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First-Order Phase Transition at the Curie Temperature in MnAs and $MnAs_{0.9}Sb_{0.1}$

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Structural transformations of MnAs and $MnAs_{0.9}Sb_{0.1}$ were investigated by X-ray diffraction in high magnetic fields up to 5 T. The temperature dependence of the magnetization was measured in a magnetic field of 0.01 T and the Curie temperature T_C was determined to be 315 K for MnAs and 290 K for $MnAs_{0.9}Sb_{0.1}$ during heating process. For both compounds, a metamagnetic transition from a paramagnetic to a ferromagnetic state was observed above T_C. The X-ray diffraction profile at 319 K for MnAs showed a single phase of an orthorhombic MnP-type structure in zero field. An applied magnetic field of 3 T induced the appearance of a hexagonal NiAs-type structure. On further increase of the magnetic field, a single phase with a hexagonal structure was realized above 3.5 T in a forced-ferromagnetic state. The X-ray diffraction profile at 295 K for $MnAs_{0.9}Sb_{0.1}$ showed a hexagonal NiAs-type structure. The coexistence of ferromagnetic and paramagnetic states with different lattice parameters was confirmed in a magnetic field of 2.5 T. The volume expansion induced by a magnetic field was found to be 2.1% for MnAs and 1.1% for $MnAs_{0.9}Sb_{0.1}$.

KEYWORDS: MnAs, X-ray diffraction, structural transformation, metamagnetic transition
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1. Introduction

It is well known that MnAs exhibits a first-order magnetic transition at the Curie temperature $T_C = 317$ K, accompanied by a structural transformation.[1–3] The crystal structure of MnAs is a hexagonal NiAs-type in a ferromagnetic state, and is transformed into an orthorhombic MnP-type structure in a paramagnetic state with thermal hysteresis. The MnP-type structure reverts to a NiAs-type at $T_t = 398$ K in the manner of a second-order transition.[2]

In recent years, much attention has been paid to MnAs as a magnetic refrigerant material because it exhibits a very large magnetocaloric effect due to the first-order transition at T_C. Wada and Tanabe have studied the giant magnetocaloric effect of MnAs and reported that MnAs has a large magnetic entropy change [$\Delta S_{mag} = 30$ J/(K kg) in a magnetic field of 5 T] and an adiabatic temperature change ($\Delta T_{ad} = 13$ K in a magnetic field of 5 T).[4] These changes are comparable with those of $Gd_5Si_2Ge_2$, which is known as a material with a huge magnetocaloric effect. MnAs is also recognized as a high-magnetostrictive material. Chernenko *et al.* reported magnetic field-induced uniaxial strains of up to 0.7% in a magnetic field of 10 T near room temperature.[5]

The substitution of Sb for As changes T_C without a significant loss of the magnetocaloric effect.[6] The magnetic properties of $MnAs_{1-x}Sb_x$ have been reported by various groups.[6–10] These reports show that the dependence of T_C on Sb concentration shows a minimum around $x = 0.3$ and that T_C of MnSb is higher than that of MnAs. The substitution of Sb for As reduces the thermal hysteresis at T_C, but the magnetization change in the transition is still quite sharp in the range of concentration $0.1 < x < 0.5$.[8] Moreover, metamagnetic behavior was observed for the compounds $x = 0$, 0.1, 0.3, and 0.4 above T_C.[6,8,11,12] The $x = 0$ compound, MnAs, shows very large magnetic hysteresis in the metamagnetic transition. For example, the transition field values for increasing and decreasing fields are $B_{c,i} = 3.5$ T and $B_{c,d} = 1.5$ T at 320 K, respectively.[12] However, $MnAs_{0.7}Sb_{0.3}$ shows no hysteresis in the metamagnetic transition, and hence this transition is considered to be second-order.[11,13]

The temperature dependence of the lattice parameters for $MnAs_{1-x}Sb_x$ compounds has also been reported by several researchers.[3,8,13,14] For MnAs, the lattice parameter of the hexagonal *a*-axis was found to abruptly decrease with increasing temperature, and a structural transformation from the hexagonal *a*-axis to an orthorhombic *b*-axis occurs at T_C.[3]

Ido *et al.* reported that the temperature dependence of the lattice parameters for $MnAs_{1-x}Sb_x$ with $x = 0.1$, 0.2, 0.3, and 0.5[8] shows anomalous changes at T_C. With increasing temperature to T_C, the lattice parameters *a* and *c* rapidly decrease and increase, respectively, as T_C is approached. Above T_C both parameters increase linearly. Thus, the temperature dependence of the lattice parameters of the $MnAs_{1-x}Sb_x$ system seems to have a close relationship with the magnetic state. However, there have been no reports on the lattice parameters under a magnetic field.

