Multisite Exchange-Enhanced Barocaloric Response in Mn$_3$NiN

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We study the barocaloric effect (BCE) in the geometrically frustrated antiferromagnet Mn$_3$NiN across the Néel transition temperature. Experimentally, we find a larger barocaloric entropy change by a factor of 1.6 than that recently discovered in the isostructural antiperovskite Mn$_3$GaN despite significantly greater magnetovolume coupling in Mn$_3$GaN. By fitting experimental data to theory, we show that the larger BCE of Mn$_3$NiN originates from multisite exchange interactions amongst the local Mn magnetic moments and their coupling with itinerant electron spins. Using this framework, we discuss the route to maximize the BCE in the wider Mn$_3$AN family.

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I. INTRODUCTION

The emerging field of solid-state caloric cooling offers opportunities for greater energy-efficient refrigeration without the need for environmentally harmful chemicals. Magnetocaloric properties are by far the most studied, whereas mechanocalorics including baro- and elastocalorics are only beginning to gain prominence [1–3]. In magnetocalorics, the largest effects are found in materials with contributions from both localized and itinerant magnetic moments, so called mixed magnetism with competing exchange interactions. In the intermetallics RCo$_2$ ($R$ = rare earth) [4], Mn-Fe(P,Si) [2], and La(Fe, Si)$_{13}$ [5,6] mixing of magnetic contributions and a strong coupling to the crystal lattice results in first-order transition behavior while maintaining large magnetization and a high transition temperature. These properties also lend themselves to attractive barocaloric effects (BCEs), and this complementary behavior has guided initial research in this field [3,7–11]. Recent efforts have also focused on qualitatively different material families such as ferrielectric inorganic salts [12], superionic conductors [13], and hybrid inorganic organic materials [14]. While impressive BCEs are achieved in these materials, low density of the materials, poor thermal conductivity, and long-term stability are issues that may limit their applicability. An alternative and promising family of magnetic systems which we explore here is geometrically frustrated antiferromagnets (AFMs) [15]. The most prominent example is the metallic alloy Mn$_3$GaN with giant BCEs and a large volume change at the transition where the BCE is thought to be enhanced due to the stabilization of the local moment in the non-collinear AFM phase. The authors of Ref. [15] propose that the frustrated exchange interactions in the non-collinear AFM phase lead to a relative insensitivity of the transition temperature to pressure in comparison with other magnetic barocaloric materials, and it is this feature combined with the large volume change that underlies the impressive performance of the material. Thus, the combination of geometric frustration of exchange between local Mn moments and itinerant electrons, akin to the local and itinerant character of the optimum magnetocalorics, may provide a fruitful playground through which to explore new barocaloric materials.

The Mn$_3$AN family displays a number of unusual properties, such as anomalous coefficient of resistivity.
The temperature refined from the neutron-diffraction data. (e) The shown in Figs. 1(a) and 1(b) and are hereafter termed

\[ \Gamma^{5g} \] and \[ \Gamma^{5g} \], respectively. These structures are similar to

\[ \Gamma_{\text{NiN}} \] is a fully compensated antiferromagnetic structure stable at low temperatures. \[ \Gamma^{5g} \] is also an antiferromagnetic structure (purple arrows) but has a symmetry-allowed ferromagnetic component (gray arrows) causing canting of the spins out of the (111) plane.

(c) Thermodiffractogram measured using neutron powder diffraction (\( \lambda = 1.544 \) Å) at ILL, France [24]. Rietveld refinement of the data confirms that the sample is the antiperovskite Mn\(_3\)NiN phase with only a minor MnO impurity (see Fig. S1 in the Supplemental Material [25]). The refined lattice parameter at room temperature is 3.880 75(3) Å, in excellent agreement with the literature [26], and all atomic sites are refined to within 98% occupation, thus, confirming that the sample is close to stoichiometric with a fully occupied N site. The N site occupation is particularly noteworthy, as nitrogen deficiency is reported to occur in manganese nitride compounds [27].

