

## Research Article

# Origin of the Giant Negative Thermal Expansion in $\text{Mn}_3(\text{Cu}_{0.5}\text{Ge}_{0.5})\text{N}$

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The giant negative thermal expansion in the Ge-doped antiperovskite  $\text{Mn}_3\text{CuN}$  compound is theoretically studied by using the first principles calculations. We propose that such a negative thermal expansion property is essentially attributed to the magnetic phase transition, rather than to the lattice vibration of the Ge-doped compound. Furthermore, we found that the doped Ge atoms in the compound significantly enhance the antiferromagnetic couplings between the nearest neighboring Mn ions, which effectively stabilizes the magnetic ground states. In addition, the nature of the temperature-dependent changes in the volume of the Ge-doped compound was revealed.

## 1. Introduction

Controlling the thermal expansion behavior of materials is eagerly required in modern advanced industries [1, 2]. Commonly, such control can be realized through mixing a kind of positive thermal expansion (PTE) materials with a kind of negative thermal expansion (NTE) materials whose volumes contract on heating. As we know, there are many PTE materials in the world, but the NTE ones rarely exist yet. Therefore, a challenging issue in controlling the thermal expansion behavior of the materials is to synthesize materials possessing NTE property.

$\text{Mn}_3\text{CuN}$ , a member of the anti-perovskite manganese nitride  $\text{Mn}_3\text{MN}$  ( $M = \text{Zn}, \text{Cu}, \text{etc.}$ ) [3–5], does not possess the negative thermal expansion property. However, recent experiments [6] reported that, with partial substitution of Ge for Cu in the  $\text{Mn}_3\text{CuN}$  compound, the synthesized  $\text{Mn}_3(\text{Cu}_{1-x}\text{Ge}_x)\text{N}$  compounds exhibited isotropic negative thermal expansion. Typically, the Ge-doped compound,  $\text{Mn}_3(\text{Cu}_{1-x}\text{Ge}_x)\text{N}$  ( $x = 0.5$ ), showed the NTE property in a wide temperature window of 316–386 K, together with a giant negative thermal expansion coefficient (The linear thermal expansion coefficient of a material is defined as  $\alpha = (1/L)(\Delta L/\Delta T)$ . Here,  $L$  is the length of the material at

temperature  $T_0$ , and  $\Delta L$  is the change of the length when temperature has a change of  $\Delta T = T - T_0$ ) of  $\alpha_L = -16 \times 10^{-6} \text{ K}^{-1}$ . More importantly, the working temperature and the width of the temperature window as well as the negative thermal expansion coefficient of the Ge-doped compound were modulated through the introduction of Ge dopant.

Prompted by the pioneering research [6], many other groups have studied the doping effect on the NTE property for some counterparts of  $\text{Mn}_3(\text{Cu}_{1-x}\text{Ge}_x)\text{N}$ , typically like  $\text{Mn}_3(\text{Cu}_{1-x}\text{Sn}_x)\text{N}$  [7],  $\text{Mn}_3(\text{Zn}_{1-x}\text{Ge}_x)\text{N}$  [8],  $\text{Mn}_3(\text{Cu}_{0.6}\text{Si}_x\text{Ge}_{0.4-x})\text{N}$  [9], and so on [10, 11]. All the efforts reported in these papers showed that it was the doped Ge that brought the NTE property into these anti-perovskite compounds, just like that of the  $\text{Mn}_3(\text{Cu}_{1-x}\text{Ge}_x)\text{N}$  compound. Therefore, the doped Ge was regarded as a “magic element” for the observed NTE property in the class of the anti-perovskite manganese nitride compounds [6].