Recently, Mira *et al.* examined the structural transformation of MnAs induced by magnetic fields using a neutron diffraction technique.[15] Our group has independently studied the field-induced structural transformation of MnAs[12] and $MnAs_{0.9}Sb_{0.1}$ in detail using a high-field X-ray diffraction apparatus to investigate the structural deformation around T_C. In this paper, we present our results of the crystal structure in magnetic fields and discuss the relationship between the magnetic properties and the crystal structure.

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2. Experimental

Samples were prepared by a solid–vapor reaction at facilities at Kyoto University.[4] Powders of Mn and As were sealed in an evacuated quartz tube and sintered at 800 °C. The sintered samples were crushed and annealed at 1000 °C and then quenched using liquid nitrogen. We performed a second annealing process at 800 °C. The magnetization was measured with a conventional SQUID-type magnetometer (MPMS-XL, Quantum Design). The temperature dependence of the magnetization was measured at 0.01 T. The Curie temperature was determined to be 315 K for MnAs and 290 K for $MnAs_{0.9}Sb_{0.1}$ during heating process.

We performed powder X-ray diffraction measurements in magnetic fields up to 5 T at the High Field Laboratory for Superconducting Materials, Institute for Materials Research, Tohoku University.[16] The X-ray diffraction measurements were made with Cu $K\alpha$ radiation at various temperatures from 260 to 319 K using a conventional Gifford-McMahon cycle cryocooler controlled by a resistive heater. The temperature accuracy was 0.1 K. The magnetic field was produced by a cryocooled split-pair superconducting magnet using NbTi wires.

3. Results

3.1 MnAs

Figure 1 shows the isothermal magnetization curves at several temperatures for MnAs. The curve at 280 K shows ferromagnetic behavior and the curves at 316 and 320 K, above T_C, show paramagnetic behavior at low fields. At a critical field, a metamagnetic transition from a paramagnetic to a forced-ferromagnetic state occurs as the field increases. The metamagnetic transition field values at 316 K for increasing and decreasing fields are $B_{c,i} = 2.4$ T and $B_{c,d} = 0.2$ T, respectively. Both transition field values increase with increasing temperature; at 320 K the metamagnetic transition fields are $B_{c,i} = 3.5$ T for an increasing field and $B_{c,d} = 1.5$ T for a decreasing field.

Figure 2 shows X-ray diffraction profiles around T_C in the range $20 < 2\theta < 90^\circ$ with a step size of 0.05°. Here, hkl_o and hkl_h denote the Miller indices for the orthorhombic and hexagonal structures, respectively. In the ferromagnetic state at 285 K, MnAs has a hexagonal NiAs-type structure. With increasing temperature, additional peaks that indicate the existence of the orthorhombic MnP-type structure appear, and a single phase of the MnP-type is observed at 319 K. At 316 K, both the NiAs-type and the MnP-type structures coexist. Mira *et al.* also observed the hexagonal–orthorhombic transformation starting at 313 K and completed at 317 K by neutron diffraction measurements.[15]

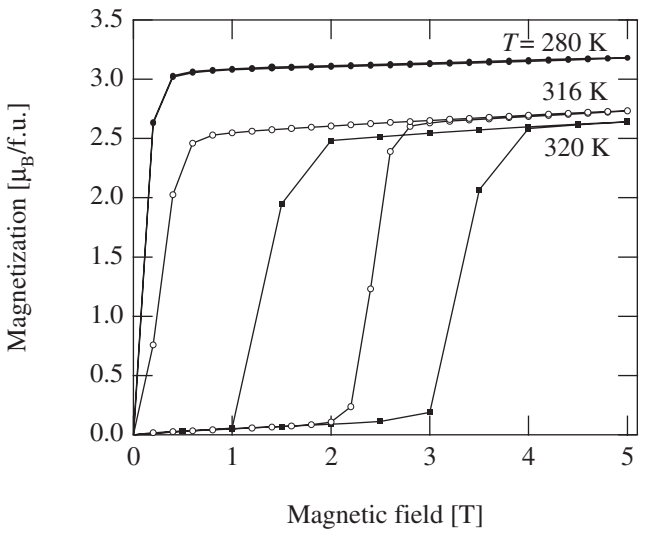

Fig. 1. Magnetization curves for MnAs around T_C.