The temperature dependence of the neutron-diffraction data is summarized in Fig. 1(c). At \( T_N \), a clear shift in the nuclear Bragg peaks indicates a significant change in lattice parameters concomitant with the appearance of magnetic Bragg peaks. The refined lattice parameter across the transition reveals a volume change of \( \Delta V \approx 0.4\% \) [Fig. 1(d)], which is similar to that found in previous studies on this material [27,28]. The magnetic Bragg peaks are centered on the nuclear peaks, thus, confirming a \( k = 0 \) magnetic propagation vector. The temperature dependence of the magnetic structure is similar to that found previously [26]. At \( T_N \), the magnetic moments are rotated within the (111) plane roughly between the \[ \Gamma^{5g} \] and \[ \Gamma^{5g} \] structures, and upon further cooling, they rotate towards the \[ \Gamma^{5g} \] structure until approximately 220 K when this rotation is complete.
This temperature window coincides with an enlarged magnetization evidenced from the bulk magnetometry data [Fig. 1(f)], which can be explained by the symmetry-allowed ferromagnetic component of the Γ4g structure [Fig. 1(b)] [26].

Evidence of the first-order character of the transition is found in the latent heat ($Q_\ell \sim T_N \Delta S$) from the heat-flow data shown in Fig. 1(g). The total entropy change in zero pressure $S - S_{320}$ calculated from the same data as $S - S_{210} = \int_{0}^{T_{N}} [1/T]\left[(dQ)/(dT)\right]_{p=0} dT$ is presented in Fig. 1(h). We find the entropy change across $T_N$, $\Delta S_N$, at zero pressure is 43 J K$^{-1}$ kg$^{-1}$, approximately double the value found in Mn$_3$GaN [15].

### III. PRESSURE-DEPENDENT AND BAROCALORIC EFFECT MEASUREMENTS

We now turn to measurements performed under pressure (see the experimental details in the Supplemental Material [25]). The vibrating sample magnetometry (VSM) data of Fig. 2(a) show that $T_N$ shifts to lower $T$ with increased pressure. Moreover, in zero pressure the thermal hysteresis is 8 K, while under a pressure of 0.61 GPa, the hysteresis is reduced to 7 K and the transition is broadened noticeably. As shown in Fig. 2(b), the pressure sensitivity of $T_N$ ranges between $-13 \pm 1$ and $-14 \pm 1$ K GPa$^{-1}$, as determined by either high-pressure calorimetry (HC, explained below) or VSM, showing that they are in excellent agreement.

The results under pressure allow us to make a direct comparison with available data on the Mn$_3$GaN antiperovskite [15]. First, $\Delta\omega_{TN}$ at the transition of 0.4% is roughly half the value of that in the Ga system [27]. However, the sensitivity of $T_N$ with pressure $[(dT_N)/(dp)]$ of 13.5 K GPa$^{-1}$ (taken from the average of the measured values) is approximately 5 times smaller. If the magnetovolume coupling were the primary underlying mechanism for first-order character, one would expect $\Delta\omega_{TN}$ and $[(dT_N)/(dp)]$ to scale linearly, given the chemical and magnetic similarities of the two systems and that both parameters are heavily dependent on the strength of the magnetovolume coupling. By combining these values, we find the FOM $\Delta\omega_{TN}[(dT_N)/(dp)]^{-1}$ in Mn$_3$NiN is 0.03% GPa K$^{-1}$, more than double that of Mn$_3$GaN and several other known barocaloric systems [15].