Recently, revealing the nature of such a “magic element” in the elegant performance of the NTE property has aroused many attractions, Matsuno and coworkers [12] proposed that the Ge dopant caused a local structural distortion in the  $\text{Mn}_3(\text{Cu}_{0.7}\text{Ge}_{0.3})\text{N}$  compound, leading to the negative thermal expansion of the system in a broad temperature range. This was supported by the neutron powder diffraction

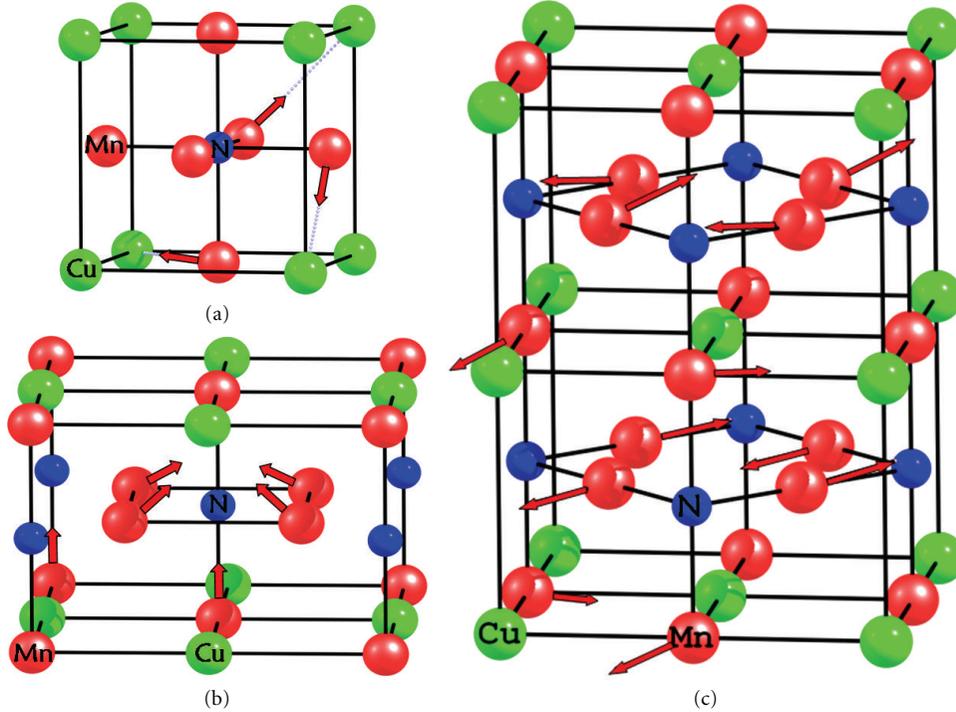


FIGURE 1: The magnetic configurations of (a)  $\Gamma^{5g}$ , (b) C0, and (c) C1. The arrows in the figures indicate the orientations of the local magnetic moments at the ions.

and NMR measurements on  $\text{Mn}_3(\text{Cu}_{1-x}\text{Ge}_x)\text{N}$  [13]. On the other hand, through fitting the possible magnetic configurations to their experimental data, Kodama et al. [14] found that the ordering moment of the ground state known as the anti-ferromagnetic  $\Gamma^{5g}$  (seen in Figure 1(a)) of the  $\text{Mn}_3(\text{Cu}_{1-x}\text{Ge}_x)\text{N}$  compound gradually increased with decreasing temperature. This might also be responsible for the NTE property of the concerned compound. Even so, it is still unclear why the doped Ge atoms make the  $\text{Mn}_3(\text{Cu}_{1-x}\text{Ge}_x)\text{N}$  compound be of NTE property.

Usually, the thermal expansion property of a compound arises from different mechanisms, such as the lattice vibration, the temperature-excited magnetic phase transition, and the diffusion of ions/atoms between interstitial sites. Among these different mechanisms, both the lattice vibration and the phase transition are mainly responsible for the thermal expansion property of many materials. However, for our concerned  $\text{Mn}_3(\text{Cu}_{1-x}\text{Ge}_x)\text{N}$  compound, the relation between its thermal expansion behavior and the lattice vibration is still puzzling.