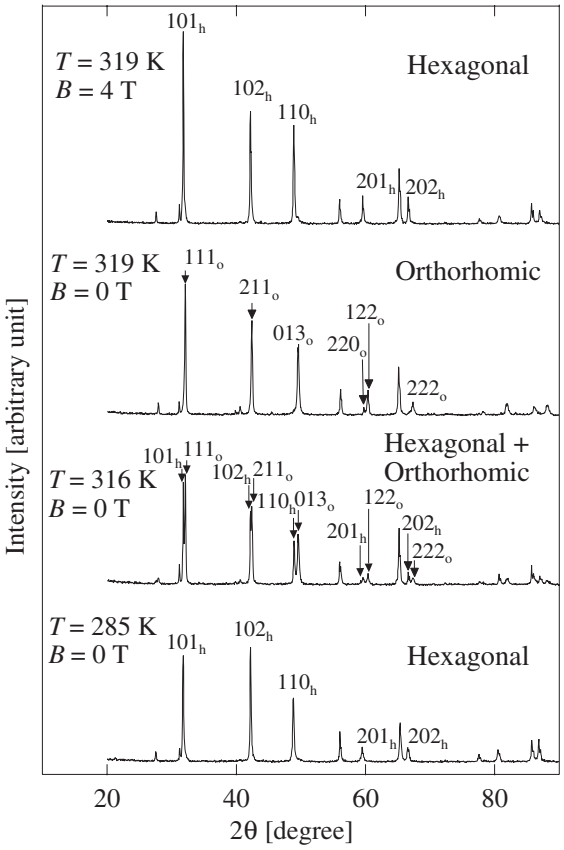

Fig. 2. X-ray diffraction profiles of MnAs at temperatures around T_C. The indices hkl_o and hkl_h denote the Miller indices for the orthorhombic and hexagonal structures, respectively. Only the indices showing the structural transition clearly are annotated.

Applying a magnetic field of 4 T induces a transformation from a MnP-type to a NiAs-type structure at 319 K. Detailed measurements under various magnetic fields at 316 and 319 K were made in the diffraction angle range $58 < 2\theta < 68^\circ$ with a step size of 0.01°. The results at 319 K are shown in the right panel of Fig. 3. Only the orthorhombic MnP-type phase is seen at 0 T in the paramagnetic state at 319 K. With increasing magnetic field, the intensities of the peaks of the MnP-type structure become weaker, while the intensities of the peaks of the NiAs-type become stronger. A single phase of the NiAs-type structure is seen above 3.5 T without any trace of the MnP-type structure. For a decreasing field, the field-induced NiAs-type structure remains down to 1 T. The results at 316 K are shown in the left panel of Fig. 3. At 316 K, the NiAs-type and the MnP-type phases coexist at 0 T. However, when a magnetic field is applied, the MnP-type phase reduces. Applying a magnetic field over 3 T completely suppresses the MnP-type phase. Moreover, on removing the magnetic field, the state for coexistence of two

