Magnetovolume Effect and Negative Thermal Expansion in $Mn_3(Cu_{1-x}Ge_x)N$

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Metallic manganese nitrides Mn_3AN (A = Zn, Ga, etc) are well-known for their large magnetovolume effect (MVE), *i.e.*, a discontinuous volume expansion at the magnetic transition. However, MVE is exceptionally absent in Mn_3CuN. We found that MVE is recovered by a small amount of Ge in the Cu site. This revival seems to coincide with recovery of the cubic structure. By further Ge doping, the volume expansion becomes gradual ($\Delta T \sim 100$ K) and large negative thermal expansion (NTE) is exhibited around room temperature [$\alpha = -12 \times 10^{-6}$ K^{-1} (α: coefficient of linear thermal expansion) for $Mn_3(Cu_{0.5}Ge_{0.5})N$]. Such a large, isotropic and non-hysteretic NTE is desirable for practical applications.

1. Introduction

Magnetovolume effect (MVE) of magnetic metals and alloys is one of the fundamental problems in condensed-matter physics, because it gives us crucial information on a long-standing problem, magnetism in itinerant-electron systems. In addition, it is also important from a technological viewpoint; large magnetostriction and anomaly in thermal expansion due to MVE are utilized as, for example, actuators (Terfenol-D[1]) and low-expansion materials (Fe$_{64}$Ni$_{36}$ Invar alloy[2]). In particular, MVE is one of the rare mechanisms producing negative thermal expansion (NTE).[3] Indeed, pronounced NTE behaviors are observed in Fe–Pt alloys[4] and Laves phase intermetallic compounds.[5] 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, printed circuit boards, heat sinks, and an athermalizer for a Bragg grating.[6,7]

Antiperovskite manganese nitrides Mn_3AN (A = Zn, Ga, etc) are well-known for their large MVE.[8–15] For these nitrides the large volume expansion is triggered by the magnetic transition from the high-temperature (high-T) paramagnetic phase to the low-T antiferromagnetic (AF) ordered phase with the triangular Γ^{5g} structure. This expansion is isotropic because the crystal structure remains cubic at the transition. For a prototypical material Mn_3GaN,[9] Néel temperature T_N is 298 K and a discontinuous jump in lattice constant a at T_N is estimated to be $\Delta a/a \sim 3.8 \times 10^{-3}$. However, it manifests as a sharp first-order transition. As a result, Mn_3AN has not been considered for any industrial applications to date. Although a full understanding of the MVE for Mn_3AN was still lacking, the interest turned to other materials.

Recently, we discovered that the discontinuous volume expansion of Mn_3AN becomes broad to an order of 100 K and NTE is exhibited by partial substitution of Ge for A.[16] Here,

we thought that understanding of the mechanism of the MVE and control of the thermal and magnetic properties are helpful for fabrication of better NTE materials using Mn_3AN. We recognized importance of Mn_3CuN. It is a puzzling exception among the stoichiometric Mn_3AN family. It becomes ferromagnetic (FM) with the spin structure different from Γ^{5g} at Curie temperature $T_C = 143$ K, accompanied by the transition from cubic to tetragonal T_1 structure.[8,14] At the magnetic transition, Mn_3CuN does not exhibit a large change in volume. However, we found that MVE is restored, surprisingly, by substituting Cu with a small amount of Ge and NTE is also exhibited by further Ge doping.[16] We have investigated suppression and revival of MVE in Mn_3-$(Cu_{1-x}Ge_x)N$. Here we discuss variation in the structural and magnetic properties with Ge doping.

2. Experimental

All of the measurements were performed using sintered polycrystalline samples. We obtained Mn_3AN by solid state reaction.[14,15,17] Powders of Mn_2N and pure element A (purity: 99.9% or higher) were mixed in a bag filled with nitrogen gas and then sealed in a quartz tube under vacuum ($<10^{-1}$ Pa). The sealed quartz tube was heated at 760°C for 40–70 h. To obtain a solid solution $Mn_3(A_{1-x}B_x)N$, we mixed Mn_3AN and Mn_3BN in an appropriate molar ratio, pressed into a pellet, and sealed it in a quartz tube under vacuum. The final sintering was carried out at 800°C for 60 h. Linear thermal expansion $\Delta L(T)/L(300$ K$)$ was measured using a strain gage (KYOWA; type KFL). Because we used the sintered polycrystalline samples, the obtained $\Delta L/L$ is, to be precise, related directly to the volume V expansion in a manner $\Delta L/L = (1/3)\Delta V/V$. This method is simple but requires a material of known expansion. We used copper (purity 99.99%) and the corresponding thermal expansion data of pure copper.[18,19] The T dependence of lattice constant measured by X-ray diffraction were reported for A = Ni,[10] Zn,[11] Ga,[13] and Ag.[12] Our $\Delta L/L$ data for stoichiometric Mn_3AN are in quantitative agreement with previous results from X-ray diffraction studies, thus validating our thermal expansion measurement. Magnetic suscepti-

