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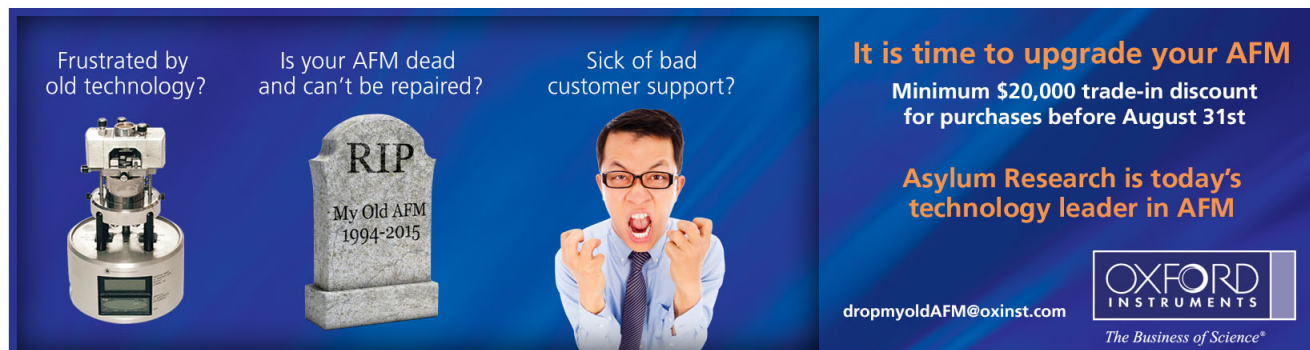
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# Giant negative thermal expansion in Ge-doped anti-perovskite manganese nitrides

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We report the discovery of a large negative thermal expansion (NTE) up to  $\alpha = -25 \times 10^{-6} \text{ K}^{-1}$  ( $\alpha$ : coefficient of linear thermal expansion) in Ge-doped anti-perovskite manganese nitrides  $\text{Mn}_3\text{AN}$  ( $A = \text{Cu}, \text{Zn}, \text{Ga}$ ). This gigantic NTE is several to ten times higher than that of commercially available NTE materials. **The discontinuous lattice expansion seen in pure  $\text{Mn}_3\text{AN}$  is broadened by Ge substitution over a wide temperature window, at widest  $\Delta T \sim 100 \text{ K}$ , around room temperature.** Such a large, isotropic and nonhysteretic NTE is desirable for practical applications. © 2005 American Institute of Physics. [DOI: 10.1063/1.2147726]

Most solids exhibit thermal expansion, i.e., their lattice parameters increase on heating under constant pressure. Due to the asymmetry of the potential well, excursions to longer interatomic distances are easier than to shorter interatomic distances. A very limited number of materials, however, contract on heating and show negative thermal expansion (NTE).<sup>1–3</sup> There has been considerable interest in these NTE materials because of their variety of potential applications. NTE materials can compensate or control (positive) thermal expansion of materials by forming composites, which have been widely used as, for example, high-precision (zero-expansion) optical and machinery parts and an athermalizer for a Bragg grating.<sup>4,5</sup> To promote an even wider range of practical applications, it has been long desired to develop materials with larger NTE over a wide temperature ( $T$ ) range.

The anti-perovskite manganese nitride  $\text{Mn}_3\text{AN}$  ( $A = \text{Zn}, \text{Ga}$ , etc.) is a potential candidate for observing large NTE effects. These nitrides are well known for their large magnetovolume effect (MVE)<sup>6–11</sup> as well as a possible large piezo-magnetic effect.<sup>12</sup> As clearly seen in Fig. 1, the lattice volume for  $A = \text{Zn}$  and  $\text{Ga}$  compounds shows a sudden and pronounced increase with decreasing temperature, as large as a few%, at 165 and 290 K, respectively.<sup>13</sup> The neutron-diffraction studies<sup>6</sup> indicate that these lattice **anomalies** are associated with an anti-ferromagnetic transition to the triangular  $\Gamma^{5g}$  spin structure [inset of Fig. 1(b)] while the cubic crystal structure is maintained.