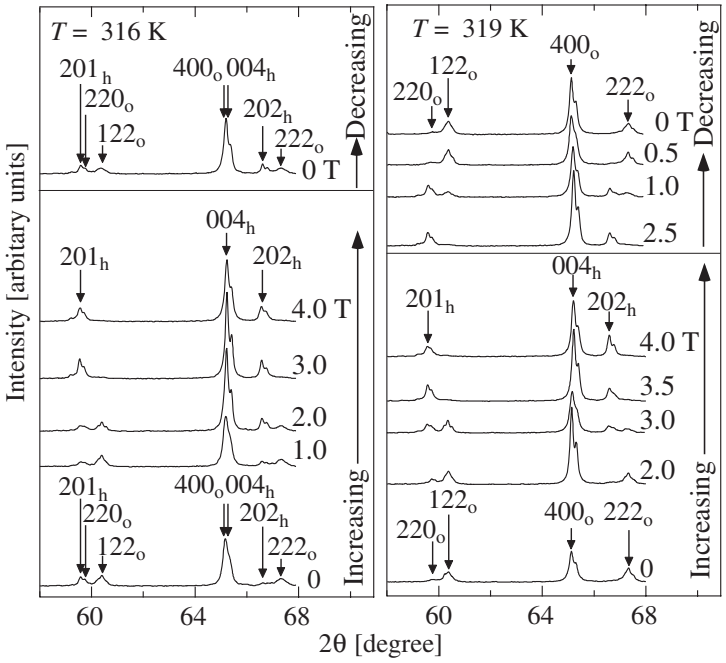

Fig. 3. X-ray diffraction profiles of MnAs in magnetic fields up to 4 T. The figures show the profiles at 316 K (left panel) and 319 K (right panel). In both left and right panels, the lower and upper panels show the profiles for increasing and decreasing magnetic fields, respectively.

phases reappears. The field-induced structural transformation above T_C was also confirmed by Mira *et al.*[15] They reported that a magnetic field of 5 T restored fully the hexagonal phase at 321 K and the phase transformation occurs at smaller values of the magnetic field with decreasing temperature.

These results for the magnetic field dependence of the crystal structure are consistent with the transition fields $B_{c,i}$ and $B_{c,d}$ observed for the magnetization, as shown in Fig. 1. The field-induced structural transformation between the MnP-type and the NiAs-type structures takes place at $B_{c,i}$ for an increasing field and $B_{c,d}$ for a decreasing field. That is, MnAs exhibits a MnP-type structure in the paramagnetic state and a NiAs-type structure in both the spontaneous and forced-ferromagnetic states.

The magnetic field dependence of the lattice parameters at 319 K is plotted in Fig. 4. The transformation of the axes between the hexagonal and the orthorhombic lattice is shown in the inset of Fig. 4. The principal change in the lattice parameters induced by a magnetic field is a transformation from B_{ortho} to a_{hex} with an expansion of 1.4%. The lattice parameters A_{ortho} and c_{hex} decrease slightly with increasing field, while the other parameters are almost independent of the magnetic field. The temperature dependence of the unit cell volume for both structures at 0 and 4 T is shown in Fig. 5. The structural transformation occurs at T_C from the ferromagnetic hexagonal structure to the paramagnetic orthorhombic structure with a volume reduction of 2.1%. Applying a magnetic field of 4 T induces the hexagonal NiAs-type structure and restores the unit cell volume. This result agrees well with the previous macroscopic measurement of the field-induced uniaxial strain of 0.66% reported by Chernenko *et al.*[5]

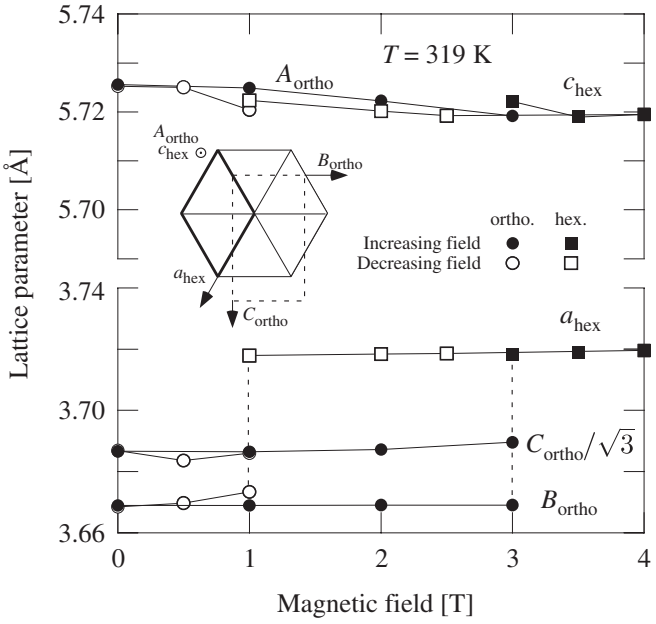

Fig. 4. Magnetic field dependence of lattice parameters of MnAs at 319 K. The closed and open symbols show the lattice parameters for increasing and decreasing fields, respectively. The dotted lines denote the coexistence of the hexagonal NiAs-type and orthorhombic MnP-type structures at 3 T for an increasing field and at 1 T for a decreasing field.

