Structural Transformation of MnAs\(_{1-x}\)Sb\(_x\) under High Magnetic Fields*

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Structural transformation induced by magnetic fields on MnAs and MnAs\(_{0.9}\)Sb\(_{0.1}\) was investigated by the X-ray diffraction measurements in high magnetic fields up to 5 T. The X-ray diffraction profiles at 319 K for MnAs showed a single phase of the orthorhombic MnP-type structure in zero field, and applying a magnetic field of 3 T caused an appearance of the hexagonal NiAs-type structure. On further increase of magnetic fields up to 5 T, the X-ray diffraction profiles at 319 K for MnAs showed a single phase of the orthorhombic MnP-type structure. These results imply that the transition at \(T_C\) for MnAs\(_{0.9}\)Sb\(_{0.1}\) is of the first-order.

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1. Introduction

MnAs forms the hexagonal NiAs-type structure at low temperature and transforms into a paramagnetic phase with the orthorhombic MnP-type structure at the Curie temperature \(T_C\).\(^{1-3}\) This transformation is of the first-order, accompanied by discontinuous changes of the magnetization and the volume. In the paramagnetic region, the magnetization curve exhibits a field-induced metamagnetic transformation.\(^4,5\)

Recently, MnAs has attracted interest for practical application. A large magnetocaloric effect for MnAs due to the first-order magnetic transition was examined by Wada et al.\(^5\) On the other hand, a giant magnetic field-induced uniaxial strain of 0.7\% in MnAs is also reported by Chernenko et al.\(^7\)

It is also known that Sb substitution for As eliminate the first-order characteristic at \(T_C\) in MnAs.\(^8,9\) At the same time, the structural transformation from the hexagonal to the orthorhombic structures disappears and the hexagonal NiAs-type structure remains in all temperature range.\(^9\) In spite of the disappearance of the first-order characteristic, the temperature dependence of magnetization shows a very sharp transition at \(T_C\) for MnAs\(_{0.9}\)Sb\(_{0.1}\) and MnAs\(_{0.7}\)Sb\(_{0.3}\).\(^6,10\) Moreover, a large magnetocaloric effect has been reported for the MnAs\(_{1-x}\)Sb\(_x\), \(0 \leq x \leq 0.4\) without thermal hysteresis.\(^6,11\)

There are several previous reports about the temperature dependence of the lattice parameters for the MnAs\(_{1-x}\)Sb\(_x\) system.\(^2,3,12,13\) However, the crystal structure in magnetic fields has not been clarified so far. Quite recently, Mira et al. measured the structural transformation induced by magnetic fields by neutron diffraction experiments for MnAs.\(^14\) In our group, the magnetic field dependence of the crystal structure of MnAs and MnAs\(_{0.9}\)Sb\(_{0.1}\) has been studied in detail using the high-field X-ray diffraction apparatus to investigate the structural deformation around \(T_C\). In this paper, we present the results of the crystal structure in magnetic fields and discuss the relationships between the magnetism and the crystal structure.

2. Experimental

The polycrystalline sample was prepared by a solid-vapor reaction at Kyoto University.\(^6,11\) Magnetization was measured with a conventional SQUID magnetometer. Temperature dependence of magnetization was measured in a magnetic field of 0.01 T and the Curie temperatures for the present samples were determined to be 315 K for MnAs and 290 K for MnAs\(_{0.9}\)Sb\(_{0.1}\) in heating process.

Powder X-ray diffraction measurements with Cu \(K\alpha\) radiation at various temperatures from 200 to 319 K in magnetic fields up to 5 T were carried out at the High Field Laboratory for Superconducting Materials, Institute for Materials Research, Tohoku University.\(^6\) We confirmed the single phases with the hexagonal NiAs-type structure at 295 K and with the orthorhombic MnP-type structure at 319 K for the present sample of MnAs. The X-ray diffraction profiles indicated that the MnAs\(_{0.9}\)Sb\(_{0.1}\) sample was almost in a single phase with the NiAs-type at 270 K and 305 K. The determined lattice parameters of MnAs\(_{0.9}\)Sb\(_{0.1}\) agreed well with the previous report.\(^13\)

3. Results and Discussion

Figure 1 shows the X-ray diffraction profiles for MnAs in the range of 20\(^\circ\) \(\leq 2\theta \leq 90\(^\circ\)\) with a step size of 0.05\(^\circ\) at 319 K in the magnetic fields of 0 T and 4 T. Here, \(h0k\) and \(hkl_b\) denote the Miller indices for the orthorhombic-type and the hexagonal-type structure, respectively. At this temperature, MnAs is in a single phase with the orthorhombic MnP-type structure in zero field. However, the diffraction profile under the magnetic field of 4 T shows clearly the single phase with the hexagonal NiAs-type structure. That is, the applying a magnetic field of 4 T restores the NiAs-type structure from the MnP-type structure above \(T_C\). Detailed measurements were also carried out in the diffraction angle range of 58\(^\circ\) \(\leq 2\theta \leq 90\(^\circ\)\).

