

Superstructure of NiAs

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The structural transition in NiAs was studied by neutron diffraction on the single crystalline sample. The crystal structure of NiAs has been reported to be bottom-centered orthorhombic with $Cmc2_1$ symmetry (*niccolite*-type). The measurement of temperature dependence of the powder X-ray diffraction revealed that NiAs undergoes a structural transition to the NiAs-type at $T_t=335$ K. In present neutron diffraction experiment at room temperature, we observed the reflections indexed on the basis of the orthorhombic unit cell. The intensities of these reflections are qualitatively explained in terms of the *niccolite*-type structure with taking account of three domain structures, except for the weak reflections indexed as (001), (003) and (012). Then, the intensities of (001), (002) and (004) reflections were measured in temperature range of 20 to 420 K. The temperature dependences of (002) and (004) reflections qualitatively agree with those of the calculated intensities using the atomic positions of *niccolite*-type structure. However, the temperature dependence of (001) reflection shows the anomaly around T_t , which suggests the symmetry of crystal structure of NiAs is not the $Cmc2_1$ symmetry.

KEYWORDS: NiAs, superstructure, structural transition, neutron diffraction

§1. Introduction

The 3d transition metal monpnictides have mainly a NiAs-type ($P6_3/mmc$) or MnP-type structure ($Pnma$). Among them, CrAs, MnAs and CoAs show the structural transition from MnP-type to NiAs-type with increasing temperature. Then these structural instabilities have been experimentally and theoretically investigated. Though NiAs was thought to have the NiAs-type structure, Vincent *et al.*¹⁾ reported using a convergent-beam electron diffraction measurement that the crystal structure of NiAs is a bottom-centered orthorhombic structure belonging to the symmetry group $Cmc2_1$ with lattice constants, $A = 3a$, $B = \sqrt{3}a$ and $C = c$, where a and c are the lattice constants of the hexagonal NiAs-type as shown in Fig. 1. In this structure which is called *niccolite*-type structure from now on, the Ni and As atoms form sinusoidal displacements from the ideal atomic position in the NiAs-type with $\vec{q} = \frac{1}{3}(a^* + b^*)$. It was found that the sample has a domain structure where the directions of $\vec{q}$ have $[11\bar{2}0]$, $[1\bar{2}10]$ and $[2\bar{1}10]$ related to the hexagonal symmetry in three domains, respectively. The atomic position parameters were obtained from the X-ray diffraction measurement at 100 K using the small single crystal prepared by a chemical transport reaction.²⁾ The Ni and As atoms are mainly displaced along the B and C axes, respectively, and their amplitudes of the sinusoidal displacements are $0.0066B$ and $0.0088C$, respectively. However, it was reported that the sign of the p_1 parameter for the Ni atoms was not distinguished within their experimental error.

We have collected the powder X-ray diffraction data in the temperature range from 15 to 400K.³⁾ The value of $\delta (= A/\sqrt{3}B - 1)$ which is a measure of orthorhombic distortion from the hexagonal cell is evaluated to be less than 0.2% at 15 K. Moreover, the very weak reflec-

tions which are related to this superstructure disappear around 300 K with increasing temperature. This result suggests a structural transition to the NiAs-type. The electrical resistivity and the magnetic susceptibility show significant anomalies at this structural transition temperature, T_t , which is estimated be 335 K.³⁾

We have measured the dHvA effect on NiAs.⁴⁾ Some of the observed branches are not explained with the Fermi surfaces obtained from the band calculation based on the NiAs-type lattice. As a result, the accurate knowledge of crystal structure of NiAs is required to analyze the results of dHvA effect on NiAs. In this study, we have measured neutron diffraction using the single crystalline sample and observed reflections which are not explained in terms of the $Cmc2_1$ symmetry.

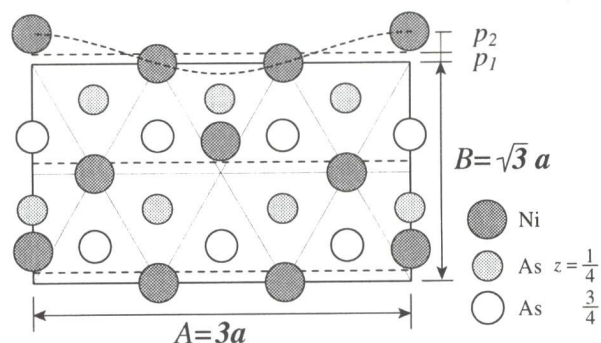


Fig.1. Crystal structure of NiAs in projection to the (001) plane (*niccolite*-type). The Ni atoms are displaced at the distance of p_1 from the atomic positions of NiAs-type and form sinusoidal displacements with the amplitude of p_2 on the base line as indicated by the dashed curve. The As atoms are also displaced sinusoidally along the C axis.