We determine the BCE by quasidirect caloric measurements under pressure (see the experimental details in the Supplemental Material [25]). Temperature-dependent heat-flow measurements under pressure $[(dQ)/(dT)]_p$ recorded on cooling [Fig. 3(a)] show a sharp peak at $T_N$ that shifts to lower temperatures with applied pressure. Figure 3(b) shows that the entropy change under applied pressures decreases, falling to a value upon cooling of 34 J K$^{-1}$ kg$^{-1}$ in 0.56 GPa. This decrease is not due to additional entropy

![FIG. 2.](image)

![FIG. 3.](image)
changes associated with the thermal expansion on either side of the transition [12], as these are negligible [Fig. 1(d)]. One explanation could be that the transition broadens (becomes more weakly first order) with increased pressure, which is consistent with the shape of the $M(T)$ curve in the transition region [Fig. 2(a)]. The reduction in magnetization at the peak (of about 16% under 0.61 GPa and 0.05 T) can also contribute to the drop in the entropy change seen in Fig. 3(b). As only $\Gamma^{4g}$ has a symmetry-allowed ferromagnetic component [Fig. 1(b)], the reduced magnetization under pressure likely results from a variation of the $\Gamma^{4g}; \Gamma^{5g}$ ratio in this transitional region. However, a detailed understanding of the magnetic structure requires neutron-diffraction studies under pressure.

To calculate pressure-driven isothermal changes in entropy $\Delta S$ and pressure-driven adiabatic changes in temperature $\Delta T$, we use the total entropy curves $S = S_{210 \text{ K}}$ [Fig. 3(c)] measured under various applied pressures. The isothermal entropy changes [Fig. 3(d)] are calculated upon the release of pressure to atmospheric. The peak value of $|\Delta S|$ increases to a value of approximately $35 \text{ J K}^{-1} \text{kg}^{-1}$ by removing 0.28 GPa and subsequently saturates upon removing pressure from higher values, whereas the temperature window at which the values of $|\Delta S|$ are large increases continuously with removal of higher pressures. This maximum value of $|\Delta S|$ is approximately 1.6 times larger than Mn$_3$GaN, in approximate agreement with the relative FOM values. These entropy change values are comparable to those observed in the best-performing barocaloric materials (Table I). Moreover, the high density of Mn$_3$AN compared to other barocaloric materials means that when measured per unit volume, Mn$_3$NiN is outperformed only by two materials, AgI and MnCoGe$_{0.99}$In$_{0.01}$. Considering now $\Delta T$, both the peak value and temperature range for which $\Delta T > 0$ continuously increase upon removal of the largest applied pressure of 0.56 GPa. The largest peak value of $\Delta T$ is 5.8 K; therefore, the available adiabatic temperature change for a given pressure release $[\Delta T]/(dp)$ is 10.4 K GPa$^{-1}$. However, these values are estimated from quasidirect measurements and direct measurement of the adiabatic temperature change is required. Note that in order to drive these BCEs in a reversible manner, pressures larger than 0.56 GPa are required.

**IV. THEORETICAL MODELING**

The lack of scaling between $\Delta S_{\text{TR}}$ and $[\Delta T]/(dp)$ suggests properties beyond magnetovolume coupling contribute to $|\Delta S|$. To further understand the giant barocaloric entropy changes in Mn$_3$NiN, we carry out an analysis of our experimental data based on a description of the Gibbs free energy $G$. We design a simple generic form of $G$ drawing from our previous detailed ab initio density functional theory-based disordered local moment theory modeling of the complex magnetic phase diagrams of the heavy rare-earth metals [30], transition-metal alloys such as FeRh [21], and pertinent to this work Mn$_4$GaN [18]. Using this model, full details of which are in the Supplemental Material [25], we are able to write $G$ as

$$G = -a_2(M_1^4 + M_2^4 + M_3^4) - a_4(M_1^4 + M_2^4 + M_3^4) - c_{\text{MV}} \Delta \omega(M_1^2 + M_2^2 + M_3^2) + \frac{1}{2} \Omega T \Delta \omega^2 + \Omega T \omega p - TS_{\text{tot}},$$

where the last term is the total entropy composed by the entropy contributions from the three sublattices and AgI represent reversible effects. Other entries represent irreversible effects. Entropy changes are obtained from quasidirect calorimetric methods for all entries, expect for MnCoGe$_{0.99}$In$_{0.01}$ where entropy changes are estimated from pressure-dependent neutron diffraction.