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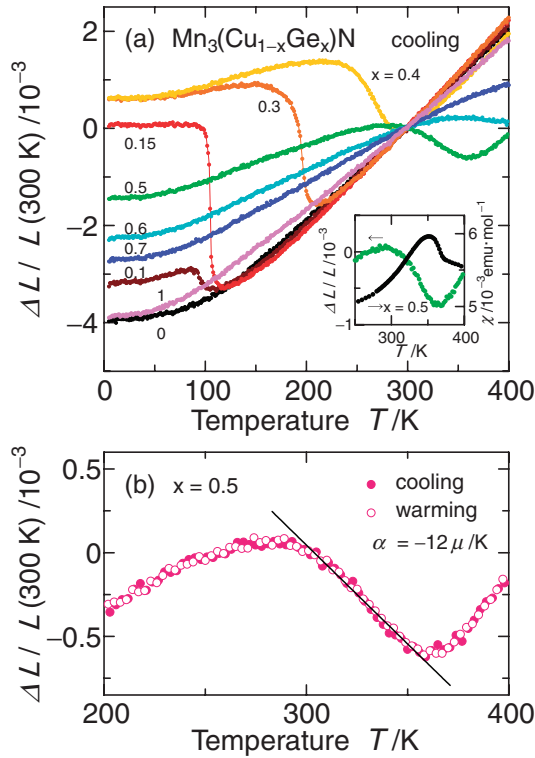
Fig. 1 (color) (a) Linear thermal expansion of solid solution Mn_3-$(Cu_{1-x}Ge_x)N$. Inset: Deviation from the Curie-Weiss behavior in $\chi(T)$ coincides with the onset of NTE ($x = 0.5$). (b) Negative thermal expansion of $Mn_3(Cu_{0.5}Ge_{0.5})N$. Data collected in cooling and warming processes are identical.

bility $\chi(T)$ was measured at 5000 Oe by a SQUID magnetometer. The crystal structure was investigated by means of X-ray powder diffraction.

3. Results and Discussion

Figure 1 displays linear thermal expansion $\Delta L/L$ data for $Mn_3(Cu_{1-x}Ge_x)N$. Although Mn_3CuN does not show MVE, it is recovered by a small amount of Ge and drastically enhanced by a small increment of x from $x = 0.1$ to 0.15 [Fig. 1(a)]. The discontinuous jump in $\Delta L/L$ at the transition is estimated to be 3.3×10^{-3} for $x = 0.15$, which is comparable to those of Mn_3ZnN (4.6×10^{-3})[11,15] and Mn_3GaN (3.8×10^{-3}),[9,13] and one of the largest among Mn_3AX ($X = N$, C) members. At the same compositional region, the cubic structure is recovered. The present X-ray diffraction study revealed that the crystal structure changes from high-T cubic to low-T tetragonal T_1 at the anomaly temperature in $\Delta L/L$ for $x \leq 0.1$, while it remains cubic over a whole temperature range for $0.15 \leq x \leq 0.7$.

As Ge substitution proceeds, the transition temperature increases, the volume expansion becomes gradual, and the magnitude of the anomaly in $\Delta L/L$ decreases. It is known empirically that the transition temperature of Mn_3AN is scaled by the number of valence electrons on A, n_v.[8] 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.) It should be noticed that the gradual lattice change gives rise to a large negative slope
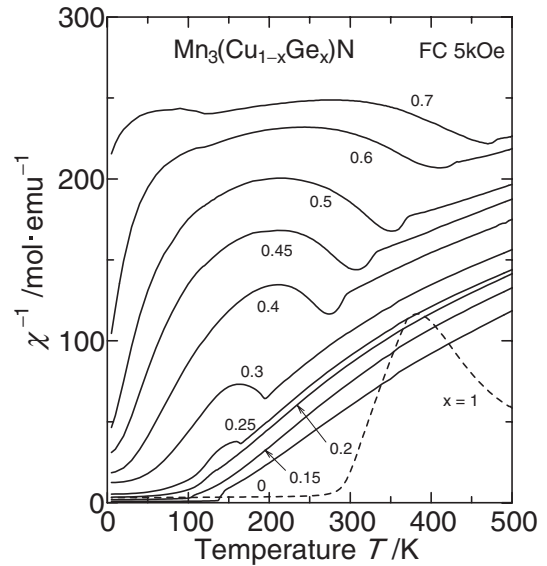

Fig. 2 Inverse suceptibility of $Mn_3(Cu_{1-x}Ge_x)N$ measured in cooling process under 5 kOe.