In this theoretical study, the  $\text{Mn}_3(\text{Cu}_{0.5}\text{Ge}_{0.5})\text{N}$  compound is selected as a representative, since it exhibited a striking NTE property in experiment. Our calculations indicate that the lattice vibration contributes to the positive thermal expansion, and the magnetic phase transition from anti-ferromagnetic phase to paramagnetic phase contributes to the negative thermal expansion. Both of the PTE and NTE are compensative to each other, resulting in the observed thermal expansion behavior of the  $\text{Mn}_3(\text{Cu}_{0.5}\text{Ge}_{0.5})\text{N}$  compound. Furthermore, a novel mechanism is proposed to explain the role of the doped Ge for the broad working

temperature range of NTE in the  $\text{Mn}_3(\text{Cu}_{0.5}\text{Ge}_{0.5})\text{N}$  compound.

## 2. Computational Details

In our calculations, a  $\sqrt{2} \times \sqrt{2} \times 2$  supercell consisting of 20 atoms is used to simulate the magnetic structures of  $\text{Mn}_3(\text{Cu}_{0.5}\text{Ge}_{0.5})\text{N}$  compound, where half of Cu atoms were replaced by Ge atoms. Based on the symmetry of the supercell, there are three kinds of distributions of Ge in it. These configurations are all optimized by using the VASP code [15, 16], in which the projector augmented wave (PAW) pseudopotentials and the Perdew-Burke-Ernzerhof (PBE) parameterizations of the generalized gradient approximation [17] are adopted. The cut-off energy is 400 eV and a gamma-centered k-point mesh of  $5 \times 5 \times 3$  is used for the geometry optimization. Optimizations are performed until the residual forces acting on the atoms are smaller than  $0.01 \text{ eV}/\text{\AA}$ .

By calculations, the energies of the supercell with three kinds of distributions of Ge in the compound are achieved, respectively. We find that the energy differences between the Ge distributions are less than 18 meV per unit cell. Such very small energy differences imply that these different distributions of Ge in  $\text{Mn}_3(\text{Cu}_{0.5}\text{Ge}_{0.5})\text{N}$  compound may exist at finite temperatures. Even so, we select the lowest-energy one to serve our following calculations.

## 3. Results and Discussions

*3.1. Vibrational Effect on the Variation of Volume.* Structurally,  $\text{Mn}_3(\text{Cu}_{0.5}\text{Ge}_{0.5})\text{N}$  is composed of the corner-shared

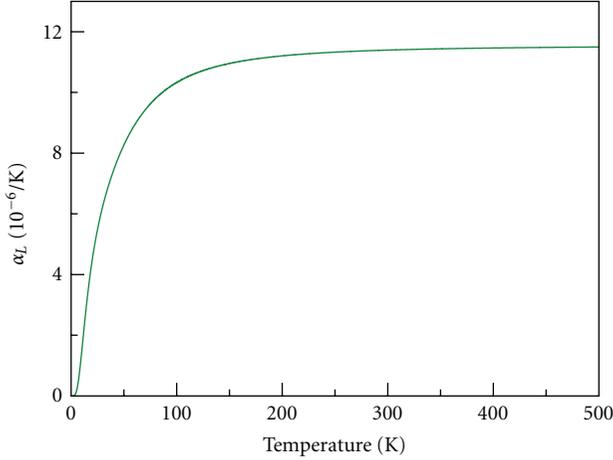


FIGURE 2: The coefficient of the thermal expansion  $\alpha_L$  caused by the lattice vibration as a function of the temperature.

$\text{Mn}_6\text{N}$  octahedron, somewhat like the structural feature in the  $\text{ZrW}_2\text{O}_8$  compound [18], where an open-framework structure consisting of corner-linked rigid polyhedra associates with the transverse vibrational modes that cause NTE. Thus, it is necessary to examine the thermal expansion behavior induced by the vibrational modes. Within the quasiharmonic approximation, the thermal expansion coefficient  $\alpha_L$  is related to the vibrational modes of a material, which is calculated through the formula [19]

$$\alpha_L = \frac{k_B}{3BV} \sum_{j=1}^n \gamma_j \left( \frac{\hbar\omega_j}{k_B T} \right)^2 \frac{\exp(\hbar\omega_j/k_B T)}{[\exp(\hbar\omega_j/k_B T) - 1]^2}, \quad (1)$$

where  $\omega_j$  is the  $j$ th frequency,  $B$  the bulk modulus,  $V$  the volume of the system, and  $\gamma_j$  the Grüneisen parameter relevant to the  $j$ th vibrational mode. Here, the Grüneisen parameter is defined as

$$\gamma_j = - \left( \frac{\partial \ln \omega_j}{\partial \ln V} \right)_T. \quad (2)$$

