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Yoshihiro Kuroiwa [a], Masanosuke Kunikata [b] & Yukio Noda [c]

[a] Department of Physics, Okayama University, Tsushima, Okayama, 700-8530, Japan

[b] Department of Physics, Chiba University, Yayoi, Inage, Chiba, 263-8522, Japan

[c] Research Institute for Scientific Measurements, Tohoku University, Katahira, Aoba, Sendai, 980-8577, Japan

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Structural Phase Transition of an Intercalation Compound $Mn_{1/4}NbS_2$

YOSHIHIRO KUROIWA[a*], MASANOSUKE KUNIKATA[b] and YUKIO NODA[c]

[a]*Department of Physics, Okayama University, Tsushima, Okayama 700–8530, Japan,* [b]*Department of Physics, Chiba University, Yayoi, Inage, Chiba 263–8522, Japan and* [c]*Research Institute for Scientific Measurements, Tohoku University, Katahira, Aoba, Sendai 980–8577, Japan*

A structural phase transition of an intercalation compound $Mn_{1/4}NbS_2$ has been investigated by X-ray diffraction at high temperatures. The lattice parameter c exhibited a discontinuous change at 640K. The superlattice reflections observed below 640K disappeared suddenly above 640K. The phase transition at 640K took an aspect of the first-order phase transition. The precise structure analyses were performed at various temperatures above and below the phase-transition temperature. It was revealed that Mn atoms were arranged in disorder in the high-temperature phase, while the Mn atoms were ordered forming the $2a_0 \times 2a_0 \times c_0$ superlattice in the low-temperature phase. The Nb and S atoms around the ordered Mn atoms slightly shifted from the high-symmetry position in the low-temperature phase. The order parameters were the degree of order of the Mn atoms and the degree of displacement of the Nb and S atoms.

Keywords: $Mn_{1/4}NbS_2$; intercalation; phase transition; crystal structure analysis; X-ray diffraction

INTRODUCTION

The 3d transition-metals M are intercalated into layered compounds of 2H-type transition-metal dichalcogenides TX_2 (T = Nb, Ta; X = S, Se). It is believed that the metals M form the $2a_0 \times 2a_0 \times c_0$ and the $\sqrt{3}\ a_0 \times \sqrt{3}\ a_0 \times c_0$ superlattice structures near the concentration x = 1/4 and 1/3, respectively, on the intercalation compounds M_xTX_2, where a_0 and c_0 are the lattice parameters of

* Corresponding author. e-mail kuroiwa@science.okayama-u.ac.jp

the host materials TX_2. Among these intercalation compounds, magnetic properties of $Mn_{1/4}NbS_2$ and $Mn_{1/4}TaS_2$ have been investigated in details.

The intercalation compounds $Mn_{1/4}NbS_2$ and $Mn_{1/4}TaS_2$ show a ferromagnetic transition at 100K and 75K, respectively[1]. The magnetization density in $Mn_{1/4}TaS_2$ is measured by polarized neutron scattering at low temperatures[2]. The electronic band calculation is carried out for $Mn_{1/4}TaS_2$[3]. On the other hand, magnetic properties at high temperatures are investigated by van Laar *et al.*[4]. They found a discontinuous change in the magnetic susceptibility curve of $Mn_{1/4}NbS_2$ and $Mn_{1/4}TaS_2$ at 689K and 690K, respectively, and suggested the existence of a phase transition at the temperature. They also carried out the crystal-structure analyses of $Mn_{1/4}TaS_2$ by neutron powder-diffraction with so-called Rietveld analysis. However, no significant difference on the crystal structure between the high-temperature phase and the low-temperature phase was found, except the discontinuous change of the lattice parameter c at the phase-transition temperature.

In the preceding paper[5], we measured the magnetic susceptibilities, the lattice parameters and the X-ray intensities of the superlattice reflections of $Mn_{1/4}NbS_2$ and $Mn_{1/4}TaS_2$, and suggested that the order-disorder of Mn atoms and the displacement of Nb and S atoms occurred at 640K and 670K, respectively.

In the present paper, we show the results of X-ray structural studies at high temperatures on the phase transition of $Mn_{1/4}NbS_2$. The order parameter on the phase transition is discussed based on the precise structure-analyses at various temperatures above and below the phase-transition temperature.

EXPERIMENTAL AND RESULTS

A single crystal of the $Mn_{1/4}NbS_2$ sample was grown by a chemical vapor transport method with iodine as a transporter[5]. Structure analyses were performed on an off-center type four-circle diffractometer equipped with a vacuum-type high-temperature furnace. Other X-ray measurements were carried out on a two-axis diffractometer with a furnace. Mo K_α radiation was used in all measurements.