| Material       | Transition temperature (K) | Applied pressure (GPa) | $\Delta S_{\text{max}}$ (J K$^{-1}$ kg$^{-1}$) | $\Delta S_{\text{max}}$ (J K$^{-1}$ cm$^{-3}$) | Reference |
|----------------|---------------------------|------------------------|---------------------------------------------|---------------------------------------------|-----------|
| MnCoGe$_{0.99}$In$_{0.01}$ | 310                        | 0.3                    | 52                                          | 0.42                                        | [11]      |
| (NH$_4$)$_2$SO$_4$     | 224                        | 0.1                    | 61                                          | 0.11                                        | [12]      |
| (NH$_4$)$_2$SnF$_6$    | 110                        | 0.14                   | 61                                          | 0.18                                        | [29]      |
| AgI                   | 420                        | 0.22                   | 63                                          | 0.36                                        | [13]      |
| Mn$_3$NiN             | 262                        | 0.28                   | 35                                          | 0.24                                        | This work |

TABLE I. Pressure-driven entropy changes for selected state-of-the-art barocaloric materials, listing their transition temperatures, applied pressures, and corresponding entropy changes normalized by mass or volume. Entries for (NH$_4$)$_2$SO$_4$ and AgI represent reversible effects. Other entries represent irreversible effects. Entropy changes are obtained from quasidirect calorimetric methods for all entries, expect for MnCoGe$_{0.99}$In$_{0.01}$ where entropy changes are estimated from pressure-dependent neutron diffraction.
\[ \Delta \omega = \frac{1}{\gamma \Omega} \left[ c_{\text{MV}} \left( M_1^2 + M_2^2 + M_3^2 \right) - \Omega p \right], \]

which substituted into Eq. (1) gives

\[ G = - \left[ a_2 - \frac{c_{\text{MV}}}{\gamma} p \right] \left( M_1^2 + M_2^2 + M_3^2 \right) - a_4 \left( M_1^4 + M_2^4 + M_3^4 \right) - \frac{c_{\text{MV}}^2}{2\gamma} \left( M_1^2 + M_2^2 + M_3^2 \right)^2 \]
\[ - \frac{\Omega p^2}{2\gamma} - T S_{\text{tot}}. \]  

The free energy expressed above can be minimized with respect to the magnetic order parameters for given values of \( T \) and \( p \), and, consequently, the theoretical quantities of \( T_N \), \( \left[ \frac{\langle dT_N \rangle}{\langle dp \rangle} \right] \), and \( \Delta \omega_{T_N} \) can be suitably calculated as functions of the model parameters \( a_2, a_4 \), and \( c_{\text{MV}} \).

To conclude this section, we derive the condition for which the transition from the paramagnetic state \(( M_1 = M_2 = M_3 = 0 )\) to the triangular state \(( M_1 = M_2 = M_3 \neq 0 )\) changes from second order to first order. As shown by Bean and Rodbell [31], this condition follows from requiring that the fourth-order coefficient in the order parameters of \( G \) is negative. To find this, we first write the entropy contributions \( S_n \) as an expansion in terms of \( M_n \) (see the Supplemental Material [25]),

\[ S_n = k_B \left( \log 4\pi - \frac{3}{2} M_n^2 - \frac{9}{20} M_n^4 - \ldots \right). \]

Now, from Eqs. (3) and (4) it directly follows that the condition is

\[ a_4 = \frac{3}{10} a_2 - \frac{3c_{\text{MV}}^2}{2\gamma}. \]

