

Research Article

Thermodynamic, Electromagnetic, and Lattice Properties of Antiperovskite Mn_3SbN

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The physical properties of polycrystalline Mn_3SbN were investigated using measurements of the magnetic, calorimetric, and electronic transport properties. At room temperature, the phase crystallizes in a tetragonal structure with $P4/mmm$ symmetry. A remarkably sharp peak in the heat capacity versus temperature curve was found near 353 K. The peak reaches $723 \text{ J mol}^{-1} \text{ K}^{-1}$ at its highest, which corresponds to a transition entropy of $10.2 \text{ J mol}^{-1} \text{ K}^{-1}$. The majority of the large entropy change appears to be due to lattice distortion from the high-temperature cubic structure to the room-temperature tetragonal structure and the accompanying Ferrimagnetic transition.

1. Introduction

Antiperovskite compounds with the formula Mn_3XN or Mn_3XC ($X = \text{Cu, Zn, Ga, Cu, In, or Sn}$) were discovered in the middle of the last century [1]. Recently, interest in these materials has intensively renewed owing to discoveries of new, potentially useful properties [2–4] such as the giant magnetoresistance of Mn_3GaC [5], negative thermal expansion (NTE) of $\text{Mn}_3\text{Cu}(\text{Ge})\text{N}$ [6] and $\text{Mn}_3\text{Zn}(\text{Ge})\text{N}$ [7], magnetostriction of Mn_3CuN [8] and Mn_3SbN [9], and near-zero temperature coefficient of the resistivity of Mn_3CuN [10] and Mn_3NiN [11]. Specifically, Takenaka and Takagi found that Ge-doped Mn_3CuN compound has a large NTE (NTE parameter = $-25 \times 10^{-6} \text{ K}^{-1}$) [12]; using neutron diffraction, the broad NTE was determined to be associated with the local T_4 structure [6]. Asano et al. discovered large magnetostriction in tetragonal Mn_3CuN ; it expands 0.2% and shrinks 0.1% in the directions parallel and perpendicular to an external 90 kOe magnetic field, respectively [8]. In

previous studies, we found a peculiar phase separation and accompanying anomaly in the electronic transport properties of Mn_3ZnN [13, 14], while further study indicated that the thermal expansion properties of Mn_3ZnN can be controlled by introducing Zn vacancies [15]. In addition, Song et al. observed a canonical spin-glass state in Mn_3GaN below the spin-freezing temperature of 133 K [16]. Lukashev et al. systematically studied the spin density of the spin-frustrated state of a Mn-based antiperovskite under mechanical stress [17].

The above-mentioned properties enable a variety of potential applications for this type of material. Although the prospective industrial markets are expected to be large and much effort has already been devoted to studying their structural, electromagnetic, and transport properties, further investigations on antiperovskite materials are still required. In this study, the thermodynamic, electromagnetic, and electronic transport properties of Mn_3SbN are investigated. In particular, we focused on the notable transition entropy that

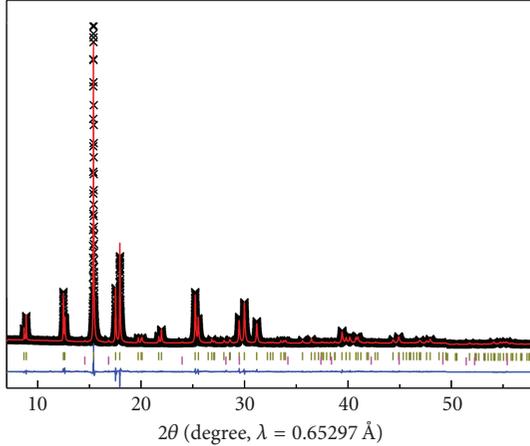


FIGURE 1: Rietveld refinement of the synchrotron XRD pattern of Mn_3SbN . The crosses and solid lines represent the observed and calculated profiles, respectively, and the difference between the curves is shown at the bottom. Bragg positions are marked by small ticks (upper: Mn_3ZnN , lower: MnO).

accompanies the magnetic and crystal structure transition above room temperature.

2. Experimental Details

A polycrystalline Mn_3SbN sample was prepared via the solid-state reaction of fine powders of Sb (99.99%, Rare Metallic Co.) and Mn_2N , which was synthesized by firing Mn powder (99.99%, Sigma Aldrich Co.) in nitrogen at 800°C for 60 h. Stoichiometric amounts of the starting materials were thoroughly mixed, and the mixture was pressed into a pellet. The pellet was sealed in an evacuated quartz tube, heated in a box furnace at 800°C for three days, and then slowly cooled to room temperature in the furnace.