This MVE, giving rise to a large change in volume, is reminiscent of Invar alloys.<sup>14</sup> However, unlike Invar alloys where the transition is second order, here it is **manifest** as a sharp first-order transition. As a result,  $\text{Mn}_3\text{AN}$  has not been considered for any industrial applications to date. If a kind of **relaxor** concept can be introduced to  $\text{Mn}_3\text{AN}$  and the discontinuous expansion can be broadened, we might be able to develop NTE materials for potential application. We explored this possibility by examining partial substitution of the constituent elements. After searching through a variety of

elements, we found that partial substitution of Ge for  $A$  is quite effective at broadening the volume expansion. Here, we report details of this discovery.

All of the measurements were performed using sintered polycrystalline samples made by solid-state reaction.<sup>10,11</sup> Powders of  $\text{Mn}_2\text{N}$ ,  $\text{Fe}_4\text{N}$ , C, and pure elemental  $A$  (purity: 99.9% or higher) were used as the starting materials.

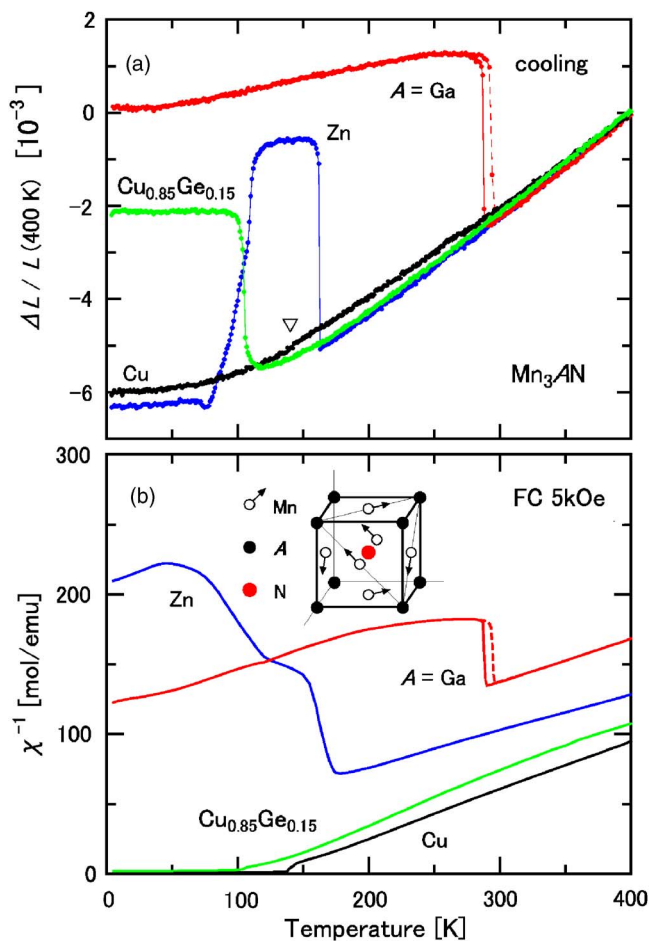


FIG. 1. (Color online) Linear thermal expansion (a) and inverse magnetic susceptibility (b) of  $\text{Mn}_3\text{AN}$ . Solid line: cooling process; dashed line: warming process. For sintered polycrystalline samples,  $\Delta L/L$  is related directly to the volume ( $V$ ) expansion in a manner  $\Delta L/L = (1/3)\Delta V/V$ . Inset shows the antiferromagnetic  $\Gamma^{5g}$  spin structure of  $\text{Mn}_3\text{ZnN}$  and  $\text{Mn}_3\text{GaN}$ .

