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Physica B 346–347 (2004) 408–412
PHYSICA B
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X-ray diffraction study of the structural phase transition in MnAs under high magnetic fields

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Abstract

The structural phase transition induced by magnetic fields on MnAs was observed by the X-ray diffraction measurements in high magnetic fields up to 4 T. Magnetization measurements showed that Curie temperature T_C was 315.5 K for increasing temperatures and a metamagnetic transition from the paramagnetic to the ferromagnetic state occurred above T_C. The structural transformation from the hexagonal NiAs-type to the orthorhombic MnP-type structure was confirmed at T_C with increasing temperature from 290 to 319 K via two-phase coexistence region. The X-ray diffraction profiles at 319 K showed the single phase of the MnP-type structure in zero field and applying magnetic field of 3 T caused appearance of the Brag peak of the hexagonal structure. On further increase of magnetic fields, the single phase of the hexagonal structure was observed above 3.5 T in the forced ferromagnetic state. Both the magnetic and structural transitions induced by magnetic fields above T_C were first order with a hysteresis and had a close relationship between each other.

PACS: 61.10.Nz; 61.50.Ks; 75.50.Cc

Keywords: MnAs; X-ray diffraction; Structural transformation; Metamagnetic transition

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 Curie temperature T_C [1–3]. This transformation is a first-order transition accompanied by a discontinuous change of magnetization and volume. Furthermore, a second-order transformation occurs at $T_t = 398$ K from the MnP-type to the NiAs-type structure [2]. In the paramagnetic region of $T_C < T < T_t$, the magnetization curve exhibits a field-induced metamagnetic transition [4–6].

The first-order transition for MnAs is characterized by the structural transformation as mentioned above. But the crystal structure in magnetic fields has not been clarified so far. Quite recently, Mira et al. examined the structural transformation induced by magnetic fields on MnAs by neutron diffraction experiments [7]. Independently,we have investigated that the field-induced structural transformation in MnAs in detail using the high-field X-ray diffraction apparatus to clarify the structural deformation around T_C. In this paper, we will

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0921-4526/$ - see front matter
doi:10.1016/j.physb.2004.01.116

present our results of the crystal structure in magnetic fields and the relationships between the magnetic property and the crystal structure.

2. Experimental

The sample was prepared by a solid–vapor reaction at Kyoto University [8]. Powders of Mn and As were sealed in evacuated quartz tubes and sintered at 800°C for 7 days. The reaction products were crushed and the same heat treatment was performed again. Magnetization was measured with a conventional SQUID-type magnetometer Quantum Design's MPMS-XL. Temperature dependence of magnetization was measured at 0.01 T and Curie temperature for the present sample was determined to be 315.5 K in heating process. Powder X-ray diffraction measurements in magnetic fields up to 4 T were carried out at the High Field Laboratory for Superconducting Materials, Institute for Materials Research, Tohoku University [9]. We performed the X-ray diffraction measurements with Cu Kα radiation at various temperatures from 280 to 319 K using a conventional GM cryocooler controlled by a resistive heater. Magnetic fields were produced with a cryocooled split-pair NbTi superconducting magnet.

3. Results and discussion

Fig. 1 shows the results of magnetization curves at several temperature. Magnetization curve shows ferromagnetic behavior at 280 K. At 316 and 320 K (above T_C), the magnetization curves show paramagnetic behavior at low fields. On reaching a critical field, $B_{c,i}$, a metamagnetic transition from the paramagnetic to the forced ferromagnetic state occurs. Hysteric behavior is observed on the decreasing process and the critical field for the decreasing field, $B_{c,d}$, is smaller than $B_{c,i}$. The critical fields are determined to be $B_{c,i} = 2.4$ T, $B_{c,d} = 0.2$ T at 316 K and $B_{c,i} = 3.5$ T, $B_{c,d} = 1.5$ T at 320 K. It is noted that the transition field increases and the hysteresis becomes smaller with increasing temperature. These magnetic behaviors