The crystal structure of Mn_3SbN was analyzed by synchrotron X-ray diffraction (SXRD) using a large Debye-Scherrer camera at the BL15XU NIMS beam line of the SPring-8 facility in Hyogo, Japan. The SXRD data were collected for 2θ ranging from 2° to 60° at intervals of 0.003° . The incident beam was monochromatized at $\lambda = 0.65297 \text{ \AA}$. The evolution of the Mn_3SbN crystal structure with temperature was also determined via the measurement of the SXRD patterns.

The temperature dependence of magnetization was measured between 2 and 400 K with applied magnetic fields of 0.1 and 5 kOe using a Magnetic Property Measurements System (Quantum Design). The measurements were conducted on loosely gathered powder under both zero-field cooling (ZFC) and field cooling (FC) conditions. The isothermal magnetization curve was recorded at 10 K between -50 and 50 kOe.

Specific heat (C_p) values were measured between 2 and 400 K with cooling using a Physical Properties Measurement System (Quantum Design). The sample was fixed on a stage using a small amount of grease; the heat capacity of the grease was measured first and subtracted from the total C_p .

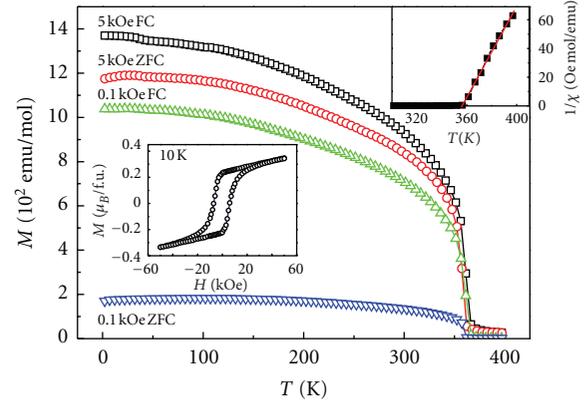


FIGURE 2: Temperature dependence of magnetization in magnetic fields of 0.1 and 5 kOe. The left and right insets show the isothermal magnetization curve at 10 K and χ^{-1} versus T plot of the FC data at 0.1 kOe, respectively.

The electrical resistivity (ρ) was measured between 2 and 400 K with cooling and heating using a conventional four-probe techniques with the same apparatus. The AC gauge current and frequency were 10 mA and 30 Hz, respectively. The electrical contacts were prepared on the surface of a bar-shaped piece of the pellet using silver paste and Pt wires.

3. Results and Discussion

As shown in Figure 1, the synchrotron XRD pattern at room temperature fit well with a model pattern of the proposed structure (space group: $P4/mmm$). The structural parameters of Mn_3SbN were refined by the Rietveld method using the RIETAN-FP program [18]. The occupancy factors of Sb, N, Mn1, and Mn2 were refined to be 1 (fixed), 1 (fixed), 0.97(1), and 0.99(1), respectively, while the isotropic atomic displacement parameters were 0.42(1), 0.84(5), 0.86(1), and $0.78(1) \text{ \AA}^2$, respectively. The lattice constants were calculated to be $a = b = 4.17994(4) \text{ \AA}$ and $c = 4.27718(5) \text{ \AA}$. The final R_{wp} and R_p reliability indexes were below 5.56% and 4.09%, respectively. The analysis revealed 1.91 mass% MnO in the sample as an impurity; as shown later, the magnetic, C_p , and ρ measurements suggest that the impurity does not significantly impact the measurements of Mn_3SbN in this study.

Figure 2 displays the temperature dependence of magnetization of polycrystalline Mn_3SbN . The magnetization steeply increases upon cooling to around 353 K, which suggests the establishment of long-range magnetic order at the magnetic transition temperature (T_c). In addition, a small hysteresis can be observed between the heating and cooling process, implying the first-order character of the magnetic transition. The remarkable bifurcation between the ZFC and FC curves may originate from the spontaneous alignment of random magnetic Mn moments in domain boundaries. It is worth noting that the hysteresis is less significant at a higher magnetic field of 5 kOe, which supports the domain picture.

