Magnetic structure and local lattice distortion in giant negative thermal expansion material
\(\text{Mn}_3\text{Cu}_{1-x}\text{Ge}_x\text{N}\)

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Abstract. Magnetic and local structures in an antiperovskite system, \(\text{Mn}_3\text{Cu}_{1-x}\text{Ge}_x\text{N}\), with a giant negative thermal expansion have been studied by neutron powder diffraction measurement. We discuss (1) an importance of an averaged cubic crystal structure and a \(\Gamma_5\) antiferromagnetic spin structure for the large magneto-volume effect (MVE) in this itinerant electron system, (2) an unique role of a local lattice distortion well described by the low temperature tetragonal structure of \(\text{Mn}_3\text{GeN}\) for the broadening of MVE.

1. Introduction

Negative thermal expansion (NTE) materials have already been used in a wide area of technical applications in which it is desperately needed to control the thermal expansion\[^1\,^2\]. The NTE occurs as a result of the gradual volume expansion accompanied by magnetic ordering, the so-called magneto-volume effect (MVE). The MVE of itinerant electron systems has been investigated since the discovery of extraordinarily small thermal expansion in Invar alloys \[^3\]. Antiperovskite manganese nitrides \(\text{Mn}_3\text{AN}\), where \(A\) is a metal or a semiconducting element, are well known for their large MVE \[^4\]. However, this system has not been considered as a practical NTE material to date, because all the MVEs reported in \(\text{Mn}_3\text{AN}\) members have been associated with first-order phase transitions. Recently, Takenaka and Takagi reported that the MVE is broadened against temperature \(T\) in \(\text{Mn}_3\text{Cu}_{1-x}\text{Ge}_x\text{N}\) and leads to a giant negative thermal expansion coefficient \[^5\,^6\,^7\]. At \(x\sim0.5\), linear thermal expansion \(\Delta L/L\) is almost linear to \(T\) in the temperature range of \(270 \leq T \leq 350\) K. The large negative coefficient of linear thermal expansion \(\alpha\) is about \(-2 \times 10^{-5}/\text{K}\), the largest value among all NTE materials. The clarification of the microscopic mechanism of the MVE may provide us a useful guideline for designing NTE materials with better performance. Especially, to clarify the mechanism for the broadening of MVE (the Invar problem) has been a challenge in solid state physics over a century. We have studied the magnetic and local structures in \(\text{Mn}_3\text{Cu}_{1-x}\text{Ge}_x\text{N}\) using neutron
Figure 1. (a) Neutron powder diffraction patterns of Mn$_3$Cu$_{0.5}$Ge$_{0.5}$N above and below magnetic ordering temperatures, which are at $T=400$ (solid line) and 15 K (dotted line), respectively. The diffraction pattern contains weak reflections from MnO impurity and Al$_2$O$_3$, marked by stars, in the furnace. The inset shows the $\Gamma^{5g}$ Antiferromagnetic structure of Mn$_3$Cu$_{1-x}$Ge$_x$N. (b) $T$ dependence of (100) magnetic reflection intensity and (c) $T$-dependence of lattice constants of Mn$_3$Cu$_{1-x}$Ge$_x$N for $x=0.15$, 0.5 and 0.7.

In this paper, we review the present understanding of the Ge-doping effect on the magnetic properties and MVE in Mn$_3$Cu$_{1-x}$Ge$_x$N.

2. Magnetic structure

Figure 1 (a) shows neutron diffraction patterns of Mn$_3$Cu$_{0.5}$Ge$_{0.5}$N. Solid and dotted lines show the data collected above and below magnetic ordering temperatures. Miller indices are given in reciprocal lattice units of primitive cubic perovskite. We can see magnetic reflections corresponding to magnetic ordering vector $\mathbf{q}=(0 \ 0 \ 0)$, where the (100) and the (210) magnetic reflection are strong. Figures 1 (b) and (c) show the $T$ dependence of the (100) magnetic reflections and $T$-dependence of lattice constants of Mn$_3$Cu$_{1-x}$Ge$_x$N for $x=0.15$, 0.5, and 0.7. The $T$-dependence of lattice constants are consistent with the linear thermal expansions previously reported by Takenaka and Takagi [5]. Both the 1 0 0 magnetic reflection and the lattice constant exhibit sharp increases at $x=0.15$ with decreasing $T$. For $x=0.5$, they gradually increase with decreasing $T$ in the temperature range from 360 to 320 K. The magnetic reflection intensity grows in a progressively wider $T$ range with increasing Ge content. The width of the magnetic peaks is nearly resolution-limited, suggesting long-range Neel ordering. Based on the neutron and the NMR results [9], we conclude that the systems with a gradual volume change exhibit a gradual change in the magnitude of the ordered moments.