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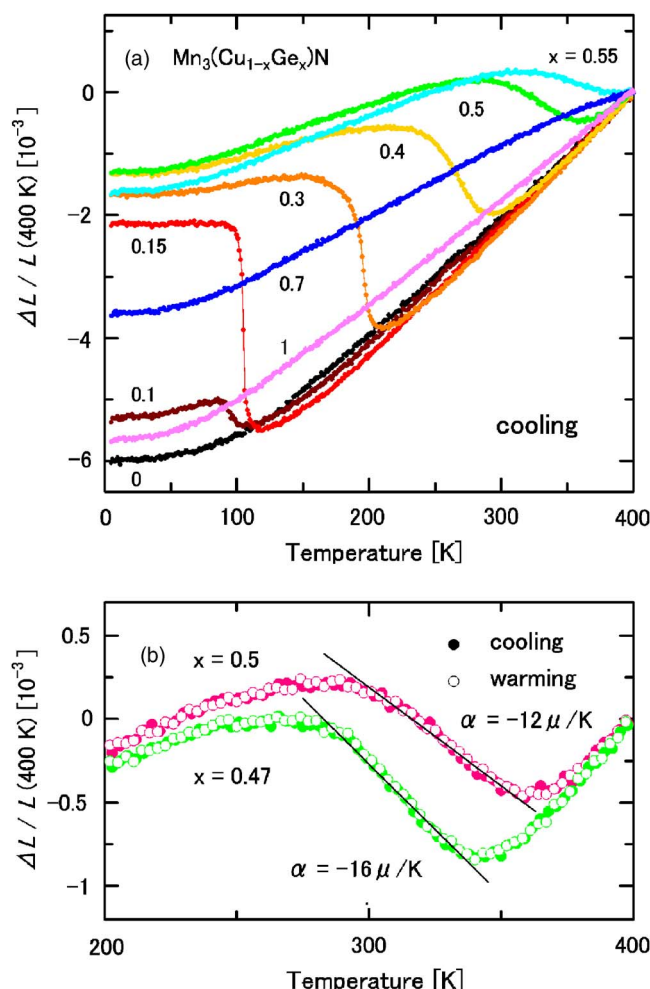


FIG. 2. (Color online) (a) Linear thermal expansion of solid solution  $\text{Mn}_3(\text{Cu}_{1-x}\text{Ge}_x)\text{N}$ . (b) Negative thermal expansion for  $x=0.47$  and  $0.5$ . Data collected in cooling and warming processes are identical.

$\Delta L/L(400\text{ K})$  was measured using a strain gauge (KYOWA; type KFL). This method is simple but requires a reference material of known expansion. Here we used copper (purity 99.99%) and the corresponding thermal expansion data of pure copper.<sup>15,16</sup> Our  $\Delta L/L$  data for stoichiometric  $\text{Mn}_3\text{AN}$  are in quantitative agreement with previous results from x-ray diffraction studies,<sup>7-9</sup> thus validating our thermal expansion measurement.  $\chi(T)$  was measured at 5000 Oe by a superconducting quantum interference device magnetometer. The crystal structure was investigated by means of powder x-ray diffraction.

Figure 2 displays linear thermal expansion  $\Delta L/L$  data for  $\text{Mn}_3(\text{Cu}_{1-x}\text{Ge}_x)\text{N}$ . Unlike other  $\text{Mn}_3\text{AN}$ ,  $\text{Mn}_3\text{CuN}$  does not show MVE. Instead it becomes ferromagnetic at the Curie temperature  $T_C=143\text{ K}$  with a spin structure different from  $\Gamma^{5g}$ . In contrast to the other  $\text{Mn}_3\text{AN}$  compounds, this ferromagnetic transition is accompanied by a transition to the tetragonal  $T_1$  structure (Fig. 1).<sup>6,10</sup> We found from x-ray diffraction that, by substituting Cu with a small amount of Ge, the low temperature structure switches from tetragonal to cubic for  $x>0.1$ . In accord with this structural change, a pronounced MVE is restored for  $x>0.1$  as clearly seen in Fig. 2. Incidentally, the magnetic ordering still remains ferromagnetic even above  $x=0.1$  [Fig. 1(b)] but eventually changes to anti-ferromagnetic at  $x=0.3$ . The detailed spin structure is yet to be determined. The discontinuous jump in

$\Delta L/L$  at the transition is estimated to be  $3.3 \times 10^{-3}$  for  $x=0.15$ , which is comparable to those of  $\text{Mn}_3\text{ZnN}$  ( $4.6 \times 10^{-3}$ ) and  $\text{Mn}_3\text{GaN}$  ( $3.8 \times 10^{-3}$ ), and one of the largest among  $\text{Mn}_3\text{AX}$  ( $X=\text{N}, \text{C}$ ) members [Fig. 1(a)]. The magnetic transition temperature (accompanied by a large MVE) is drastically enhanced by further increasing Ge content. It is known empirically that the transition temperature of  $\text{Mn}_3\text{AN}$  is scaled by the number of valence electrons on A,  $n_v$ .<sup>6</sup> The drastic increase of transition temperature with Ge substitution is consistent with the empirical rule ( $n_v$  is 1, 2, 3, and 4 for Cu, Zn, Ga, and Ge, respectively).