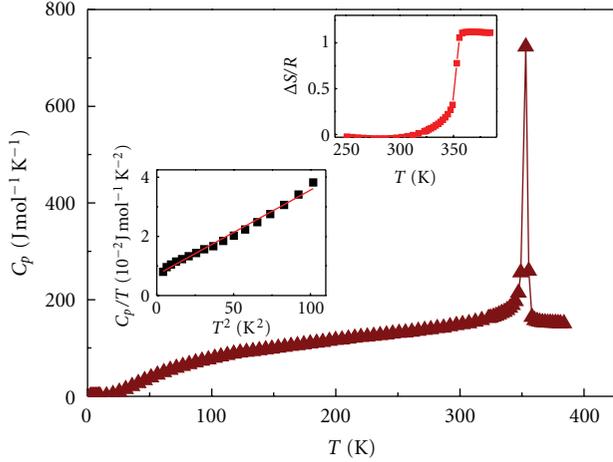


FIGURE 3: Temperature dependence of the C_p of Mn_3SbN . The left and right insets show a linear fit to the C_p/T versus T^2 curve and an estimation of ΔS , respectively.

To further study the magnetic properties, we applied the Curie-Weiss law to the paramagnetic portion. As shown in the right inset of Figure 2, the $\chi^{-1}-T$ plot is well represented by the Curie-Weiss law, that is, the spin-only expression for magnetic susceptibility: $\chi(T) = C/(T - \Theta_W)$, where C is the Curie constant and Θ_W is the Weiss temperature. The value of Θ_W was determined to be 354 K, which suggests that ferromagnetic correlation is dominant in the spin system. The effective Bohr magneton (μ_{eff}) was estimated to be $1.28 \mu_B/\text{Mn}$ from $\mu_{\text{eff}} = 2.83(C/\eta)^{0.5} \mu_B$, where η is the number of magnetic atoms in the molecular formula ($\eta = 3$ in the present case). The value of μ_{eff} is much lower than that of other antiperovskite manganese nitrides (e.g., $2.87 \mu_B$ for Mn_3ZnN [14]) and even lower than the expected moment for localized $S = 1/2$ spins, suggesting an itinerant character of the 3d electrons in Mn_3SbN .

From the isothermal magnetization curve (see the inset of Figure 2), it was found that the magnetization at 50 kOe is $\sim 0.35 \mu_B/\text{Mn}$, which is too small to be caused by full ferromagnetic order. The gap suggests that the spins of the Mn atoms are possibly Ferrimagnetically ordered. This Ferrimagnetic interaction is also suggested by the magnetization characteristics above 10 kOe, that is, the magnetization continuously increases with increasing magnetic field without approaching saturation. The Ferrimagnetic order of a related Mn-based antiperovskite compound was explained by a Γ^{4g} spin structure, where two of the three Mn magnetic moments are antiferromagnetically coupled and the third exhibits FM behavior [19]. It is possible that a similar magnetic structure is established in Mn_3SbN below 353 K.

To further characterize the magnetic transition, the specific heat was measured from 400 to 2 K. As shown in Figure 3, the temperature dependence of C_p features a sharp and narrow peak around T_c ($\Delta C_p/R = 87$ and $\Delta T = 3$ K, where R is the ideal gas constant). This is indicative of a first-order-like transition, as discussed in [20].

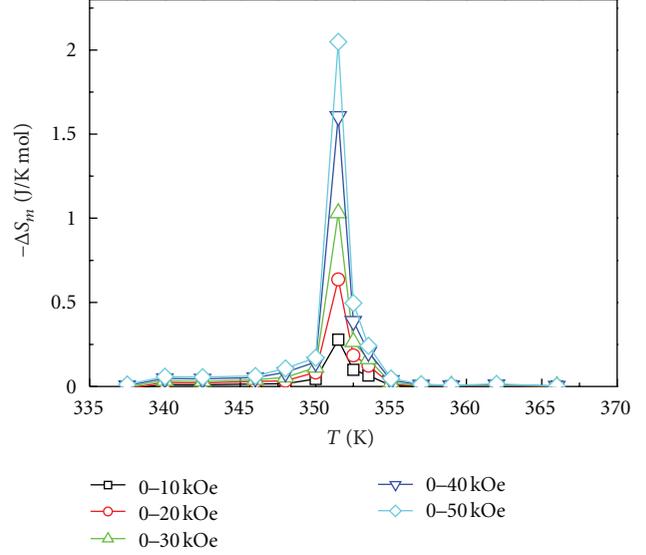


FIGURE 4: Temperature dependence of the magnetic entropy change when the magnetic field changes from 0 to 10, 20, 30, 40, and 50 kOe, respectively.