V. DETERMINING THE MULTISITE INTERACTION STRENGTH

By minimizing \( G \) of Eq. (3) with respect to the magnetic order parameters for given values of \( T \) and \( p \), the theoretical quantities of \( T_N \), \( \left[ \frac{\langle dT_N \rangle}{\langle dp \rangle} \right] \), and \( \Delta \omega_{T_N} \) can be calculated as a function of the model parameters \( a_2, a_4 \), and \( c_{\text{MV}} \). For instance, we show in Figs. 4(a) and 4(b) how \( T_N \) and \( \left[ \frac{\langle dT_N \rangle}{\langle dp \rangle} \right] \) depend on \( a_2 \) and \( c_{\text{MV}} \), respectively, while dependences of \( a_4 \) on (i) \( c_{\text{MV}} \) and \( \left[ \frac{\langle dT_N \rangle}{\langle dp \rangle} \right] \) and (ii) \( c_{\text{MV}} \) and \( \Delta S \) are shown in Figs. 4(c) and 4(d), respectively. Using this model combined with our experimental data on Mn$_3$NiN and literature data on Mn$_3$GaN [15], the constants \( a_2, a_4 \), and \( c_{\text{MV}} \) are determined by an iterative fitting process for both systems. The final parameters are shown in Table II.

Mn$_3$GaN has a significantly larger \( c_{\text{MV}} \) of 1107 meV compared to the small value of 250 meV for Mn$_3$NiN, consistent with the larger volume change at the transition. We propose that the 5-times-larger ratio \( \left[ \frac{\langle dT_N \rangle}{\langle dp \rangle} \right] \) observed experimentally in Mn$_3$GaN mainly originates from the larger magnetovolume coupling. Turning now to the \( a_2 \) and \( a_4 \) terms, we observe that \( a_2 \) scales mainly with \( T_N \), while positive \( a_4 \) contributes to the first-order character of the transition [see Eq. (3)], in agreement with other models based on expanding the free energy in terms of the magnetic order parameter [31,32]. Therefore, while \( \Delta \omega_{T_N} \) at the transition is smaller in Mn$_3$NiN compared to Mn$_3$GaN, the entropy change can be at least as large due to the smaller but positive \( a_1 \) term preserving a substantial \( \Delta \omega_{T_N} \), relative to the low \( \left[ \frac{\langle dT_N \rangle}{\langle dp \rangle} \right] \) from the small magnetovolume coupling. This explanation is exemplified in Fig. 4(c), which shows the dependence of \( \left[ \frac{\langle dT_N \rangle}{\langle dp \rangle} \right] \) on \( a_4 \) and \( c_{\text{MV}} \). It is clear from this plot that \( \left[ \frac{\langle dT_N \rangle}{\langle dp \rangle} \right] \) scales with \( c_{\text{MV}} \), while increasing positive \( a_4 \) leads to more first-order behavior. Hence, we understand that Ni is pushed towards the region displaying first-order behavior and, therefore, larger \( \Delta S \) [see Fig. 4(d)]. As the \( a_4 \) term originates from the
TABLE II. Experimental values of $T_N$, $\Delta \sigma_{T_x}$, and $([dT_N]/[dp])$ for Mn$_3$NiN and Mn$_3$GaN along with the calculated values of $c_{\text{MV}}$, $a_2$, $a_4$, and $\Delta S$ as described in the text. The latter, $\Delta S_{\text{CC}}$, is calculated from the Clausius-Clapeyron equation but in excellent agreement with that determined from calorimetry. The maximum magnetic entropy available for an $S = \frac{1}{2}$ Mn ion, commonly given by $\Delta S = k_B \ln(2S + 1)$ in Mn$_3$NiN and Mn$_3$GaN is 188.2 and 179.8 J kg$^{-1}$ K$^{-1}$, respectively. As such, the Mn$_3$AN family has the potential to realize much larger entropy changes.