3.2 $MnAs_{0.9}Sb_{0.1}$

Isothermal magnetization curves for $MnAs_{0.9}Sb_{0.1}$ around $T_C = 290$ K are shown in Fig. 6. Metamagnetic behavior appears above 290 K and the curve at 290 K suggests that the temperature is in the vicinity of T_C; the curve is initially in a paramagnetic state and a ferromagnetic state is induced by a small magnetic field with a small hysteresis less than 0.2 T. The transition field increases with increasing temperature and the transition becomes broader. The metamagnetic transition field was determined to be 0.5 T at 290 K, 2.0 T at 295 K and 3.8 T at 300 K from the peak position of the derivative of the magnetization with respect to the field, dM/dB. No metamagnetic transition was observed at 310 K in the magnetic field range we investigated.

Figure 7 shows the X-ray diffraction profiles around T_C in

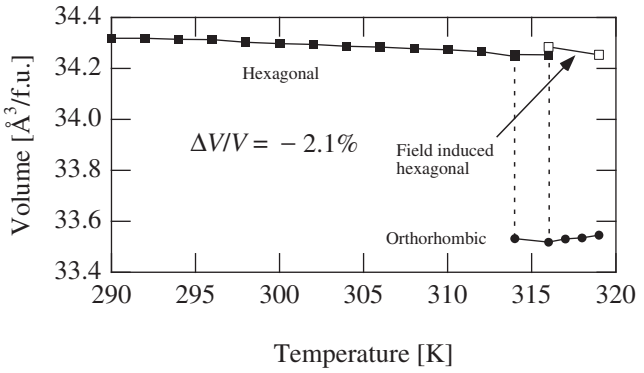

Fig. 5. Temperature dependence of unit cell volume of MnAs. The square and circle symbols represent the hexagonal NiAs-type and orthorhombic MnP-type structures, respectively. The volume of the field-induced hexagonal structure at 4 T is also plotted as open squares.

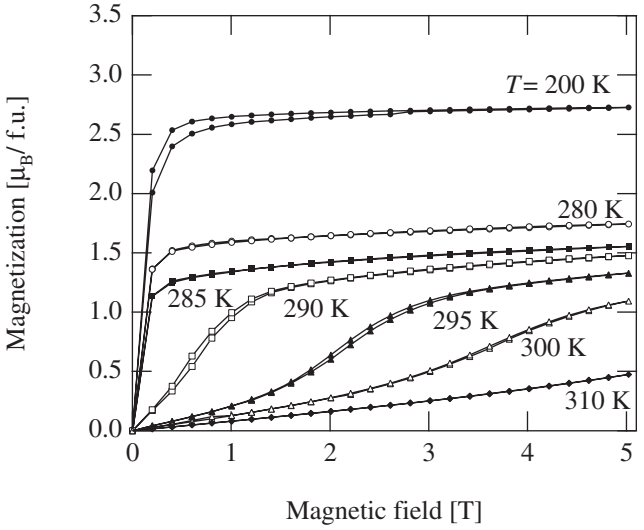

Fig. 6. Magnetization curves for $MnAs_{0.9}Sb_{0.1}$ at various temperatures.

the range $20 < 2\theta < 90^\circ$ with a step size of 0.05°. The profiles indicate that $MnAs_{0.9}Sb_{0.1}$ has a hexagonal NiAs-type structure below and above T_C. Moreover, $MnAs_{0.9}Sb_{0.1}$ retains the same structure in a magnetic field of 4 T. We also made detailed measurements in the range $64 < 2\theta < 67^\circ$ with a step size of 0.01°. The results for the temperature dependence in zero magnetic field (left panel) and the magnetic field dependence at 295 K (right panel) are shown in Fig. 8. As shown in the left panel of Fig. 8, the X-ray diffraction profiles show a single phase of a hexagonal NiAs-type structure below 280 K. In the temperature range of 285 – 289 K, further 004 and 202 reflections appear and grow with increasing temperature, substituting for the original peaks, suggesting the appearance of high- and low-temperature phases. Above 290 K, only the high-temperature phase exists. This structural transformation temperature agrees well with T_C, and hence the low- and high-temperature phases correspond to the ferromagnetic and paramagnetic states, respectively.