§2. Experimental

A single crystalline sample of NiAs was grown by a Bridgman method in a silica crucible and the details for the sample preparation were reported in the previous paper.⁴⁾ The lattice constants, A , B and C , were estimated to be 10.854(1), 6.267(1) and 5.033(1) Å, respectively, at room temperature from an analysis of the powder X-ray diffraction data. Nickel arsenide, Ni_{1-x}As , has a substantial deficiency at Ni sites in the range $0 \leq x \leq 0.05$. The deficiency at Ni sites in this sample is evaluated to be less than 2% using the empirical relation for the concentration of Ni in Ni_{1-x}As versus the lattice constants with the NiAs-type structure.⁵⁾

Neutron diffraction was carried out at the KSD diffractometer installed at the thermal neutron guide of JRR-3M reactor in JAERI using an incident neutron beam with $\lambda=1.53$ Å. The single crystal NiAs has a $6\phi \times 15$ mm³ cylindrical form. The integrated intensities of the $(h0l)$ and $(k0l)$ reflections were measured in the range of $0 \leq h \leq 8$, $0 \leq k \leq 4$ and $0 \leq l \leq 4$ at room temperature. Detailed studies of the temperature dependences of the integrated intensities were carried out for the (001), (002) and (004) reflections.

§3. Results and Discussion

The integrated intensities of observed $(h0l)$ and $(k0l)$ reflections are summarized in Table I. All reflections are indexed on the basis of orthorhombic unit cell reported by Vincent *et al.*¹⁾ Among them, however, the reflections indexed by $(h0l)$ with $l = \text{odd}$ and (012) which are marked by asterisk in Table I disappear by the extinction rule for the $Cmc2_1$ symmetry. As mentioned above, NiAs has three domain structures related to three possible $\vec{q}$ vectors. Because δ is estimated to be about 2×10^{-3} from X-ray diffraction, the reflections in one domain overlap with those in the other domains as shown in Fig. 2. In this experimental condition, the $(h0l)$ and $(0kl)$ reflections overlaps with $(\frac{h}{2}\frac{h}{2}l)$ and $(\frac{3k}{2}\frac{k}{2}l)$, respectively. Therefore, the observed reflections except for (001), (003) and (012) correspond to the expected ones of the *niccolite*-type structure with taking into account the domain structure.

The integrated intensities of (001) and (003) reflections are about 50 times smaller than that of the (002) reflection. The (300) reflection was not observed within the experimental accuracy although the intensity of (600) reflection is larger than that of the (002) reflection. Therefore, the (001) and (003) reflections are not attributed to the neutron beam with $\lambda/2$. The (012) reflection has also the very weak intensity. Since there are not the plane parallel to (012) with the twice interplane distance, this reflection is considered as intrinsic. These reflections were not observed in the careful X-ray diffraction measurement using the powdered sample because their intensities are very weak.

The intensities of reflections were calculated using the position parameters determined by Thompson *et al.*²⁾ In this procedure, we take into account the secondary extinction effect and assume that the sample contains each

domain structure in an equal ratio of 1/3. The calculated intensities are also summarized in Table I. Thus, the observed intensities except for the (001), (003) and (012) reflections are qualitatively explained in terms of the *niccolite*-type structure model.

Table I. Summary of the observed and calculated intensities of $(h0l)$ and $(k0l)$ reflections. The reflections marked by asterisk indicate those which disappear by the extinction rule for the $Cmc2_1$ symmetry. The right indices mean the overlapped reflection due to the domain structure in this experimental condition.

$(h0l)$	$(\frac{h}{2}\frac{h}{2}l)$	$I_{\text{obs.}}$	$I_{\text{cal.}}$	$(0kl)$	$(\frac{3k}{2}\frac{k}{2}l)$	$I_{\text{obs.}}$	$I_{\text{cal.}}$
(001)*		5.9	0	(001)*		17.6	0
(002)		345.3	264.7	(002)		367.2	631.9
(003)*		7.7	0	(003)*		0.4	0
(004)		552.2	579.6	(004)		755.9	949.0
(600) (330)		575.3	590.8	(012)*		1.7	0
(201)* (111)		0.7	22.7	(021) (311)		361.2	514.4
(401)* (221)		2.9	18.4	(022) (312)		1176.8	1100.9
(601)* (331)		1.4	7.0	(023) (313)		493.5	340.9
(801)* (441)		4.1	11.4	(024) (314)		483.7	288.2
(202) (112)		1.0	8.6	(042) (622)		783.3	658.6
(402) (222)		0.8	6.6	(043) (623)		299.7	202.2
(602) (332)		119.5	117.7				
(802) (442)		0.4	4.3				
(203)* (113)		4.7	4.8				
(603)* (333)		4.8	14.5				
(803)* (443)		12.3	6.2				
(204) (114)		1.4	12.7				
(404) (224)		1.9	10.7				
(604) (334)		409.1	367.0				

Figure 3 shows temperature dependences of the integrated intensities of (001), (002) and (004) reflections. The intensity of (002) reflection decreases monotonously with increasing temperature. On the other hand, the intensity of (004) reflection shows slightly temperature dependence with a broad peak around 360 K. The (001)