| Material     | $T_N$ (K) | $\Delta \sigma_{T_x}$ (%) | $([dT_N]/[dp])$ (K GPa$^{-1}$) | $c_{\text{MV}}$ (meV) | $a_2$ (meV) | $a_4$ (meV) | $\Delta S_{\text{CC}}$ (J K$^{-1}$ kg$^{-1}$) |
|--------------|-----------|---------------------------|---------------------------------|------------------------|-------------|-------------|------------------------------------------|
| Mn$_3$NiN   | 262       | 0.4                       | 13.5                            | 250                    | 33          | 13          | 47                                       |
| Mn$_3$GaN   | 290 [15]  | 1.0 [15]                  | 65 [15]                         | 1107                   | 37          | −25         | 22                                       |

multisite interactions among the Mn local moments and the itinerant electron spin, it appears consistent that the larger BCE in Mn$_3$NiN relative to Mn$_3$GaN is due to these multisite terms providing an additional contribution that strongly favors the triangular state. This information provides a useful handle on the barocaloric properties of Mn$_3$AN and stimulates research on those with small magnetovolume coupling that may have been overlooked. For instance, $A =$ Co, Pd, and Rh all have significantly lower magnetovolume effects than $A =$ Ni [27], but their magnetism may have a contribution from the multisite exchange that enhances the BCE based on their potential to hybridize with the Mn $d$ band (as is the case for Ni) [19]. Moreover, it is possible to tailor quaternary compounds that offer large BCE at room temperature [27].

VI. CONCLUSION AND OUTLOOK

In conclusion, we measure the barocaloric properties of the geometrically frustrated antiferromagnet Mn$_3$NiN, a member of the Mn-based antiperovskite family Mn$_3$AN. This material displays large pressure-driven isothermal entropy changes and adiabatic temperature changes of $\Delta S = 35$ J K$^{-1}$ kg$^{-1}$ ($p = 0.28$ GPa) and $\Delta T = 5.8$ K ($p = 0.56$ GPa) near the paramagnetic to antiferromagnetic transition. The isothermal entropy change is larger than the closely related antiperovskite Mn$_3$GaN by a factor of 1.6 and within a factor of 2 of the largest entropy changes reported in the literature once normalization by density is taken into account. Considering that the magnetovolume coupling is a factor of 5 smaller in Mn$_3$NiN compared to $A =$ Ga, the results are in stark contrast to the anticipated trend that larger magnetovolume coupling naturally leads to a larger BCE. Our theoretical insights reveal that their properties are strongly linked to a combination of electronic spin effects and lattice changes. The interactions between the local moments associated with the magnetic Mn sites depend on the overall magnetic order described by the multisite interactions. Their positive value, which is set by our experimental data, acts to enhance the first-order nature of the transition in Mn$_3$NiN, and, consequently, the material retains a large volume change despite the relatively small magnetovolume coupling. This improved understanding can be used to tune the BCE in Mn$_3$AN materials and highlights the potential of discovering new materials with enhanced properties in this broad and chemically flexible family as well as frustrated magnets in general.

VII. DATA AVAILABILITY

All relevant data are presented via this publication and Supplemental Material [25].