The most important finding of this study is the broadening of MVE with increasing Ge concentration. The lattice expansion associated with the magnetic transition is a well-defined discontinuous jump at  $x=0.15$  but gradually becomes broadened with further increasing Ge content. This gradual lattice change gives rise to a large negative slope (large NTE) over a wide  $T$  range. For example,  $\text{Mn}_3(\text{Cu}_{0.53}\text{Ge}_{0.47})\text{N}$  and  $\text{Mn}_3(\text{Cu}_{0.5}\text{Ge}_{0.5})\text{N}$  [Fig. 2(b)] show NTE of  $\alpha=-16 \times 10^{-6}\text{ K}^{-1}$  at  $T=267-342$  ( $\Delta T=75\text{ K}$ ) and  $\alpha=-12 \times 10^{-6}\text{ K}^{-1}$  at  $T=280-365$  ( $\Delta T=85\text{ K}$ ), respectively. This NTE is isotropic because the cubic structure is maintained down to low temperatures. With further Ge substitution, the transition temperature exceeds 400 K and the anomaly in  $\Delta L/L$  could not be identified within the covered  $T$  range. The end member  $\text{Mn}_3\text{GeN}$  shows a structural and magnetic transition around 400 K but this is complicated by a set of multi-transitions.<sup>6</sup>

We also investigated chemical substitution with elements other than Ge. However, while the transition temperature was changed in accord with the empirical rule, we have yet to obtain volume expansion as broad as that seen in the Ge-containing compounds. This suggests the uniqueness of Ge as a dopant. Indeed,  $\text{Mn}_3\text{GeN}$  shows crystal and spin structures that are distinct from other  $\text{Mn}_3\text{AN}$  members.<sup>6</sup> We suspect that Ge dopants give rise to a strong local disorder, which might give rise to a relaxor-like behavior as in relaxor ferroelectrics<sup>17</sup> or relaxor ferromagnets.<sup>18</sup> Alternatively, the transition may become the Invar-type, second-order transition. The microscopic origin of this broadening is worthy of further exploration. In particular, relation to  $\text{ZrV}_{2-x}\text{P}_x\text{O}_7$  is an interesting future issue. In both  $\text{ZrV}_2\text{O}_7$  and  $\text{ZrP}_2\text{O}_7$ , phase transitions occur, but the transition becomes broad or disappears in a solid solution of these compounds. Thus, abrupt changes in thermal expansion disappeared, and a material with very low thermal expansion was produced.<sup>19</sup>

Our empirical observations in  $\text{Mn}_3(\text{Cu}_{1-x}\text{Ge}_x)\text{N}$  offer the prospect that other members such as  $\text{Mn}_3\text{ZnN}$  and  $\text{Mn}_3\text{GaN}$  may also show a broadened MVE and resultant NTE behavior upon Ge substitution. Initial attempts have so far proved unsuccessful, however. In accord with the empirical rule, the transition temperature rapidly increases upon Ge substitution, rising far above 400 K, but none of the compounds exhibited a broadened MVE. In order to produce NTE materials operative around room temperature, we realized that we have to compensate this rapid increase by "co-doping" with another element (Fig. 3). Partial replacement of A by Mn or N by C, for example, lowers the transition temperature, presumably due to the reduction in the number of valence electrons. By employing the co-doping of Ge at 30%–40% level plus Mn or C, we did manage to achieve a NTE over a wide  $T$  range around room temperature. In



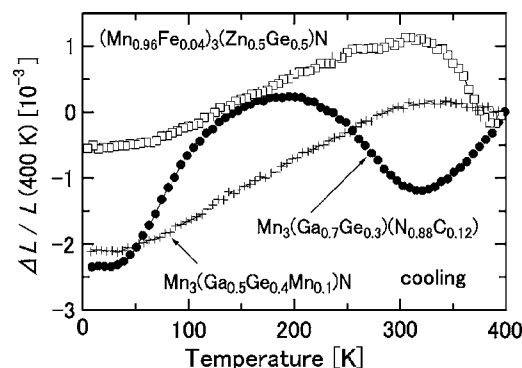


FIG. 3. Linear thermal expansion of the Ge-contained solid solutions.