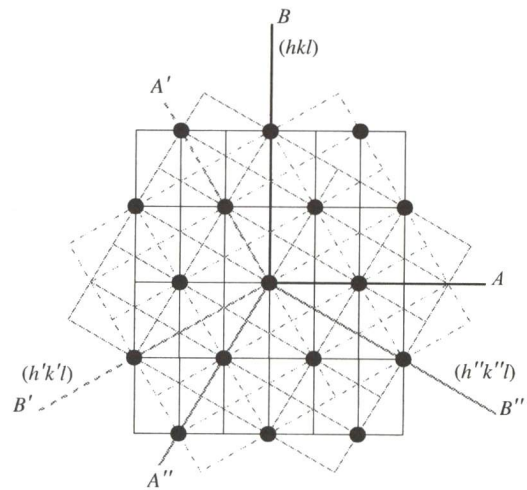


Fig. 2. Reciprocal lattice points of the *niccolite*-type structure. Three grids mean the coordinates of three domain structures. A point (hkl) in one domain overlaps with $(h'k'l)$: $h' = -\frac{1}{2}(h - 3k)$, $k' = -\frac{1}{2}(h + k)$ and $(h''k''l)$: $h'' = -\frac{1}{2}(h + 3k)$, $k'' = \frac{1}{2}(h - k)$ in the other domains rotated by 120° and 240° , respectively.

intensity decreases with increasing temperature up to 330 K and have an almost constant value above 330 K where the crystal structure has been considered to be the NiAs-type from the X-ray diffraction.³⁾ Thus this temperature is in agreement with T_t . If NiAs has the NiAs-type structure above T_t , the (00 l) reflection with l =odd is probably caused by vacancies in alternate Ni layers normal to the c axis. The amount of vacancies is estimated to be 2% in the Ni sites from the intensity of (001) reflection on an assumption of random vacancies in these Ni layers. This amount of vacancies is comparable with the deficiency of Ni evaluated from the lattice constants.

It was found by the X-ray diffraction measurements³⁾ that the structure of NiAs almost transforms continuously at T_t . Thus on the assumption of the continuous structure transition with random vacancies in the alternate Ni layers, the intensity of (002) reflection increases below T_t and that of the (004) reflection slightly decreases with decreasing temperature. The temperature dependences of intensities of these reflections qualitatively agree with the calculated intensities with considering the temperature factor. It is expected on this assumption that the intensity of (001) reflection slightly decreases with decreasing temperature below T_t . However, it is found that the intensity of (001) reflection increases with decreasing temperature below T_t . Consequently, it is suggested that the symmetry of the crystal structure of NiAs below T_t is lower than the $Cmc2_1$ symmetry.

We have examined the structural phase transition in NiAs by means of neutron diffraction measurements on the single crystalline sample. It was found that the very weak reflections indexed as (001), (003) and (012) were observed at room temperature and the temperature dependence of (001) reflection shows anomaly at 330 K. The crystal structure is not determined by this preliminary analysis of intensity at room temperature. More precise measurements above and below T_t and analysis will be in progress. It seems from the temperature dependence of (001) reflection that the (001) and (003) reflections are caused by the modification of the crystal structures in both phases below and above T_t .

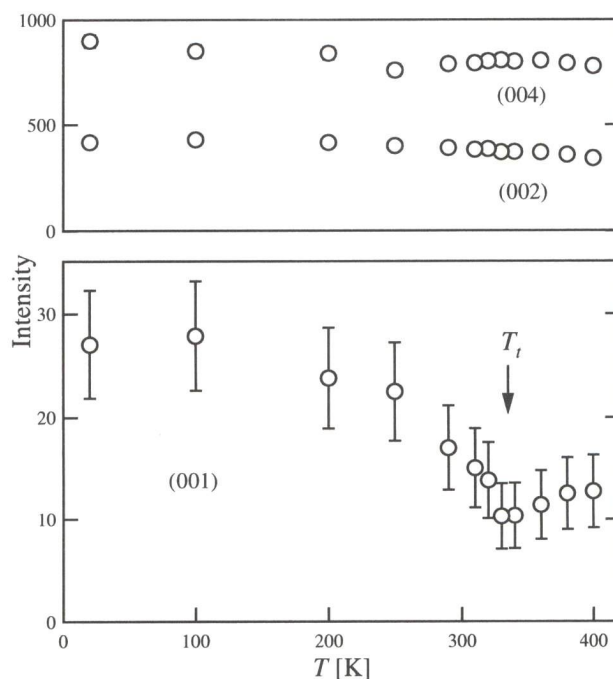


Fig. 3. Temperature dependences of integrated intensities of (002), (004) and (001) reflections. The arrow indicates the temperature of the structural transition determined by the powder X-ray diffraction.

Acknowledgments

We are grateful to thank Mr. K. Nemoto of IMR, Tohoku University for helpful assistance in the neutron diffraction experiment. We wish to thank Dr. K. Ohoyama for his kind support to utilize T-1-2 KSD.

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