Superlattice reflections on the $2a_0 \times 2a_0 \times c_0$ structure disappeared all above 640K. The unit-cell size changed to $a_0 \times a_0 \times c_0$ the same size as the host material NbS_2. The lattice parameters of $Mn_{1/4}NbS_2$, referred to the unit cell of

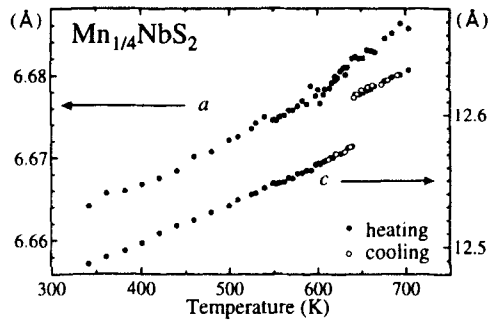

FIGURE 1 Lattice parameters a and c of $Mn_{1/4}NbS_2$ referred to the unit-cell size of the low-temperature phase[5].

the low-temperature phase, are shown in Fig. 1 as a function of temperature. A clear discontinuity on the lattice parameter c was found at 640K, while no anomaly was found on the lattice parameter a at 640K.

The space groups of the low-temperature phase and the high-temperature phase were both $P6_3/mmc$. The atomic sites used for the structure analyses were as follows: Mn1(2a) 0, 0, 0; Mn2(6g) 1/2, 0, 0; Nb1(2b) 0, 0, 1/4; Nb2(6h) x, $2x$, 1/4, x~1/2; S1(4f) 1/3, 2/3, z, z~1/8; S2(12k) x, $2x$, z, x~5/6, z~1/8 for the low-temperature phase, and Mn(2a) 0, 0, 0; Nb(2b) 0, 0, 1/4; S(4f) 1/3, 2/3, z, z~1/8 for the high-temperature phase. Results of the structure analyses are summarized in TABLE I. The occupancy number of the Mn1(2a) site, σ_{2a}, as shown in TABLE I, was treated as a parameter for the analyses at 300K, 370K, 500K and 630K in the low-temperature phase. The occupancy

TABLE I Structure parameters of $Mn_{1/4}NbS_2$ for various temperatures.

Temp. (K)	Nb2(6h) (x)	S1(4f) (z)	S2(12k) (x)	S2(12k) (z)	σ_{2a}	R(F) (%)
300	0.4938(1)	0.1213(3)	0.8308(1)	0.1259(1)	0.92(1)	3.08
370	0.4937(2)	0.1209(8)	0.8308(4)	0.1268(3)	0.92(2)	4.24
500	0.4942(2)	0.1223(8)	0.8308(4)	0.1269(4)	0.91(2)	4.25
630	0.4946(3)	0.1232(9)	0.8310(5)	0.1271(4)	0.86(2)	4.83
666	-	0.1262(2)	-	-	0.23	3.64

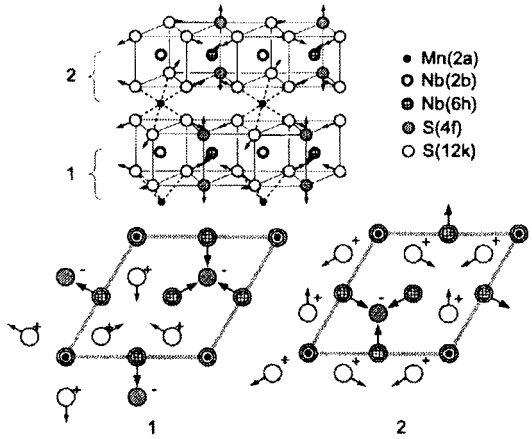

FIGURE 2 Ordered structure of the low-temperature phase of $Mn_{1/4}NbS_2$.

number of the Mn2(6g) site, σ_{6g}, was calculated at 0.00(1) for 300K as well. For other analyses at 370K, 500K and 630K, σ_{6g} was fixed at zero to avoid divergence of the number. Most of Mn atoms were found by the structure analyses to be ordered on the Mn1(2a) site in the low-temperature phase. The actual Mn-concentration of the sample was determined by 0.23 based on the analysis at 300K. We still write the sample name down as $Mn_{1/4}NbS_2$ here since the concentration was almost equal to 0.25. At 666K in the high-temperature phase, on the other hand, Mn atoms were arranged in disorder on the every Mn site in the unit cell. Accordingly, the occupancy number of the Mn(2a) site in the high-temperature phase was fixed at 0.23 for the analysis.

