16] [39] appears to contribute also significantly to the estimated isothermal entropy changes (here, we somewhat arbitrarily define “anharmonicity” as any other effect different from ionic diffusivity). By carrying out additional MD simulations in which non-zero ionic charges were adopted, and thus avoiding the appearance of ionic diffusion in the system (Sec.III), we found that the magnitude of the resulting barocaloric effects decreased by $\sim 60\%$ of their original values. Therefore, we conclude that the influence of thermodynamic mechanisms different from Cu diffusion on the barocaloric performance of $\beta$–Cu$_2$Se is about 40%.

Figure 2d shows the adiabatic temperature changes estimated directly with Eq.(4) in the high-$T$ phase of copper selenide by considering a maximum compression of 1 GPa. Large positive $\Delta T$ values of 8.50–10.25 K are obtained within the selected temperature range. The calculated adiabatic temperature shifts increase steadily with temperature for $T \geq 500$ K and are slightly larger in the stoichiometric system at temperatures below that point. In Sec.IV we will discuss and compare the magnitude of
the barocaloric effects predicted for $\beta$–Cu$_2$Se with those known from other materials reported in the literature.

In Fig.3 we represent the value of the estimated $T$-induced volume variations and heat capacity as a function of temperature, pressure and composition. Such properties are used directly for computing $\Delta S$ and $\Delta T$ (Eqs.2 and 4), hence they are very relevant from a numerical point of view. The variation of the volume with respect to temperature behaves quite regularly as a function of $T$ and $P$. In particular, $\left(\frac{\partial V}{\partial T}\right)_P$ displays a parabolic-like temperature dependence and it decreases under pressure (Figs.3a-b). The heat capacities computed for $\beta$–Cu$_2$Se and Cu$_{1.96}$Se exhibit similar dependences on $P$ and $T$ than their corresponding $T$-derivatives of the volume (Figs.3c-d). However, the $C_P$ of $\beta$–Cu$_{1.96}$Se presents an anomalous behaviour since it increases noticeably under compression (we tentatively ascribe this tendency to some sort of effective interaction between point defects that is induced by $P$). We note that the results enclosed in Figs.3a-d indicate a need for explicitly considering the $P$-dependence of $C_P$ in the calculation of $\Delta S$ and $\Delta T$, since this quantity may vary quite broadly under pressure (for instance, at 700 K we calculate 2280 and 4141 J kg$^{-1}$ K$^{-1}$ for the stoichiometric system at 1 GPa and zero pressure, respectively).

In the insets of Figs.3a-b, we enclose the thermal expansion coefficients, $\alpha_T = \frac{1}{V} \frac{\partial V}{\partial T}$, calculated for $\beta$–Cu$_2$Se at different pressures, temperatures and compositions. In general, we obtain much larger $\alpha_T$ values than measured experimentally at zero pressure [14]. For instance, at $T = 400$ K we compute $11.4 \cdot 10^{-5}$ K$^{-1}$, which is about 5 times larger than the corresponding value determined in the experiments. A possible cause for these discrepancies may be the neglect of electrostatic cohesion in our MD simulations. We note that such a $\alpha_T$ overestimation is likely to propagate into a certain overestimation of the $\Delta S$ values reported in this work. Regarding the heat capacity, our calculations also tend to amplify considerably this quantity. For instance, at $T = 600$ K and zero pressure we compute 2383 J kg$^{-1}$ K$^{-1}$, which is about 6 times larger than the corresponding value determined in the experiments.

By simultaneously considering the molecular dynamics overestimations of both $\alpha_T$ and $C_P$, however, we may conclude that our reported $\Delta T$ results should be pretty accurate due to a cancellation error between those two quantities (Eq.4). Moreover, at high temperatures our $\Delta T$ results may be regarded as a lower bound of the adiabatic temperature changes that can be achieved in practice. For instance, at $T = 700$ K the simulated $\alpha_T/C_P$ ratio turns out to be three times smaller than the corresponding experimental value [14]. Therefore, in spite of the inevitable shortcomings deriving from the use of classical potentials for simulating materials [33, 41], we are confident that the $\Delta T$ results reported in this work are reliable.

B. Elastocaloric effects

We have also investigated the potential of $\beta$–Cu$_2$Se as a candidate elastocaloric material. In particular, we have analysed the caloric response of the crystal under a maximum uniaxial compressive and tensile load of 1 GPa at different temperatures. Figure 4 shows the numerical $\Delta S$ and $\Delta T$ values obtained from molecular dynamics simulations in which we have considered uniaxial tensile stresses. The size of the estimated adiabatic temperature and isothermal entropy changes are about one order of magnitude smaller than calculated in the barocaloric case. For example, at $T = 400$ K we compute $\Delta S = -0.35$ J kg$^{-1}$ K$^{-1}$ and $\Delta T = 0.20$ K for stoichiometric $\beta$–Cu$_2$Se (to be compared with $\Delta S = -17.5$ J kg$^{-1}$ K$^{-1}$ and $\Delta T = 8.7$ K obtained in the barocaloric case). We note that the predicted elastocaloric effects present a practically negligible dependence on composition (Figs.4a-d). Very similar $\Delta S$ and $\Delta T$ values have been obtained for the case of considering compressive uniaxial stresses in the simulations, which are not shown here.