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[1] L. Mañosa and A. Planes, *Materials with Giant Magnetocaloric Effects: Cooling by Strength*, Adv. Mater. 29, 1603607 (2017).
[2] N. H. Dung, Z. Q. Ou, L. Caron, L. Zhang, D. T. C. Thanh, G. A. De Wijs, R. A. De Groot, K. H. J. Buschow, and E. Brück, *Mixed Magnetism for Refrigeration and Energy Conversion*, Adv. Energy Mater. 1, 1215 (2011).
[3] X. Moya, S. Kar-Narayan, and N. D. Mathur, *Caloric Materials near Ferroic Phase Transitions*, Nat. Mater. 13, 439 (2014).
[4] N. K. Singh, K. G. Suresh, A. K. Nigam, S. K. Malik, A. A. Coelho, and S. Gama, *Itinerant Electron Metamagnetism and Magnetocaloric Effect in RCo$_2$-based Laves Phase Compounds*, J. Magn. Magn. Mater. 317, 68 (2007).
[5] A. Fujita and K. Fukamichi, *Giant Volume Magnetostriction due to the Itinerant Electron Metamagnetic Transition in La[Fe-Si]$_{13}$ Compounds*, IEEE Trans. Magn. 35, 3796 (1999).
[6] M. E. Gruner, W. Keune, B. R. Cuenya, C. Weis, J. Landers, S. I. Makarov, D. Klar, M. Y. Hu, E. E. Alp, J. Zhao, M. Krautz, O. Gutfleisch, and H. Wende, *Element-Resolved Thermodynamics of Magnetocaloric LaFe$_{13-x}$Si$_x$*, Phys. Rev. Lett. 114, 057202 (2015).
[7] S. Yuce, M. Barrio, B. Emre, E. Stern-Taftals, A. Planes, J.-L. Tamarit, Y. Mudryk, K. A. Gschneidner, V. K. Pecharsky, and L. Mañosa, *Barocaloric Effect in the Magnetocaloric Prototype Gd$_3$Si$_2$Ge$_2$*, Appl. Phys. Lett. 101, 071906 (2012).
[8] L. Mañosa, D. González-Alonso, A. Planes, E. Bonnot, M. Barrio, J.-L. Tamarit, S. Aksoy, and M. Acet, *Giant
Solid-State Barocaloric Effect in the NiMnIn Magnetic Shape-Memory Alloy, Nat. Mater. 9, 478 (2010).

[9] L. Mañosa, D. González-Alonso, A. Planes, M. Barrio, J.-L. Tamarit, A. Planes, M. Barrio, J.-L. Tamarit, I. S. Titov, M. Acet, A. Bhattacharyya, and S. Majumdar, Inverse Barocaloric Effect in the Giant Magnetocaloric LaFeSiCo Compound, Nat. Commun. 2, 595 (2011).

[10] E. Stern-Taulats, A. Planes, P. Lloveras, M. Barrio, J.-L. Tamarit, S. Castro-P. Lloveras, E. Stern-Taulats, M. Barrio, J.-L. Tamarit, C. Cazorla, D. Errandonea, N. D. Mathur, A. Planes, X. Moya, and L. Mañosa, Barocaloric and Magnetocaloric Effects in Fe₉₀Rhs₅₁, Phys. Rev. B 89, 214105 (2014).

[11] R.-R. Wu et al., Giant Barocaloric Effect in Hexagonal Ni₂In-type Mn-Co-Ge-In Compounds around Room Temperature, Sci. Rep. 5, 18027 (2015).

[12] E. O. Chi, W. S. Kim, and N. H. Hur, Nearly Zero Temperature Coefficient of Resistivity in Antiperovskite Compound Cu₄Mn₃, Solid State Commun. 120, 307 (2001).

[13] S. Deng, Y. Sun, L. Wang, Z. Shi, H. Wu, Q. Huang, J. Yan, K. Shi, P. Hu, A. Zaoui, and C. Wang, Frustrated Triangular Magnetic Structures of Mn₃Sn: Applications in Thermal Expansion, J. Phys. Chem. C 119, 24983 (2015).

[14] J. M. Bermudez-Garcia, M. Sanchez-Andujar, S. Castro-Garcia, J. Lopez-Beceiro, R. Artiaga, and M. A. Senaris-Rodriguez, Giant Barocaloric Effect in the Ferroic Organic-Inorganic Hybrid [TPyA][Mn(dca)₃] Perovskite under Easily Accessible Pressures, Nat. Commun. 8, 15715 (2017).

[15] D. Matsunami, A. Fujita, K. Takenaka, and M. Kano, Giant Barocaloric Effect Enhanced by the Frustration of the Antiferromagnetic Phase in Mn₃GaN, Nat. Mater. 14, 73 (2015).

[16] J. Zemen, Z. Gercsi, and K. G. Sandeman, Piezomagnetic Effect as a Counterpart of Negative Thermal Expansion in Magnetically Frustrated Mn-based Antiperovskite Nitrides, Phys. Rev. B 96, 024451 (2017).