$\text{Mn}_3(\text{Ga}_{0.7}\text{Ge}_{0.3})(\text{N}_{0.88}\text{C}_{0.12})$ , for example,  $\alpha = -18 \times 10^{-6} \text{ K}^{-1}$  at  $T = 197\text{--}319$  ( $\Delta T = 122 \text{ K}$ ) and in  $\text{Mn}_3(\text{Ga}_{0.5}\text{Ge}_{0.4}\text{Mn}_{0.1})\text{N}$ ,  $\alpha = -3 \times 10^{-6} \text{ K}^{-1}$  above  $334 \text{ K}$ . We also found that partial replacement of Mn by Fe lowers the operative temperature.  $(\text{Mn}_{0.96}\text{Fe}_{0.04})_3(\text{Zn}_{0.5}\text{Ge}_{0.5})\text{N}$  shows NTE of  $\alpha = -25 \times 10^{-6} \text{ K}^{-1}$  at  $T = 316\text{--}386$  ( $\Delta T = 70 \text{ K}$ ). Note that the  $T$  window for NTE is comparable to the criterion for practical use ( $\Delta T \sim 100 \text{ K}$ ).

Although a wider  $T$  range of NTE, both below and above room temperature, is favorable for practical applications, manganese nitride has a number of advantages over existing NTE materials. **(1)** The operation temperature and the coefficient of NTE can be controllable in a pure form without forming composites. **(2)** The negative  $\alpha$  coefficient is tunable across a wide range of values. Indeed, at its largest, it can be  $-25 \times 10^{-6} \text{ K}^{-1}$ , one order of magnitude larger than commercial NTE materials. (Typically,  $\alpha$  is of order  $10^{-6} \text{ K}^{-1}$ ,<sup>1</sup> though for  $\text{ZrW}_2\text{O}_8$ ,  $\alpha = -9 \times 10^{-6} \text{ K}^{-1}$ <sup>20</sup>). In fact, the magnitude of  $\alpha$  in manganese nitrides is comparable to or higher than that of the highest NTE materials known to date, such as Fe–Pt Invar alloys<sup>21</sup> and  $\text{Zn}_{1-x}\text{Cd}_x(\text{CN})_2$ .<sup>22</sup> We should also note that the absolute magnitude of the negative  $\alpha$  found in the anti-perovskite is larger than its positive counterpart seen in high-expansion ceramics such as  $\text{Al}_2\text{O}_3$  ( $9 \times 10^{-6} \text{ K}^{-1}$ ) and typical metals such as Fe ( $12 \times 10^{-6} \text{ K}^{-1}$ ) and is comparable with those of high-expansion metals such as Al ( $23 \times 10^{-6} \text{ K}^{-1}$ ). This impacts on practical applications for compensation of thermal expansion. **(3)** The negative thermal expansion is isotropic and does not show any hysteresis. This can be a great advantage. For example, microcracking during repeated thermal cycling may be avoided. Most of the existing NTE materials, with the exception of  $\text{ZrW}_2\text{O}_8$ , are anisotropic. **(4)** The NTE anti-perovskites consist only of ecological and economical elements such as Mn, Cu, Zn, and Ge. This contrasts with the potentially high costs of using Fe–Pt alloys. Similarly, manganese nitride is preferable to  $\text{Zn}_{1-x}\text{Cd}_x(\text{CN})_2$  as a commercial NTE material because of the toxicity and chemical instability of the latter. **(5)** The manganese nitrides are also stable in moist air and mechanically hard. **(6)** Finally, the manganese nitrides are metallic.

For many applications, NTE materials that have high electrical or thermal conductivity would be desirable. Most of the existing NTE materials are insulating. To date, only one low-expansion metallic material is used, Fe–Ni Invar alloy.

In conclusion, by introducing the magic element Ge, the discontinuous lattice expansion, originating from a gigantic magnetovolume effect, in anti-perovskite manganese nitrides was successfully modified into continuous expansion (at widest  $\Delta T \sim 100 \text{ K}$ ). This gives rise to a “large” and “isotropic” negative thermal expansion up to  $\alpha = -25 \times 10^{-6} \text{ K}^{-1}$  around room temperature. It is argued that the performance of these series of anti-perovskites is better than those of existing negative thermal expansion materials, and thus gives us prospect that they can be used in future commercial applications.

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