To evaluate the coefficient of the thermal expansion, we first compute the bulk modulus and all vibrational frequencies at  $\Gamma$  point for the supercell. Based on the obtained energy as a function of the volume of the system the bulk modulus of the concerned system is predicted to be about 128.2 GPa (to accurately achieve the vibrational modes, a larger supercell containing  $2 \times 2 \times 2$  chemical unit cells is selected in our calculations relevant to the vibrational modes.) Meanwhile, the dynamic matrix of the considered system is generated through the forces acting on each atom, with using the frozen phonon approximation. By solving the dynamic matrix, we obtain all of the vibrational frequencies and the related eigenmodes. According to the obtained eigenmodes and the bulk modulus, the thermal expansion coefficient  $\alpha_L$  is obtained, as shown in Figure 2. Apparently, the value of  $\alpha_L$  is very small at low temperature and then increases rapidly with increasing temperature. When the temperature reaches 100 K or so,  $\alpha_L$  almost converges to the value of  $11.50 \times 10^{-6} \text{ K}^{-1}$ .

This value is in good agreement with that ( $13 \times 10^{-6} \text{ K}^{-1}$ ) from experiment [6]. Such agreement indicates that the widely used frozen phonon approximation is also reliable to evaluate the dynamical property of the compound. More importantly, the calculated values of  $\alpha_L$  shown in Figure 2 are positive in the whole considered temperature range. This strongly predicts that the transverse motion from the rigid octahedron has no contribution to the observed NTE property in the  $\text{Mn}_3(\text{Cu}_{0.5}\text{Ge}_{0.5})\text{N}$  compound.

**3.2. Magnetic Phase Transition versus the Variation of Volume.** Experiments found the observed NTE behavior in the  $\text{Mn}_3(\text{Cu}_{0.5}\text{Ge}_{0.5})\text{N}$  compound accompanied with a magnetic transition from the low temperature  $\Gamma^{5g}$ -type antiferromagnetic (AFM) phase to the high temperature paramagnetic (PM) phase [6, 20]. However, such NTE behavior was not found in the  $\text{Mn}_3\text{CuN}$  compound yet [6, 21]. Clearly, the observed NTE property of  $\text{Mn}_3(\text{Cu}_{0.5}\text{Ge}_{0.5})\text{N}$  does tightly couple with the doped Ge atoms. To understand the role of the doped Ge atoms in the concerned NTE behavior, it is valuable to study the  $\text{Mn}_3\text{CuN}$  compound firstly.

For the undoped  $\text{MnCuN}$  compound, where the Mn ions contribute to local magnetic moments, showing non-collinear magnetic configuration. Its ground state was experimentally demonstrated to be ferromagnetic. Furthermore, a magnetic configuration (notated as C0, seen in Figure 1(b)) was suggested to explain the ground state [21]. Our calculations reproduce the magnetic configuration C0, with the ferromagnetic components of local magnetic moments of  $0.18 \mu_B$  and  $0.30 \mu_B$  for the Mn ions locating at two unequal planes, respectively, which are close to the values of  $0.20 \mu_B$  and  $0.65 \mu_B$  reported in experiment [21]. However, such agreement does not directly support C0 configuration as the ground state of the  $\text{Mn}_3\text{CuN}$  compound. In fact, a ground state configuration should have the lowest energy among all of the possible magnetic configurations. To examine whether the configuration C0 is the ground state or not, we generate many kinds of magnetic configurations, followed by full relaxations. Among these considered magnetic configurations, a lowest-energy configuration (notated as C1, seen in Figure 1(c)) is found, whose energy is lower by about 0.3 eV per primitive unit cell than that of the C0 configuration. Furthermore, we find that the configuration C1 characterizes the FM feature, and the ferromagnetic component averaged on Mn ions in this configuration is about  $0.1 \mu_B$ , being smaller than the experimental value of  $0.35 \mu_B$ .