(large NTE) over a wide T range for $0.4 \leq x \leq 0.6$. For example, $Mn_3(Cu_{0.5}Ge_{0.5})N$ [Fig. 1(b)] shows NTE of $\alpha = -12 \times 10^{-6} K^{-1}$ (α: coefficient of linear thermal expansion) at $T = 280$–$365\,K$ ($\Delta T = 85\,K$). This NTE is isotropic because the cubic structure is maintained down to low temperatures. In addition, this NTE does not show any hysteresis. 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 Mn_3GeN shows a structural and magnetic transition around 400 K but this is complicated by a set of multi-transitions.[8]

The variation in the magnetic properties with Ge doping is summarized in Fig. 2. $Mn_3(Cu_{1-x}Ge_x)N$ compounds are paramagnetic at high temperatures for $x \leq 0.70$.[20] For $x = 0$ and 0.15, θ is positive and χ^{-1} shows a sudden decrease at 143 and 105 K, respectively, showing the FM transition. As Ge substitution proceeds, χ^{-1} increases and θ decreases. Around $x = 0.2$, θ becomes negative, suggesting dominating AF interaction. However, the magnetization increases at low temperatures, giving rise to a peak in χ^{-1}, which suggests that spin canting induces magnetization to a certain extent. Indeed, for $x = 0.2$, the AF transition is not clear but χ only shows a small kink at the transition (Fig. 3, solid triangle). The magnetic state around this composition is considered to be a canted weak FM state. For $x \geq 0.25$, the AF transition becomes clearer in the χ–T curve.

Another important observation in the magnetic measurement is a dip in χ^{-1} just below T_N observed for $0.4 \leq x \leq 0.6$. The dip in χ^{-1} is considered due to elongation of the magnetic moment. Namely, competition between formation of the AF spin structure and elongation of the magnetic moments yields a dip in χ^{-1}. Similar elongation of the moment is probably generic to all of Mn_3AN showing large MVE. However, if the volume expansion and hence the elongation of the moment occur in an instant at the magnetic transition, we may not see a broad peak in $\chi(T)$ below T_N, unlike the Ge-doped compounds. The NTE behavior seems to
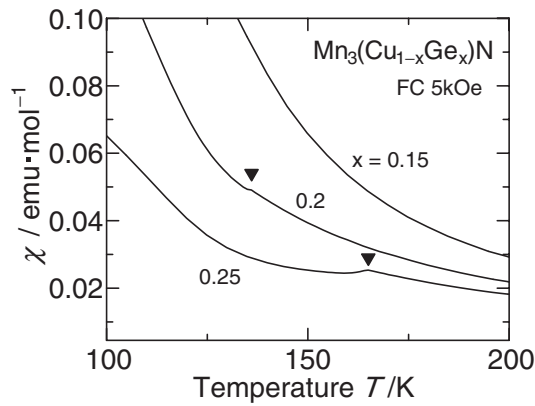
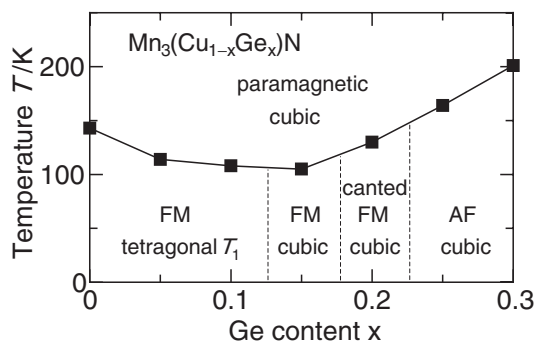Fig. 3 Magnetic suceptibility of $Mn_3(Cu_{1-x}Ge_x)N$ measured in cooling process under 5 kOe.

Fig. 4 Structural and magnetic phase diagram of $Mn_3(Cu_{1-x}Ge_x)N$.

synchronize with this elongation [inset of Fig. 1(a)]. The manganese nitrides exhibit net NTE behavior only when this magnetic contribution overcomes the ordinary lattice expansion.