An estimation of entropy change is essential to understanding the nature of the transition of Mn_3SbN . The peak was roughly separated from the baseline using a polynomial function. Analysis indicates that the total transition entropy (ΔS) is $\sim 1.23R$ (10.2 J/mol K). Since the total entropy change comprises all contributions, including the lattice, electronic, and magnetic changes [20], we evaluated each contribution independently.

For the present compound, the abrupt change of the magnetization at T_c may induce a large $\partial M/\partial T$; therefore, a large magnetic entropy change (ΔS_m) is expected. A series of magnetization curves with small temperature steps were measured; the data allow for a rough estimation of the magnetic entropy change via the thermodynamic Maxwell relation, as follows [21]:

$$\left(\frac{\partial S(T, H)}{\partial H}\right)_T = -\left(\frac{\partial M(T, H)}{\partial T}\right)_H. \quad (1)$$

The magnetic entropy change, $\Delta S_m(T, H)$, can be calculated by

$$\Delta S_m(T, H) = S_m(T, H) - S_m(T, 0) = \int_0^H \left(\frac{\partial M(T, H)}{\partial T}\right)_H dH. \quad (2)$$

The temperature dependence of ΔS_m calculated from (2) with fields of 10, 20, 30, 40, and 50 kOe is shown in Figure 4. The ΔS_m is maximized around T_c , and the maximum is estimated to be $\sim 2.1 \text{ J mol}^{-1} \text{ K}^{-1}$, which implies that the lattice and electronic changes provide a fairly large contribution to the total entropy change.

To investigate the electronic contribution (i.e., the Sommerfeld coefficient or γ), the C_p/T versus T^2 plot below 10 K was analyzed by applying the approximate Debye model, as

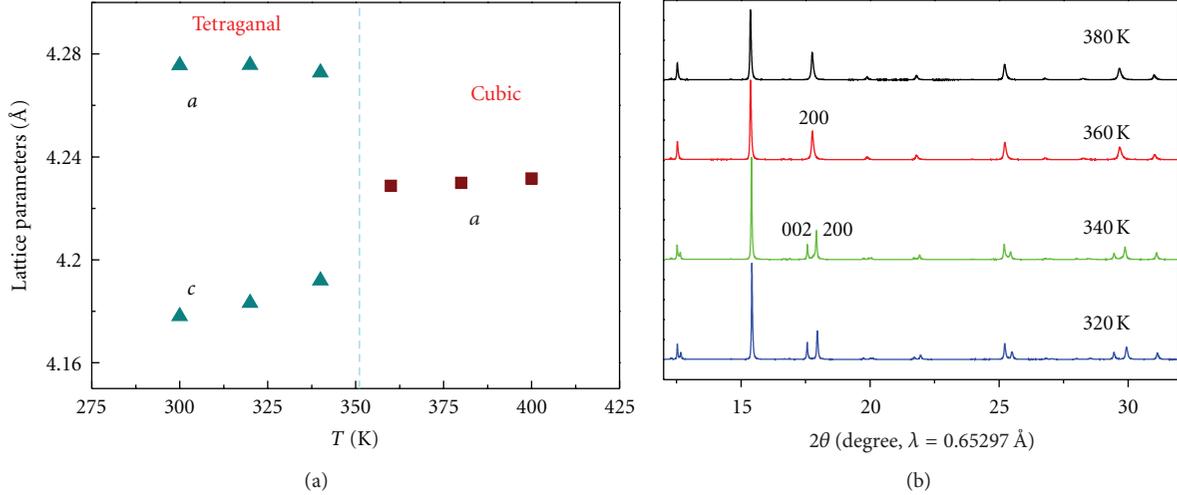


FIGURE 5: Variation in (a) lattice parameters and (b) synchrotron XRD patterns with temperature for Mn_3SbN .