The effect of a magnetic field was investigated in the high-temperature phase. The X-ray diffraction profiles at 295 K under magnetic fields for both increasing and decreasing fields are shown in the right panel of Fig. 8. At

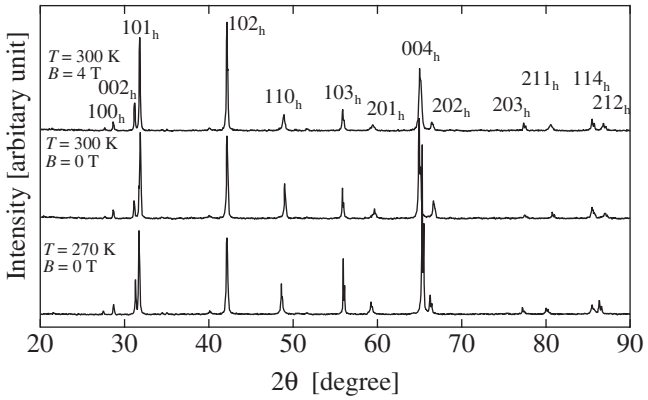

Fig. 7. X-ray diffraction profiles of $MnAs_{0.9}Sb_{0.1}$ around T_C.

zero magnetic field, only the paramagnetic phase is seen. At 2.5 T, however, further 004 and 202 reflections are induced by the magnetic field and coexist with the original reflections of the paramagnetic phase. Above 4 T, the reflections of the paramagnetic phase are not seen and only the field-induced reflections are observed. The profiles of the 004 peak at the temperatures of 290, 300, and 305 K under magnetic fields are shown in Fig. 9 together with the results at 295 K shown in Fig. 8 for comparison. These profiles indicate that the transformation field value increases with increasing temperature. This is consistent with the metamagnetic transition field value, as shown in Fig. 6. Hence, the forced-ferromagnetic phase has the same structure as the paramagnetic state with different lattice parameters. The magnetic field dependence of the lattice parameters at 295 K is plotted in Fig. 10. Applying a magnetic field of 5 T induces lattice parameter changes of -2.4% for the a-axis and 0.56% for the c-axis.

The temperature dependence of the unit cell volume for $MnAs_{0.9}Sb_{0.1}$ at $B = 0$ and 5 T is shown in Fig. 11. In the ferromagnetic region, the effect of the magnetic field is very small. In the paramagnetic region, a magnetic field induces the forced-ferromagnetic phase with a larger volume than the paramagnetic phase. The expansion of the unit cell volume is about 1.1% at 295 K, which is about half that for MnAs.

4. Discussion

In the $MnAs_{1-x}Sb_x$ system, compounds with $x \geq 0.1$ have a NiAs-type structure at all temperatures, while an MnP-type structure appears in a narrow temperature range above T_C for $x < 0.1$.[8] Thermal hysteresis at T_C, indicating a first-order transition, was only seen in the composition range $x < 0.1$.[10] Thus, the first-order transition in $MnAs_{1-x}Sb_x$ is considered to depend on the structural transformation between the NiAs-type and the MnP-type structures.

The present results show that MnAs undergoes a first-order transition induced by magnetic fields from a paramagnetic to a forced-ferromagnetic state above T_C. This transition is accompanied by a structural transformation from an orthorhombic MnP-type to a hexagonal NiAs-type structure via a region where the two phases coexist. These results are similar with the temperature-induced transition at T_C. This structural transformation exhibits hysteresis in a magnetic field, demonstrating that it is a first-order transition.