Figures 4a-b show the influence of uniaxial tensile stress, $\sigma$, on the copper ionic diffusion coefficient of $\beta$–Cu$_2$Se at several temperatures. As it is appreciated therein, under a load of 1 GPa the estimated $D_\text{Cu}$’s hardly change in comparison to the values obtained at zero stress. For example, for stoichiometric Cu$_2$Se at $T = 700$ K and $\sigma = 0$ we estimate $1.3 \cdot 10^{-6}$ cm$^2$s$^{-1}$ whereas at the same temperature and $\sigma = 1$ GPa we obtain $1.0 \cdot 10^{-6}$ cm$^2$s$^{-1}$. Such a small $\sigma$-induced reduction in the ionic diffusivity explains the minuteness and sign of the elastocaloric effects predicted for $\beta$–Cu$_2$Se. Consequently, we may conclude that thermoelectric compounds presenting high ionic disorder in principle are not promising elastocaloric materials.

IV. DISCUSSION

To date, large barocaloric effects have been experimentally measured in a number of shape-memory alloys [45, 46], polar compounds [47, 48], organic-inorganic hybrid perovskites [49], molecular crystals [50-52], and the archetypal fast-ion conductor AgI [41]. In Table I, we report several representative barocaloric compounds along with some of their basic cooling features measured at or near room temperature (made the exception of Li$_3$N, for which barocaloric experiments have not been performed yet). The thermoelectric fast-ion conductor $\beta$–Cu$_2$Se in fact turns out to be competitive with those archetypal materials in terms of barocaloric performance. The isothermal entropy change induced by a hydrostatic pressure of 1 GPa in $\beta$–Cu$_2$Se at $T = 400$ K is relatively small as compared to those measured, for instance, in the shape-memory alloy Ni$_{51}$Mn$_{33}$In$_{16}$, ferroelectric salt (NH$_4$)$_2$SO$_4$, molecular crystal (CH$_3$)$_2$C(CH$_2$OH)$_2$, and fast-ion conductor AgI (Table I). On the other
FIG. 4. Elastocaloric effects in bulk Cu$_{2−δ}$Se at temperatures 400 ≤ T ≤ 700 K. a Ionic diffusion coefficients calculated at zero uniaxial tensile stress and b σ = 1 GPa. c Isothermal entropy changes induced by a maximum uniaxial tensile stress of 1 GPa. d Adiabatic temperature changes induced by a maximum uniaxial tensile stress of 1 GPa.

hand, the |ΔS| estimated for copper selenide is larger than or similar in magnitude to those found in the shape-memory alloy Fe$_{49}$Rh$_{51}$ and archetypal ferroelectric BaTiO$_3$. In terms of adiabatic temperature shift, which arguably is the most important quality of caloric materials, β–Cu$_2$Se is better positioned. The calculated |ΔT| of 8.7 K is larger than most values reported in Table I, made the remarkable exception of the molecular crystal (CH$_3$)$_2$C(CH$_2$OH)$_2$ and fast-ion conductor AgI. It should be mentioned, however, that the experimental barocaloric effects that we review here have been obtained for hydrostatic pressures significantly smaller than 1 GPa. For this reason, the predicted barocaloric strength of β–Cu$_2$Se, which is defined as the |ΔT|/P ratio, is not particularly exceptional (∼10 K GPa$^{-1}$).

It is interesting to compare the barocaloric performance of β–Cu$_2$Se with that of Li$_3$N since both compounds are superionic and the corresponding |ΔS| and |ΔT| values have been obtained with similar computational methods [42]. The isothermal entropy change estimated in Li$_3$N is practically two times larger than the value found in β–Cu$_2$Se under same T and P conditions. The main reason for such a difference is that the ionic diffusivity in Li$_3$N is much larger than that in β–Cu$_2$Se (10$^{-3}$ versus 10$^{-9}$ cm$^2$s$^{-1}$, respectively), and thus the changes in ionic mobility caused by compression also result larger in Li$_3$N. Nevertheless, the adiabatic temperature change predicted for β–Cu$_2$Se is ∼60% larger than for Li$_3$N. This outcome is essentially due to the much smaller heat capacity estimated for the thermoelectric crystal (namely, the $C_P$ of Li$_3$N is about an order of magnitude larger than that of β–Cu$_2$Se [42]). In view of these results, we propose that an effective design strategy for enhancing likely mechanoelastic effects in fast-ion conductors may consist in optimizing the corresponding heat capacities (that is, making them as small as possible by means of composition, for instance).