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with a step size of 0.01 under magnetic fields up to 4 T. As shown in Fig. 2, only the MnP-type phase is seen at 0 T in the paramagnetic state at 319 K. With increasing magnetic field, the peak intensities of the MnP-type structure become weaker, while the peak intensities of the NiAs-type become larger. The single phase of the NiAs-type structure is formed above 3.5 T without any trace of the MnP-type structure. In decreasing process of the magnetic fields, the field-induced NiAs-type structure still remains down to 1 T. These results on the magnetic field dependence of the crystal structure are consistent with the metamagnetic transition field.15)

We also measured the temperature dependence of the X-ray diffraction profile in detail at zero field.15) Two-phase coexistence of the hexagonal NiAs-type and the orthorhombic MnP-type structure also appeared around Tc. This result also suggests that the crystal structure has a close relationship with the magnetic state. That is, MnAs exhibits the MnP-type structure in the paramagnetic state and the NiAs-type in the ferromagnetic state.

Figure 3 shows the X-ray diffraction profiles for MnAs$_{0.9}$Sb$_{0.1}$ in the range of $20^{\circ} < 2\theta < 90^{\circ}$ with a step size of 0.05 around Tc. The profiles suggest that MnAs$_{0.9}$Sb$_{0.1}$ has a hexagonal NiAs-type structure above and below the Curie temperature and retains the same structure in a magnetic field of 4 T. The results of the detailed measurements in zero magnetic field around Tc are shown in Fig. 4. The coexistence of both low and high temperature phases with the NiAs-type structure is clearly seen between 280 and 290 K. This result suggests that MnAs$_{0.9}$Sb$_{0.1}$ exhibits the first-order transition at Tc.

The X-ray diffraction profiles at 295 K under the magnetic fields both increasing and decreasing process are shown in Fig. 5. The two phase coexistence is also seen at 2.5 T. These profiles suggest that magnetic fields induce the NiAs-type...
structure with the different size. The lattice parameters above 4 T for MnAs$_{0.9}$Sb$_{0.1}$ is different from those below 2 T, and these two kinds of the phases coexist around 3 T.

In MnAs$_{1-x}$Sb$_x$ system, it has been reported that the compounds with $x \geq 0.1$ have the NiAs-type structure in all temperature ranges and the MnP-type structure appears in a narrow temperature range above $T_C$ for $x < 0.1$.\(^{15}\) It has been also reported that the thermal hysteresis at $T_C$, indicating the first-order transition, was only seen in the composition range of $x < 0.1$.\(^{9}\) Thus, the first-order transition in MnAs$_{1-x}$Sb$_x$ has been considered to depend on the structural transformation between the ferromagnetic NiAs-type and the paramagnetic MnP-type structure. However, the present X-ray diffraction measurements suggest that the NiAs-type structure appears in both the ferromagnetic and paramagnetic phases, and the transition between the both states occurs via the two phase coexistence region. Moreover, we cannot find any trace of the MnP-type structure. Therefore, we can conclude that the field-induced transition between the paramagnetic and the ferromagnetic states is of the first-order with the structural transformation between the different lattice parameters of the NiAs-type structure in MnAs$_{0.9}$Sb$_{0.1}$.

Change of the lattice volume induced by magnetic fields on MnAs and MnAs$_{0.9}$Sb$_{0.1}$ is plotted in Fig. 6. The broken lines denote the coexistence field of the paramagnetic and the ferromagnetic structures. For MnAs, the volume of the forced ferromagnetic NiAs-type phase is about 2.1% larger than that of the paramagnetic MnP-type phase.\(^{15}\) This result agrees well with the previous macroscopic measurement of the field-induced uniaxial strain of 0.66% reported by Chernenko et al. on a polycrystalline sample.\(^7\) However, the magnetostriction in each phase is very small. The volume of the forced ferromagnetic NiAs-type phase is about 1.1% larger than that of the paramagnetic NiAs-type phase for MnAs$_{0.9}$Sb$_{0.1}$.

4. Conclusion

We performed the X-ray diffraction measurements in detail 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, it was confirmed that the first-order structural transformation from the orthorhombic MnP-type to the hexagonal NiAs-type structure occurs by applying magnetic fields at 319 K. The X-ray diffraction profiles at this temperature show the existence of two-phase region of MnP-type and NiAs-type structures at 1–3 T with a hysteresis. These results show that MnAs in both spontaneous and field induced ferromagnetic states has the hexagonal NiAs-type structure. After changing the crystal structure by applying magnetic fields, the volume per formula unit increases by 2.1%, while the magnetostriction in each phase is very small. For MnAs$_{0.9}$Sb$_{0.1}$, we observed the evidence for the first-order transition between the paramagnetic to the spontaneous and the ferromagnetic states for the first time. It is clearly observed that the field induced structural transformation above $T_C$ from a NiAs-type to another NiAs-type structures with different lattice parameters via the two phase coexistence region. The lattice volume expansion of 1.1% is caused by applying a magnetic field of 5 T.

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REFERENCES


Fig. 5 X-ray diffraction profiles of MnAs$_{0.9}$Sb$_{0.1}$ at 295 K in the magnetic fields up to 5 T.

Fig. 6 Change of the lattice volume induced by the magnetic field for MnAs and MnAs$_{0.9}$Sb$_{0.1}$. Closed and open symbols denote the increasing and decreasing process, respectively.