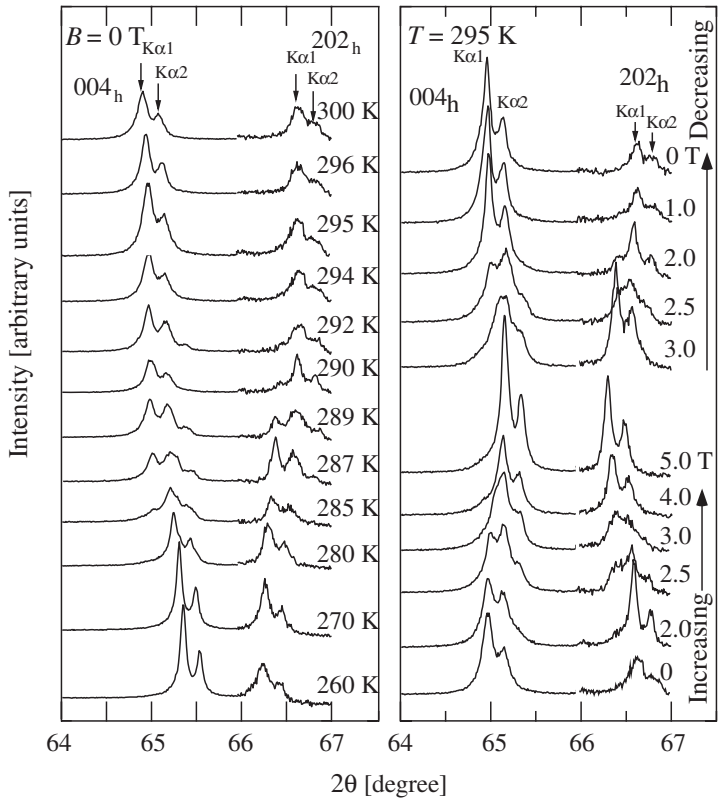

Fig. 8. X-ray diffraction profiles of $MnAs_{0.9}Sb_{0.1}$ at temperatures around T_C in zero magnetic field (left panel) and for various magnetic fields at 295 K (right panel).

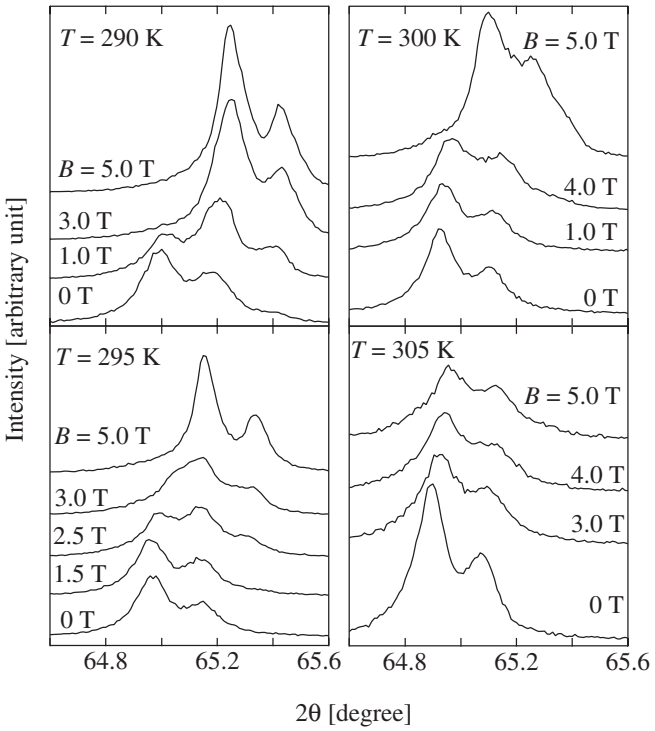

Fig. 9. X-ray diffraction profiles of the 004 reflection for $MnAs_{0.9}Sb_{0.1}$ at 290, 295, 300, and 305 K under various magnetic fields.

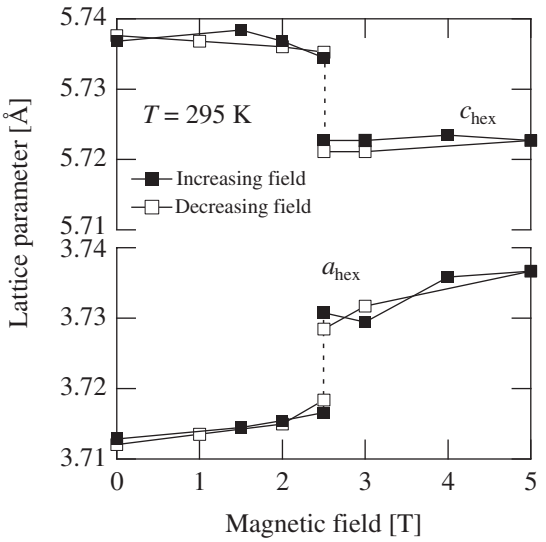

Fig. 10. Magnetic field dependence of lattice parameters of $MnAs_{0.9}Sb_{0.1}$ at 295 K. The closed and open symbols show the lattice parameters for increasing and decreasing fields, respectively.