It is worth reminding that the “giant” barocaloric effects (i.e., |ΔT| > 10 K) measured in the fast-ion conductor AgI (Table I) were obtained for its normal to superionic phase transition, which is of first-order type and has associated a large latent heat [41]. Copper se-
lelenium also presents a $\alpha \rightarrow \beta$ phase transition near room temperature [31] but for the reasons explained above (e.g., indetermination of the corresponding low-$T$ phase) we have restricted our analysis here to mechanocaloric effects occurring in the high-$T$ phase. Such mechanocaloric effects turn out to be large and are mostly due to continuous changes in the ionic diffusivity caused by pressure. Actually, the kind of second-order like changes disclosed here for $\beta$–Cu$_2$Se present great prospects in the context of refrigeration-cycle reversibility owing to the likely absence of mechanical hysteresis effects deriving from the nucleation of order-parameter domains [42]. Nevertheless, our rough estimation of $|\Delta T| \sim 80$ K for the normal to superionic phase transition in Cu$_2$Se (Sec III A), and the previous success achieved in AgI for the same type of transformation (Table I) [11], should motivate also experimental searches of giant barocaloric effects in thermoelectric fast-ion conductor materials near room temperature.

| $T$ (K) | $P$ (GPa) | $|\Delta S|$ (JK$^{-1}$K$^{-1}$) | $|\Delta T|$ (K) | $|\Delta T|/P$ (K GPa$^{-1}$) | Materials type | Reference |
|---------|-----------|-------------------------------|-----------------|-------------------------------|----------------|-----------|
| Ni$_2$Mn$_2$In$_16$ | 330 | 0.25 | 41.0 | 4.0 | 16.0 | SMA | 15 |
| Fe$_{49}$Rh$_{51}$ | 310 | 0.11 | 12.5 | 8.1 | 73.6 | SMA | 16 |
| BaTiO$_3$ | 400 | 0.10 | 2.1 | 1.5 | 10.0 | FE | 17 |
| (NH$_4$)$_2$SO$_4$ | 220 | 0.10 | 130.0 | 8.0 | 80.0 | FE | 18 |
| [TPrA][Mn(dca)$_3$] | 330 | 0.01 | 30.5 | 4.1 | 410.0 | OIH | 19 |
| [FeL$_2$][BF$_4$]$_2$ | 262 | 0.03 | 80.0 | 3.0 | 100.0 | MC | 20 |
| (CH$_3$)$_2$C(CH$_2$)OH)$_2$ | 320 | 0.52 | 510.0 | 45.0 | 86.5 | MC | 51,52 |
| AgI | 400 | 0.25 | 62.0 | 36.0 | 144.0 | FIC | 11 |
| Li$_3$N | 400 | 1.00 | 33.5 | 5.4 | 5.4 | FIC | 12 |
| Cu$_2$Se | 400 | 1.00 | 17.5 | 8.7 | 8.7 | TE/FIC | This work |

TABLE I. Materials presenting large ($|\Delta T| > 1$ K) or giant ($|\Delta T| > 10$ K) barocaloric effects at or near room temperature. $T$ represents working temperature, $P$ applied pressure, $|\Delta S|$ isothermal entropy change, $|\Delta T|$ adiabatic temperature change, $|\Delta T|/P$ barocaloric strength, “SMA” shape-memory alloy, “FE” ferroelectric, “OIH” organic-inorganic hybrid perovskite, “MC” molecular crystal, “FIC” fast-ion conductor, and “TE” thermoelectric.

V. CONCLUSIONS

Copper selenide and other similar silver- and sulfide-based compounds (e.g., Cu$_2$S, Cu$_2$Te, Ag$_2$Se, Ag$_2$S, Ag$_2$Te, and Cu$_2$–xAg$_x$X (X = S, Se and Te) alloys) are thermoelectric fast-ion conductor materials for which huge thermoelectric figures of merit have been reported. However, owing to their ionic transport properties these materials are prone to suffer severe structural degradation when subjected to intense electric fields. In this computational work, we have shown that by applying moderate hydrostatic pressures of $\sim 1$ GPa it is possible to reduce significantly the ionic diffusivity of Cu$_2$Se, thus improving its thermodynamic stability, and to induce large barocaloric effects near room temperature. It is very likely that similar $P$-induced phenomena will occur also in analogous thermoelectric superionic materials.

The caloric response of Cu$_2$Se is mostly originated by substantial changes on its ionic conductivity caused by compression. Such large barocaloric effects, namely, $|\Delta S| \sim 17.5$ J kg$^{-1}$ K$^{-1}$ and $|\Delta T| = 8.7$ K at $T = 400$ K, are very promising for engineering novel solid-state cooling applications that do not require the application of electric fields. In this context, thermoelectric superionic materials are free of the degradation and energy-efficiency problems affecting solid-state refrigeration based on the Peltier effect. Moreover, we foresee the existence of giant barocaloric effects (|$\Delta T| \gg 10$ K) associated with the normal to superionic phase transition that occurs in Cu$_2$Se near room temperature (not simulated explicitly in this study). Hence, our theoretical findings on Cu$_2$Se should stimulate new energy-conversion experiments in thermoelectric fast-ion conductors that potentially can lead to robust and highly efficient solid-state cooling applications.

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