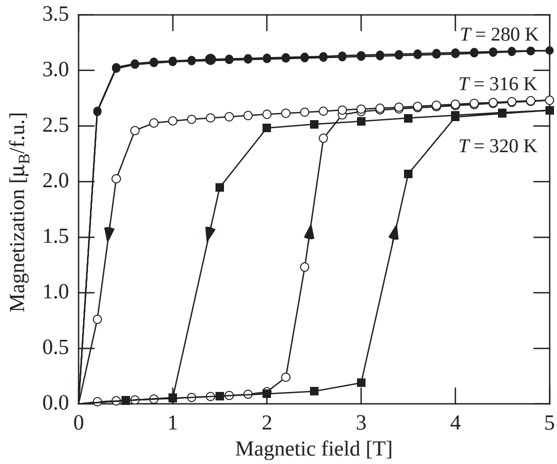

Fig. 1. Magnetization curves around T_C. The inset shows the temperature dependence of magnetization at 0.01 T.

are similar to those of typical itinerant electron metamagnets such as $Co(S, Se)_2$ [10] and $La(Fe, Si)_{13}$ [11], which exhibit the first-order metamagnetic transition just above T_C [12,13].

Fig. 2 shows the X-ray diffraction profiles in the range of $20° < 2\theta < 90°$ with a step size of 0.05° around T_C. Here, hkl_o and hkl_h denote the Miller indices for the orthorhombic-type and ones for the hexagonal-type structure, respectively. At 285 K, the X-ray profile shows the single phase of the NiAs-type structure in the ferromagnetic state. With increasing temperature, new diffraction peaks indicating the MnP-type phase appear in addition to the diffraction peaks due to the NiAs-type structure. Both the NiAs- and the MnP-type structures coexist at 316 K. And then, the single phase of the MnP-type appears at 319 K in the paramagnetic state. At 319 K, furthermore, it is clearly observed that applying magnetic field of 4 T restores the NiAs-type structure from the MnP-type structure. We also performed detailed measurements in the range of $20° < 2\theta < 90°$ with a step size of 0.05° around T_C as shown in Fig. 3 These profiles suggest that the NiAs- and the MnP-type structures coexist in the temperature range of 314–317 K and no peak of the NiAs-type hexagonal structure appeared above 318 K at last.

Fig. 4 shows the magnetic field dependence of the X-ray diffraction profiles at 319 K. Only the

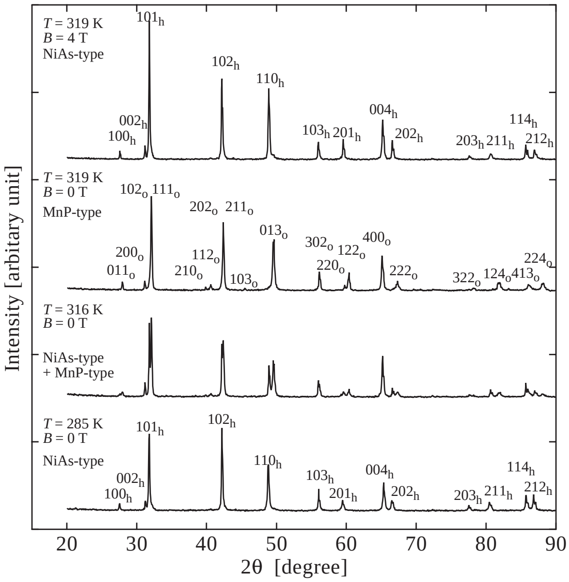

Fig. 2. X-ray diffraction profiles of MnAs at several temperatures around T_C. The Miller indices are represented as hkl_o for the orthorhombic type and hkl_h for the hexagonal type structure. Some indices of the unresolved multiplets are omitted to display.