A schematic drawing of the crystal structure of the low-temperature phase is shown in Fig. 2. The *c*-axis projections of each layer numbered 1 and 2 are depicted at the lower side in Fig. 2. In the high-temperature phase, Nb and S atoms were arranged on the high-symmetry positions, while in the low-temperature phase the Nb and S atoms around the ordered Mn atoms slightly shifted from the high-symmetry positions. The directions of the displacement of Nb and S atoms are indicated in Fig. 2 by arrows in the *a*-*b* hexagonal plane, and + and − signs for the *c*-directions. These displacements of the Nb and S atoms are considered to occur associated with the phase transition.

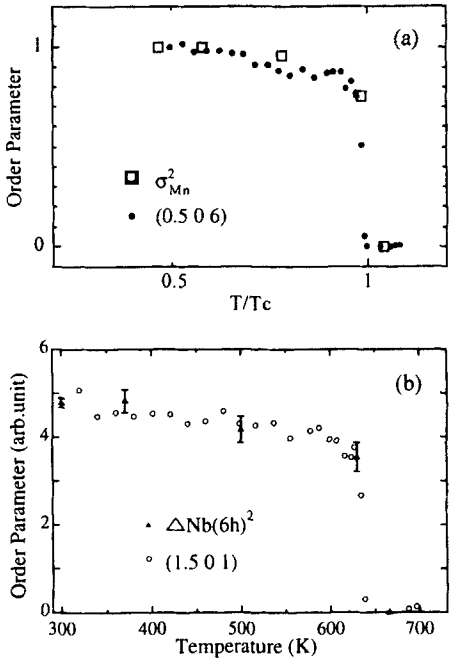

FIGURE 3 Order parameter and intensity of superlattice reflection. Intensity data from Ref. [5.].
(a) Degree of order of Mn atoms. (b) Degree of displacement of Nb atoms from the high-symmetry position in the high-temperature phase.

DISCUSSION

Degree of order of Mn atoms is defined as $\sigma_{Mn} = (\sigma_{2a} - \sigma_{6g}) / (\sigma_{2a} + \sigma_{6g})$, where σ_{2a} and σ_{6g} are occupancy numbers of the Mn sites referred to the unit-cell of the low-temperature phase, provided that extra Mn atoms not occupying the Mn1(2a) site in the low-temperature phase are assumed here to be all on the Mn2(6g) site, i.e. $\sigma_{6g} = \sigma_{2a}(300K) - \sigma_{2a}$, where $\sigma_{2a}(300K)$ is the value of σ_{2a} at 300K. The degree of order of Mn atoms σ_{Mn} are shown in Fig. 3(a) as a function of temperature with the intensity of the (0.5 0 6) superlattice reflection. The superlattice reflection is indexed based on the unit cell of the host lattice. The contribution to the structure factor of the (0.5 0 6) superlattice reflection is

almost from Mn atoms[5]. As shown in Fig. 3(a), these behaviors have a good agreement with each other. On the other hand, behaviors on the Nb atoms are shown in Fig. 3(b). In the figure, the intensity of the (1.5 0 1) superlattice reflection and degree of displacement of Nb2(6h) atoms from the high-symmetry position, *e.g.* (1/2, 1, 1/4) position, are indicated to be compared with Fig. 3(a). The contribution to the structure factor of the (1.5 0 1) superlattice reflection is almost from Nb atoms[5]. These all behaviors in Fig. 3 have a good agreement with one another. The displacement of S atoms on the S1(4f) site and the S2(12k) site had similar behavior in the consequent analyses using the parameters in Table I. Therefore, it was concluded that the phase transition at 640K in $Mn_{1/4}NbS_2$ was caused by the order-disorder of the intercalated Mn atoms coupled with the displacement of Nb and S atoms.

From the analyses of bond lengths between atoms, it has been found that the thickness of the NbS_2 layer expands along the *c*-axis at the phase-transition temperature on heating, while the van der Waals gap shortens. With regard to the absolute amplitude on the expansion and contraction, the former is larger than the latter. The bond lengths between S-S(or Nb-Nb) atoms on the *a-b* hexagonal plane also change at the phase-transition temperature. One expands, one shortens and one does not change. Resultant summation of the lengths does not change after the phase transition. This is a reason why the lattice parameter *c* changes discontinuously and the lattice parameter *a* changes continuously at the phase-transition temperature. Similar behavior on the lattice parameters is found on the order-disorder phase transition of Ag_xTiS_2[6].

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