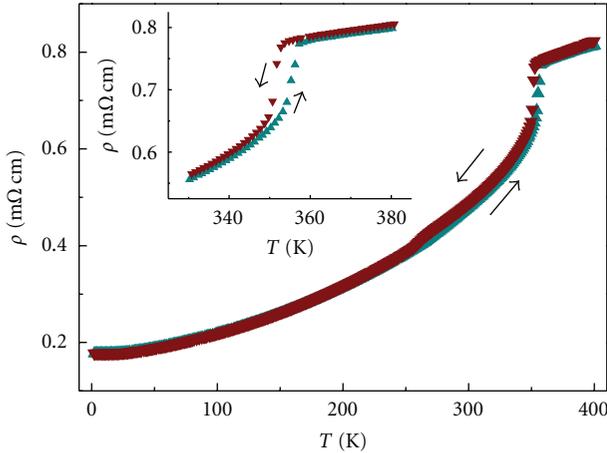


FIGURE 6: Variation of ρ with temperature for Mn_3SbN upon cooling and warming. The inset shows an enlarged view of the ρ variation around the magnetic transition.

follows: $C(T)/T = \gamma + 2.4\pi^4 n N_0 k_B (1/\Theta_D^3) T^2$ ($T \ll \Theta_D$), where n denotes the number of atoms per formula unit, k_B is the Boltzmann constant, N_0 is the Avogadro constant, and Θ_D is the Debye temperature. Fitting to the linear part of the C_p/T versus T^2 plot using the least-squares method yielded γ and Θ_D values of $\sim 7.03(1) \text{ mJ mol}^{-1} \text{ K}^{-2}$ and $326(2) \text{ K}$, respectively. Compared with the parameters determined for other antiperovskite nitrides, Mn_3SbN has a much lower γ , which indicates that the electronic correlation is somewhat weakened [20]. Thus, the electronic contribution might not be a dominant contributor to the total transition entropy.

In addition to the magnetic and electronic contributions, a possible lattice change may need to be investigated to analyze the total transition entropy. The variation of the synchrotron XRD pattern with temperature was measured. As shown in Figure 5(b). It can be seen that some typical reflections disappear with temperature, for example, the two

reflections (002) and (200) for the $P4/mmm$ lattice merge to one reflection. By the Rietveld analysis of the synchrotron XRD patterns, the structural change from tetragonal to cubic was defined, and the lattice constants were determined as a function of temperature, as shown in Figure 5(a). It is obvious that lattice parameter c increases slightly with increasing temperature, whereas a gradually decreases. When the temperature crosses T_c , the tetragonal structure completely transforms to an unidentified cubic structure. Hence, the lattice distortion must contribute to the total entropy change.

According to the thermodynamic relation, the magnetization (M) is equal to the first derivative of the magnetic free energy by the magnetic field, that is, $df(M)/dH$ [22]. Therefore, the sharp transition indicates that the energy barrier in the free energy that separates the paramagnetic and ferromagnetic states is large. Accordingly, T_c and the energy barrier height probably correlate with the electronic density of states, which exhibits a sharp peak near the Fermi level [23]; therefore, the large entropy change is possibly related to the reconstruction of the electronic structure, which could induce the magnetic and structural transition. Since such an electronic reconstruction is often sharply reflected in a ρ - T curve, the electronic transport properties of Mn_3SbN were carefully measured (shown in Figure 6). It is evident that an abnormal drop appears at T_c in the ρ - T curve, which is indicative of an electronic structure reconstruction. In addition, as shown in the inset of Figure 6, a small hysteresis was observed between the warming and cooling curves; this is in agreement with a first-order transition.

4. Conclusions

In conclusion, the thermodynamic, electromagnetic, and transport properties of antiperovskite Mn_3SbN were studied. The phase crystallizes in a tetragonal structure with $a = b = 4.17994(4) \text{ \AA}$ and $c = 4.27718(5) \text{ \AA}$ at room temperature. The C_p measurements revealed a sharp endothermic peak in the C_p - T curve at 353 K , which corresponds to a large

entropy change ($\sim 10.2 \text{ J mol}^{-1} \text{ K}^{-1}$). The present study clearly indicates that the entropy change is accompanied with a Ferrimagnetic transition and lattice distortion as well as a possible electronic structure reconstruction.

Conflict of Interests

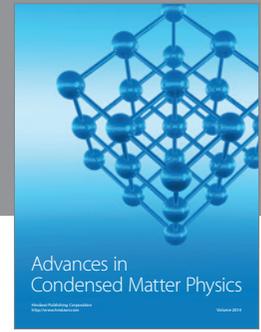
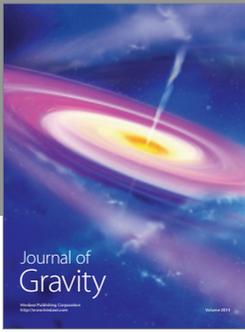
The authors declare that they have no conflict of interests.

Acknowledgments

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