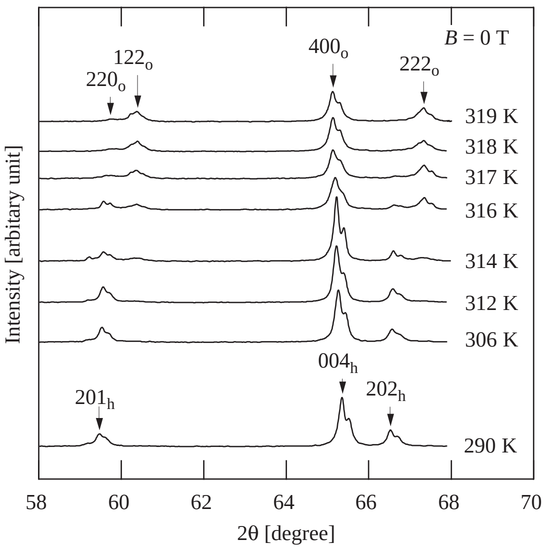

Fig. 3. X-ray diffraction profiles of MnAs at several temperatures at 0 T around T_C.

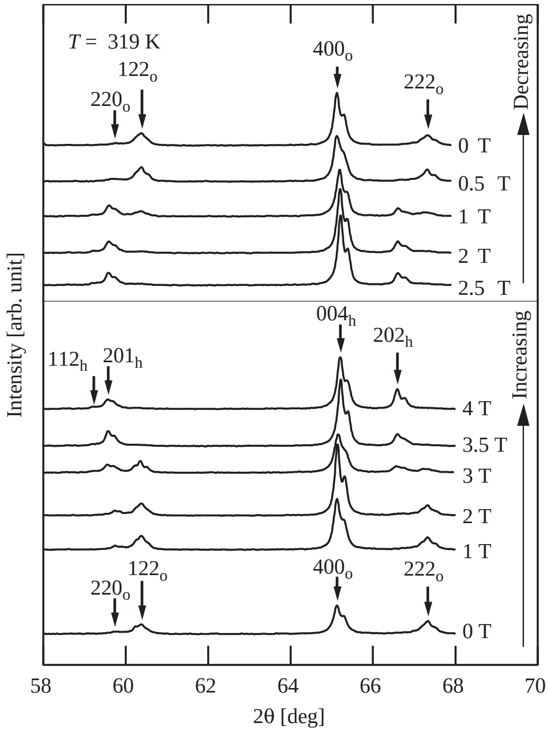

Fig. 4. X-ray diffraction profiles of MnAs at 319 K in magnetic fields up to 4 T. The lower and upper panels show the profiles with increasing and decreasing magnetic fields, respectively.

MnP-type phase is seen at 0 T in the paramagnetic state at 319 K. Increasing magnetic field reduces the intensity of hkl_o Bragg peaks and enhances one of hkl_h Bragg peaks. The single phase of the NiAs-type structure is formed without any trace of the MnP-type structure above 3.5 T. In decreasing process of magnetic fields, the phase of 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 transition fields, $B_{c,i}$ and $B_{c,d}$, observed in the magnetization process 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 increasing field and $B_{c,d}$ for decreasing field, respectively. That is, MnAs exhibits the MnP-type structure in the paramagnetic state and the NiAs-type in the ferromagnetic state even in magnetic fields.

The lattice parameters are shown in Fig. 5 as a function of temperature. The lattice parameters were determined using RIETAN-2000 [14]. Hexagonal lattice parameters of *a*- and *c*-axis are

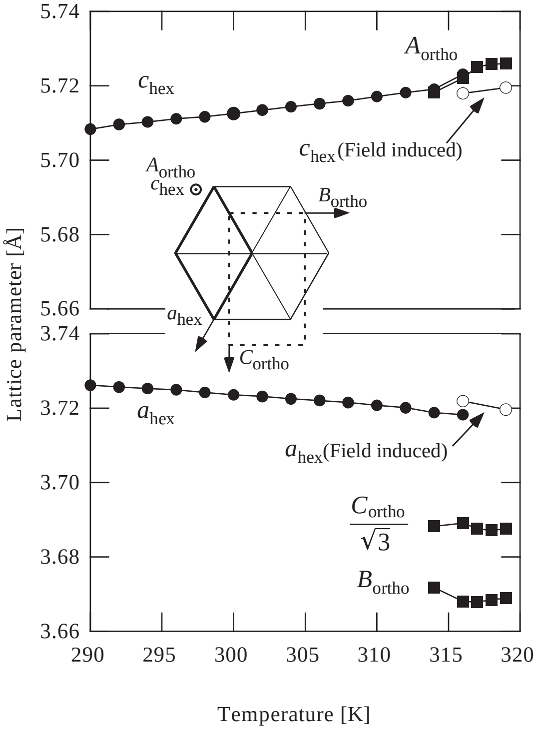

Fig. 5. Temperature dependence of lattice parameters of MnAs. The lattice parameters of the field-induced hexagonal structure at 4 T is also plotted as open circles.