Ge-doped samples have a cubic structure (space group: $Pm\bar{3}m$) and magnetic ordering vector $\mathbf{q}=(0 \ 0 \ 0)$. On the basis of these conditions, three possible models have been proposed by Fruchart and Bertaut [4]. Among three magnetic structures, so-called $\Gamma^{5g}$ antiferromagnetic (AF) structure shown in inset of Fig. 1 has large intensity of (100) reflection. Calculated intensities of all reflections assuming $\Gamma^{5g}$ AF structure can reproduce the observed intensities.

Let us now look at other antiperovskite materials. Mn$_3$GaN and Mn$_3$ZnN are well known for their large MVEs [10, 11]. Their volumes show a sudden and pronounced increase with decreasing temperature at the first-order transition, and exhibit the $\Gamma^{5g}$ antiferromagnetic structure in the cubic crystal structure below the phase transition temperature [4]. The MVE of an itinerant electron system has been discussed in terms of the amplitude of magnetic moment. However,
the intimate relationship between the $\Gamma^\text{5g}$ antiferromagnetic cubic structure and large MVE in Mn$_3$Cu$_{1-x}$Ge$_x$N indicates the necessity of a new theoretical framework for MVE, in which the ordered magnetic structure is taken into account.

3. Local structure

The technological essence of NTE in Mn$_3$AN is the discovery of Ge and Sn dopants that broaden the volume change. The strong preference of Ge and Sn for broadening the MVE in Mn$_3$AN revealed in previous studies [5, 6, 7] indicates importance of a local distortion caused by the atomic and/or chemical characteristic of dopants. Therefore we have investigated the local structure by the atomic pair distribution function (PDF) analysis [12, 13]. Although the overall crystal structure remains cubic for 0.15 $\leq$ $x$ $\leq$ 0.7 in the whole $T$ region, interestingly, the PDF shows considerable deviation of the local structure in short length from the average cubic structure.

Figure 2 (a) displays the experimental PDF obtained for $x$ = 0.15, 0.5 and 0.7 at 300 K. Negative peaks at $\sim$1.9 Å and $\sim$2.6 - 3.0 Å correspond to atomic pair bond distances related Mn atoms, because Mn nucleus has negative neutron scattering length. The first negative peak, which comes from the Mn-N correlation in Mn$_6$N octahedra. On the other hand, the second negative peak comes mainly from negative Mn-Cu (or Ge) contribution. The second negative peak around $\sim$2.8 Å is much wider than the first peak and has a double-peak structure shown in the figure, for all samples. In the ideal cubic structure, the second peak should be as sharp as the first peak at $\sim$1.9 Å. The observed PDF provides clear evidence for the local distortion on the Mn-Cu (or Ge) correlation against relatively rigid Mn-N bonds. The observed local distortion is related to the low-temperature tetragonal structure of Mn$_3$GeN. Mn$_3$GeN shows a transition from the high $T$ cubic to the low $T$ tetragonal T$_4$ ($I4/mcm$) phase at $T_t$ $\sim$540 K [14, 15]. The transition primarily involves alternate rotation of the Mn$_6$N octahedra as shown in Fig. 2(b). By this rotation, short and long Mn-Cu(Ge) bonds are generated, resulting in the splitting of the second atomic pair correlation peak.

From the structure refinement with the T$_4$ model, we found that the rotation angle $\theta$ of Mn$_6$N octahedra is a good indicator of the broadening of the MVE. At 300 K, the $\theta$s are in order of $2.3(3)(x=0.15) < 4.1(2)(x=0.5) < 4.6(3)(x=0.7)$. In Mn$_3$Cu$_{1-x}$Ge$_x$N, $\theta$ systematically increases with increasing Ge doping level $x$, corresponding to the increase of the splitting width of the
second negative peak shown in Fig. 2(a). The local octahedral rotation angle clearly correlates with the $T$ dependence of the ordered magnetic moment. Observed structural instability seems to lead to the instability of the amplitude of magnetic moment. For the Invar alloy system, the Invar effect or an instability of the amplitude of magnetic moment also appears near the phase boundary between the fcc and bcc phases [16]. So far, the variation of magnetic phase transition has been discussed on the basis of the spatially averaged information. The present study provides the first experimental result emphasizing the importance of the local structure to the related Invar problem.

4. Summary
The system with the $\Gamma^{5g}$ antiferromagnetic cubic structure exhibits a large MVE in $\text{Mn}_3\text{Cu}_{1-x}\text{Ge}_x\text{N}$. The present results establish a new MVE paradigm that will require a new theoretical framework that takes into account the ordered magnetic structure. A local $T_4$ structure in average cubic phase appears as Ge substitution proceeds. This strongly suggests that the gradual growth of magnetic moment leading to the broadening of MVE is related to the structural instability between cubic and tetragonal induced by Ge substitution.

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