Moreover, for this undoped compound, we find that these magnetic configurations have different energies, meaning that these magnetic configurations may be thermally excited at different temperatures. On the other hand, the equilibrium volumes of all considered magnetic configurations are very close to each other. Hence, the thermally excited transformation between different magnetic configurations does not change the volume of the compound nearly. In other words, the  $\text{Mn}_3\text{CuN}$  compound does not show NTE on heating. This is consistent with the observation in experiment very well [6].

Then, we turn to the  $\text{Mn}_3(\text{Cu}_{0.5}\text{Ge}_{0.5})\text{N}$  compound. For this compound, the magnetic state at low temperature

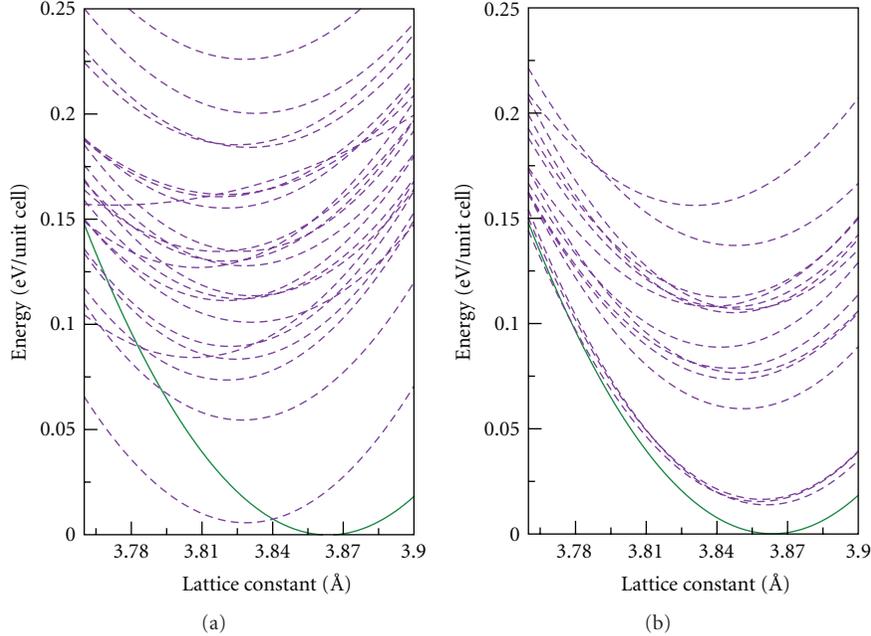


FIGURE 3: (a) The energies of the considered magnetic configurations as a function of the lattice constant for  $\text{Mn}_3(\text{Cu}_{0.5}\text{Ge}_{0.5})\text{N}$ . The solid line represents the energy curve of  $\Gamma^{5g}$  and the dashed lines represent the energy curves of the magnetic metastable configurations. (b) The energies as a function of the lattice constant for the distorted  $\Gamma^{5g}$  configurations (dashed lines) and the perfect  $\Gamma^{5g}$  configuration (solid line). The energy at the equilibrium volume of the  $\Gamma^{5g}$  configuration is taken as a reference.