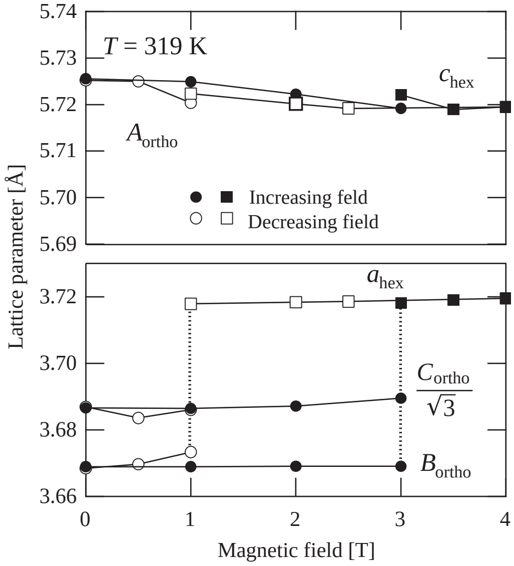

Fig. 6. Magnetic field dependence of lattice parameters of MnAs at 319 K. Closed and open symbols show the lattice parameters for the increasing and decreasing field process, respectively. Dotted lines denote the two-phase coexistence of the NiAs-type and MnP-type at 3 T for the increasing and at 1 T for decreasing field, respectively.

represented as a_{hex} and c_{hex}. In the same way, orthorhombic lattice parameters of *a*-, *b*- and *c*-axis are represented as A_{ortho}, B_{ortho} and C_{ortho}, respectively. As shown in the inset of Fig. 5, a_{hex}-axis and c_{hex}-axis are transformed to B_{ortho}-axis and A_{ortho}-axis, respectively [3]. The volume change calculated from the lattice parameters is determined about −2.1% from the hexagonal NiAs-type to the orthorhombic MnP-type structure. Temperature dependence of the lattice parameters shows the slight increasing in A_{ortho} and c_{hex} and decreasing in B_{ortho} and a_{hex}. It is noted that the lattice parameters of the field-induced hexagonal axis at 4 T, which are also plotted as open circles in Fig. 5, seem to vary smoothly from the spontaneous ferromagnetic phase.

The magnetic field dependences of the lattice parameters at 319 K are plotted in Fig. 6 including the values in the two-phase region. The lattice parameters A_{ortho} and c_{hex} decrease slightly with increasing field, but the other parameters are almost independent of the magnetic field. The volume of the forced ferromagnetic NiAs-type phase is about 2.1% larger than that of the paramagnetic MnP-type phase [16]. This value is consistent with that of structural transformation at T_C, as mentioned above. Moreover, this result agrees well with the previous macroscopic measurement of the field-induced uniaxial strain of 0.66% reported by Chernenko et al. [15].

In summary, we performed the X-ray diffraction measurements in detail on MnAs in high magnetic fields up to 4 T around T_C in order to study the structural phase transition in magnetic fields. It has been confirmed that the first-order structural transformation occurs from the orthorhombic MnP-type structure to the hexagonal NiAs-type one by applying magnetic fields at 319 K. The X-ray diffraction profiles show the existence of two-phase region of MnP-type and NiAs-type structures at 1–3 T with a hysteresis at this temperature. 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 magnetic fields, the volume per formula unit increase by 2.1% while the magnetostriction in each phase is very small. The structural transformation between the NiAs-type and the MnP-type structure has close relationships with the metamagnetic transition for MnAs above T_C.

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