It is noteworthy that the compositional phase boundary in the magnetic state is not identical to the boundary between tetragonal T_1 and cubic structures (Fig. 4). Variation in the magnetism with Ge doping is more complicated than variation in the structure. The present $\chi(T)$ measurements suggest that the magnetic state varies with Ge doping as follows: FM ($0 \leq x \leq 0.15$), canted weak FM ($x = 0.2$), and AF ($x \geq 0.25$). Because the change between $x = 0.2$ and $x = 0.25$ is rather continuous, the basic spin structure is considered to be the same (AF) structure. The intrinsic change in the magnetic properties seems to occur between $x = 0.15$ and $x = 0.2$. The spin structure is yet to be determined, but the spin structure of the canted FM and AF phases may be Γ^{5g} structure, because this structure is commonly observed for the cubic and AF Mn_3AN showing large MVE.[8] On the other hand, the FM (ferrimagnetic) structure[8] of the stoichiometric Mn_3CuN is reasonably assumed to be maintained in the FM phase. The sequence of the structural and magnetic phases (starting from low Ge doping) is summarized as follows: tetragonal T_1 and FM ($0 \leq x \leq 0.1$), cubic and FM ($x = 0.15$), cubic and canted FM ($x = 0.2$), and cubic and AF ($x \geq 0.25$). The above four phases are, indeed, realized in Mn_3CuN, Mn_3SnC, Mn_3AgN, and Mn_3GaN, respectively.[8] An important finding is co-

incidence between the revival of MVE and disappearance of tetragonal distortion.

We also investigated chemical substitution with elements other than Ge. However, whilst the transition temperature was changed in accord with the empirical rule, we have yet to obtain a volume expansion broad as that seen in the Ge-containing compounds. This suggests the uniqueness of Ge as a dopant. Indeed, Mn_3GeN shows crystal and spin structures that are distinct from other Mn_3AN members.[8] 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*[21] or *relaxor ferromagnets*.[22] Alternatively, the transition may become the Invar-type, second-order transition. The microscopic origin of this broadening is worthy for further exploration.

Manganese nitride is a unique NTE material with 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 α is tunable across a wide range of values. Indeed, at its largest, it can be $-25 \times 10^{-6}\,K^{-1}$ for $A = Zn$–Ge,[16] one order of magnitude larger than commercial NTE materials. (Typically, α is of order $10^{-6}\,K^{-1}$,[3] though for ZrW_2O_8, $\alpha = -9 \times 10^{-6}\,K^{-1}$.[23]) (3) The negative thermal expansion is isotropic and does not show any hysteresis. This can be a great advantage. For example, micro-cracking during repeated thermal cycling may be avoided. Most of the existing NTE materials, with the exception of ZrW_2O_8, are aniso-tropic. (4) The NTE antiperovskites 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. (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.

The previous arguments assume that the number of valence electrons on A, n_v, is a dominant factor for the structural and magnetic properties of the manganese ni-trides.[8] Indeed, the magnetic transition temperature is proportional to n_v. In a model by Jardin and Labbe,[24] narrow bands are formed near the Fermi level by the strong hybridization between N $2p$ and Mn $3d$ orbitals. The occupation of these narrow bands is sensitively changed according to n_v. This sensitivity is responsible for a wide variety of the magnetic and structural properties in the manganese nitrides. However, this seems to be oversimpli-fied. Firstly, magnitude of the MVE is not related to the transition temperature. Although T_N is almost two times different between Mn_3ZnN and Mn_3GaN, the magnitude of the MVE is comparable. Secondly, the revival of MVE seems to coincide with the recovery of the cubic structure in $Mn_3(Cu_{1-x}Ge_x)N$. For overall understanding, we need argu-ments beyond the above Hume–Rothery scheme. The crystal structure may not be merely a consequence of the Hume–Rothery scheme, but essentially important for the MVE.

The Ge-doping recipe for broadening volume expansion provides a new strategy to create a NTE material. A similar procedure, partial substitution of constituent elements, may be applicable to other systems for modifying their first-order MVE, discontinuous expansion in volume and/or elongation

of magnetic moments, to gradual one. Why only Ge broadens the volume expansion also provides an important clue for understanding the mechanism of the first-order magnetic transition in these nitrides. Materials showing the first-order magnetic transition are now attracting because of their possible application to solid magnetic refrigeration.[25–27]

4. Conclusion

We successfully controlled the MVE by the doping level of Ge in $Mn_3(Cu_{1-x}Ge_x)N$. The systematic structural and magnetic studies suggest the close relation between revival of MVE and recovery of the cubic structure. We also found that the volume expansion becomes gradual to an order of 100 K by further substitution of Ge and resultant NTE behavior is exhibited. The isotropic and large NTE without hysteresis is desirable for applications. The origin of the MVE and the mechanism of the broadened volume expansion by Ge deserve further explorations.

Acknowledgments

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