was demonstrated to be AFM in experiment. Moreover, experiments suggested that a special AFM configuration named as  $\Gamma^{5g}$  just corresponded to the ground state of the compound [13]. On the theoretical side, it is necessary to clarify its magnetic ground state. To do this, we randomly generate about eighty magnetic configurations plus the  $\Gamma^{5g}$  configuration in this compound. After full relaxations of the spins and atomic positions for each concerned case, we only have twenty four inequivalent magnetic configurations. Figure 3(a) displays the energy as a function of the lattice constant for each magnetic configuration. From Figure 3(a), one can find that the lowest-energy magnetic configuration is  $\Gamma^{5g}$ , and its equilibrium lattice constant is evaluated to be 3.864 Å, in agreement with the experimental value of 3.910 Å [13]. Furthermore, our calculations indicate that the local magnetic moments of the Mn ions in the  $\Gamma^{5g}$  configuration are  $2.63 \mu_B$ , being in good consistent with the experimental value of  $2.47 \pm 0.27 \mu_B$  [21]. Such agreement supports that  $\Gamma^{5g}$  is really the magnetic ground state for  $\text{Mn}_3(\text{Cu}_{0.5}\text{Ge}_{0.5})\text{N}$  compound.

The experiments revealed that with raising temperature, the  $\text{Mn}_3(\text{Cu}_{0.5}\text{Ge}_{0.5})\text{N}$  compound exhibited a volume contraction. Basically, the temperature effect not only excites more magnetic configurations of the system, but also distorts each magnetic configuration to some extent. To qualitatively evaluate the distorted magnetic configurations, we randomly deviate the orientations of the local moments of Mn ions from their initial orientations for each magnetic configuration, and thus a series of the distorted configurations can be generated through controlling the deviating extent. The volume of the compound at each distorted configuration is

optimized with fixing the orientations of the local moments. Our calculations show that the volume of the distorted magnetic configurations almost does not change, except for the  $\Gamma^{5g}$  configuration. As shown in Figure 3(b), with distorting the  $\Gamma^{5g}$  configuration seriously, the energy of the system increases significantly, and the volume of the lattice decreases largely. This predicts that the volume contraction on heating is actually contributed from the distorted  $\Gamma^{5g}$  configuration together with the thermal excited metastable configurations.

On the other hand, when the compound was heated up to the Neel temperature, it transfers from the AFM  $\Gamma^{5g}$  state to the PM state [13]. As we know, the PM state is a magnetic disorder state, which cannot be simply approximated to be either a non-magnetic state or a magnetic ordering state with lowmagnetic moment in a theoretical calculation. Since there are many different magnetic configurations in the compound, the PM state may be approximatively regarded as a mixture of many magnetic structures that can be thermally excited, when the compound is heated up above the Neel temperature. According to this, the volume of the compound at the PM state is expressed as the statistically averaged volume of many different magnetic structures including  $\Gamma^{5g}$ , by using the Boltzmann distribution function. Combining this consideration with the energy curves shown in Figure 3, we statistically compute the lattice constant ( $a(T)$ ) at each considered temperature. Of these temperature-dependent lattice constants, the lattice constant at 500 K is selected as a reference, and thus we obtain the ratio of the lattice constant contraction,  $\Delta a/a = (a(T) - a(500 \text{ K}))/a(500 \text{ K})$ . As displayed in Figure 4(a), the lattice constant exhibits a