On the other hand, our X-ray diffraction measurement results for $MnAs_{0.9}Sb_{0.1}$ reveal that the NiAs-type structure appears for all temperatures; no trace of the MnP-type structure was detected. Moreover, the coexistence of two kinds of NiAs-type structure was observed around T_C, which is an evidence of a first-order transition. The small hysteresis in the magnetization curves seen in Fig. 6 also supports the characterization of the transition in $MnAs_{0.9}Sb_{0.1}$ as a first-order. Govar *et al.* have also reported temperature-induced structural changes with the coexistence of two kinds of lattice parameters for $MnAs_{0.9}Sb_{0.1}$ single crystals.[14] The X-ray diffraction profiles shown in Figs. 7–9 suggest that $MnAs_{0.9}Sb_{0.1}$ has two kinds of NiAs-type structure, which appeared in the intermediate coexisting phase. The temperature dependence of the lattice parameters shows that the parameters change abruptly at T_C. Moreover, the structural transformation induced by a magnetic field is consistent with

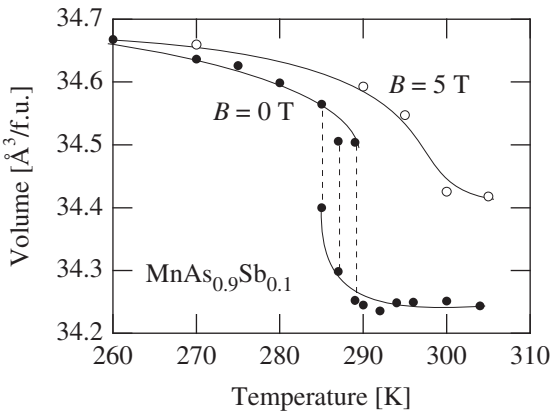

Fig. 11. Temperature dependence of unit cell volume of $MnAs_{0.9}Sb_{0.1}$. The dotted lines denote the coexistence of different lattice parameters. The solid curves are visual guides. The volume of the field-induced structure at 5 T is also plotted as open circles.

the metamagnetic transition field shown in Fig. 6. From these facts, we can conclude that the transition between the paramagnetic and the ferromagnetic states in $MnAs_{0.9}Sb_{0.1}$ is a first-order and each state has a NiAs-type structure of a different size. The coexistence of two phases was observed at 1 T for 290 K and 2.5 T for 295 K. However, it was not observed above 300 K. The structural transformation proceeds successively from the paramagnetic phase to the ferromagnetic phase. This is consistent with the broad metamagnetic transition that appears in the isothermal magnetization curve above 300 K.

5. Summary

We made detailed X-ray diffraction measurements on MnAs and $MnAs_{0.9}Sb_{0.1}$ in magnetic fields up to 5 T around T_C in order to investigate the structural transformation induced by high magnetic fields. For MnAs, a first-order structural transformation from an orthorhombic MnP-type to a hexagonal NiAs-type structure was confirmed by applying a magnetic field at 319 K. At this temperature, the X-ray diffraction profiles at 1–3 T show the coexistence of both the MnP-type and NiAs-type structures, exhibiting a hysteresis. These results show that MnAs in both spontaneous and field-induced ferromagnetic states has a hexagonal NiAs-type structure. For $MnAs_{0.9}Sb_{0.1}$, the coexistence of two kinds of NiAs-type structure was observed around T_C. The field-induced structural transformation above T_C from a NiAs-type to a different NiAs-type structure with different lattice parameters occurs via a coexistence region. This transformation originates in the paramagnetic to ferromagnetic transition. The unit cell volume change induced by a magnetic field is very large for these compounds. The maximum expansion induced by a magnetic field is 2.1% for MnAs and 1.1% for $MnAs_{0.9}Sb_{0.1}$.

Acknowledgments

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