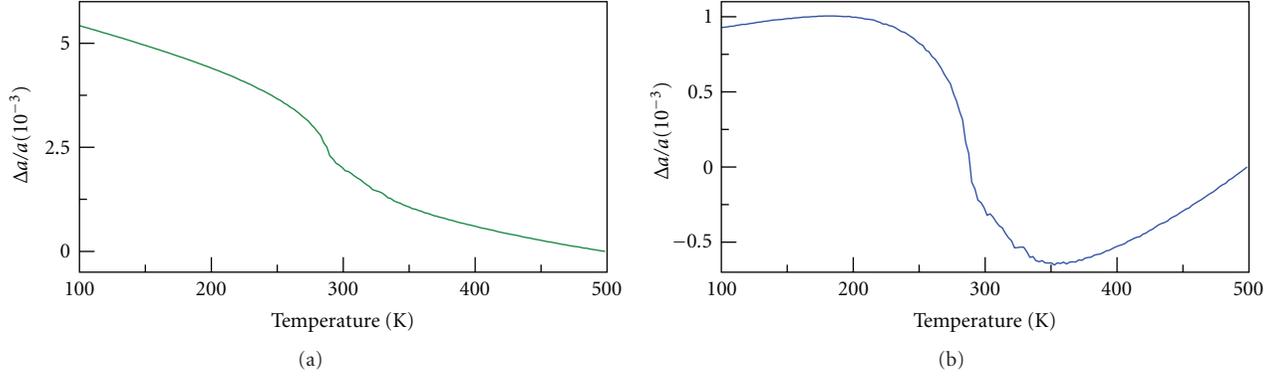


FIGURE 4: (a) The ratio of the lattice contraction caused by the magnetic interaction. (b) The ratio of the lattice change arising from the magnetic interaction and the lattice vibration.  $\Delta a$  represents the difference between the lattice constant at temperature  $T$  and the lattice constant at 500 K.

gradual decrement with increasing temperature. This implies that the considered magnetic interactions really cause the NTE property in the whole temperature range. To go further, combining this NTE behavior with the PTE behavior from the lattice dynamics shown in Figure 2, we find that the compound exhibits the NTE behavior only in a temperature range of 250–340 K, as seen in Figure 4(b), in consistent with the results reported in experiment [6]. Our calculations above reveal that the volume contraction from the magnetic couplings is actually compensated by the lattice vibrations to some extent. The effect of such compensation is strongly relevant to the temperature. Namely, when the temperature is either below 250 K or over 340 K, the volume change of the compound from the lattice vibration overpasses that from the magnetic interaction, showing the PTE behavior. And in the temperature range between 250 and 340 K, the NTE effect is much stronger than the PTE effect, so that the compound exhibits a net effect of NTE in such a temperature window.

**3.3. The Role of the Doped Ge Atoms in the NTE Property.** As mentioned above, it is the doped Ge atoms that cause the compound to be of NTE property. Meanwhile, the observed NTE property is stemmed from the magnetic interaction between ions in the  $\text{Mn}_3(\text{Cu}_{0.5}\text{Ge}_{0.5})\text{N}$  compound. So, the nature of the observed NTE property is essentially associated with how the doped Ge atoms affect the magnetic couplings between ions. Physically, the magnetic couplings between ions in a compound can be expressed by the exchange parameters between different ions within the framework of the classical isotropic Heisenberg theory [22–25]. In our concerned compound, three typical kinds of exchange parameters,  $J_1$ ,  $J_2$ , and  $J'_2$  are considered. Here,  $J_1$  is the coupling between an Mn ion and its nearest neighbor Mn;  $J_2$  is the super exchange between an Mn ion and its second neighbor Mn ion, separated by an N atom;  $J'_2$  is the coupling between an Mn ion and its second neighbor Mn ion, without any atom between them. Based on the classical isotropic Heisenberg theory [22–25], the energy gain from the magnetic couplings is expressed as  $24J_1 - 12J_2 - 24J'_2$  for  $\text{Mn}_3(\text{Cu}_{0.5}\text{Ge}_{0.5})\text{N}$  and  $8J_1 - 12J_2 + 8J'_2$  for  $\text{Mn}_3\text{CuN}$ .

TABLE 1: Exchange parameters (meV) for  $\text{Mn}_3\text{CuN}$  and  $\text{Mn}_3(\text{Cu}_{0.5}\text{Ge}_{0.5})\text{N}$  compounds.

Compound	$J_1$	$J_2$	$J'_2$
$\text{Mn}_3\text{CuN}$	-7.5	22.5	-4.9
$\text{Mn}_3(\text{Cu}_{0.5}\text{Ge}_{0.5})\text{N}$	-19.90	20.3	-8.8

Table 1 lists the calculated exchange parameters for both compounds. Among the three kinds of exchange parameters, the amplitude of  $J_1$  for the  $\text{Mn}_3(\text{Cu}_{0.5}\text{Ge}_{0.5})\text{N}$  compound is considerably bigger than that for the  $\text{Mn}_3\text{CuN}$  compound. This indicates that the doped Ge strongly enhances the magnetic interaction between the nearest-neighbor Mn ions in the  $\text{Mn}_3(\text{Cu}_{0.5}\text{Ge}_{0.5})\text{N}$  compound. It is worth noting that in our concerned anti-perovskite manganese nitride compound, the couplings between the nearest-neighbor Mn ions form a triangular structure in space. Such a triangular feature is just responsible for the noncollinear anti-ferromagnetic configuration, which is the basic characteristic of the  $\Gamma^{5g}$  configuration. So, the doped Ge atoms effectively enhance the AFM  $\Gamma^{5g}$  configuration much more than the other configurations in the  $\text{Mn}_3(\text{Cu}_{0.5}\text{Ge}_{0.5})\text{N}$  compound. This is just corresponding to the fact that  $\text{Mn}_3(\text{Cu}_{0.5}\text{Ge}_{0.5})\text{N}$  has the ground state of  $\Gamma^{5g}$ , whereas  $\text{Mn}_3\text{CuN}$  does not have yet [6, 21].

As reported in experiments, the doped Ge atoms not only caused the NTE property, but also made the NTE occurring in a broad temperature range for  $\text{Mn}_3(\text{Cu}_{0.5}\text{Ge}_{0.5})\text{N}$ . However, these features did not occur in the  $\text{Mn}_3(\text{Cu}_{1-x}\text{M}_x)\text{N}$  ( $M = \text{Zn}, \text{Si}, \text{and Ga}$ ) compounds. Basically, the different behaviors in NTE of the compounds caused by the different dopants tightly couple with the different electronic structures of the dopants. For the isolated atoms of Cu, Ge, Zn, and Mn, the energies of their highest occupied orbitals are in the order of  $E_{\text{Zn}^{4s}}(-5.93 \text{ eV}) < E_{\text{Mn}^{4s}}(-5.47 \text{ eV}) < E_{\text{Cu}^{4s}}(-4.98 \text{ eV}) < E_{\text{Ge}^{4p}}(-4.38 \text{ eV})$ . Clearly, the energy differences of the orbitals between Mn and M ( $M = \text{Cu}, \text{Zn}$  and Ge) are quite big. This means that the 4s orbital of either Cu or Zn and the 4p orbital of Ge do not significantly couple with the valence

orbital of Mn in the compound. So, in the compound, most electrons on these atomic orbitals are unpaired and thus locate at the unsaturated states which are almost at the Fermi level. Especially,  $E_{\text{Ge}4p}$  is much higher than the others, and the number of electrons on Ge 4p is larger than the other orbitals considered above. Thus the doped Ge in the compound contribute more states at the Fermi level than the other cases. Meanwhile, the local density of states (LDOS) at the Fermi level from the Mn ions drops down largely when the content of Ge is 50% [26] in the compound. With rising temperature, more electrons from the Ge 4p orbital are thermally excited into the conduction band in such metallic systems. These conduction electrons may polarize some of local electrons in the compound, altering the magnetic couplings between Mn ions and the local magnetic moments accordingly. Namely, some of magnetic states in the Ge-doped compound is easily excited by temperature, even temperature rises slightly. As a result, the Ge-doped compound shows a gradually temperature-dependent change in volume. This is corresponding to the wide temperature range for the NTE working, as reported in experiments [6].

#### 4. Conclusion

We have investigated the lattice vibrations and the magnetic phase transition for the Ge-doped metallic anti-perovskite  $\text{Mn}_3(\text{Cu}_{0.5}\text{Ge}_{0.5})\text{N}$  compound, based on first-principles calculations. We find that the lattice vibrations contribute to the PTE property rather than the NTE property. Our calculations indicate that the observed NTE is actually resulted from the magnetic phase transition from the  $\Gamma^{5g}$  phase to the PM phase. Furthermore, we suggest that the thermal effect excites more valence electrons from the doped Ge atoms to the conduction bands in the compound. These donated conduction electrons polarize the local electrons and change the local magnetic moments of Mn ions, leading to the contraction of the compound in volume.

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