X-ray structural study of the layered compounds Co$_x$NbS$_2$

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Abstract

X-ray intensity measurements have been performed on the structure of the layered compound Co$_x$NbS$_2$ single crystals ($x$$\leq$0.5) at room temperature. The $c$-axis lattice parameter changes discontinuously at around $x$$=0.2$ and remains constant with further increase of the Co content. For the lower content of Co atoms ($x$$<0.2$), no diffuse maxima appeared on the ($hk0$) and ($hk1$) reciprocal lattice planes. At $x$$=0.23$, the diffuse maxima are clearly seen at 4/3, 4/3, 1 and 5/3, 5/3, 1 reciprocal lattice points. At $x$$=0.23$, sharp intensity maxima appear at 4/3, 4/3, 0 and 5/3, 5/3, 0 in addition to at 4/3, 4/3, 1 and 5/3, 5/3, 1. It is understood that $\sqrt[3]{3}$!$\sqrt[3]{3}$R$^{30^\circ}$ ordered structure exists at the stoichiometric composition of $x$$=1/3$. At further increasing the Co content, the intensity at 4/3, 4/3, 0 and 5/3, 5/3, 0 is weakening and disappears above $x$$=0.4$. The structural model based on the space group $P6_322$ (No. 182) for Co$_{0.4}$NbS$_2$ ($x$$>0.4$) is discussed with considering both the position of the Co atoms and their occupation rate.

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1. Introduction

It is well known that the layered disulfides of transition metals MS$_2$ (M=3d transition metal) have a two-dimensional layered structure, in which in-plane atoms have strong ionic/covalent bondings and that various ions and molecules are intercalated between the layers due to weak van der Waals forces. These intercalation compounds are of interest because of the low-dimensional properties and because of the application as high energy density batteries in general. Some systems are characterized by a staged structure in which, for stage $n$, the intercalants are periodically separated by $n$ MS$_2$ layers [1,2]. After intercalation, the interlayer spacing $c$ changes discontinuously between the boundary of composition for each staging, while intralayer spacing $a$ does not change drastically for a whole range of compositions. We have already performed X-ray diffraction studies for Ag$_x$TiS$_2$, In$_x$TaS$_2$, Tl$_x$TaS$_2$ and Cu$_x$TiS$_2$ compounds for understanding of their structural characteristics [3–7].

Intercalated Co atoms in layered compounds Co$_x$NbS$_2$ are inserted into the octahedral sites between the prismatic layers of 2H NbS$_2$, whose space group is $P6_3/mcm$ (No. 194). An ordered arrangement of the intercalated Co atoms was found for the concentration of 1/3, corresponding to $\sqrt[3]{3}$!$\sqrt[3]{3}$R$^{30^\circ}$ ordered lattice, with the use of single crystal X-ray and neutron diffraction methods [8,9]. The space group of the compound is $P6_322$ (No. 182) with the Co$_{1/2}$NbS$_2$ has been indexed on the basis of a hexagonal unit cell instead of an orthorhombic one [10].

In the present study, we have performed the X-ray diffraction study to investigate both the local arrangements of intercalated Co atoms and the average crystal structures for a wide range of compositions with the use of Co$_x$NbS$_2$ ($x$$\leq0.5$) single crystals.

2. Experimental

The NbS$_2$ powdered specimens were prepared by direct reactions of Nb powder of 99.9% purity and S powder of
99.99% purity in 1:2.1 ratio in an evacuated quartz tube at 900 °C for a week. Co₃NbS₂ single crystals were grown by the chemical vapor transport reaction method in the presence of iodine as a carrier gas, where the purity of iodine was 99.8%. It took 4 weeks to grow the crystals under an optimum temperature gradient, which was created in an electric furnace kept between 800 and 950 °C. The samples grew as thin crystals with hexagonal shape. The average thickness of the crystals was 0.1 mm and their average size in the hexagonal plane was 2 mm. The compositions of the samples used were determined to be 0.16, 0.18, 0.23, 0.32, 0.39, 0.43, 0.44 and 0.50 by the electron probe microanalysis (EPMA). The X-ray diffracted intensity data for 0.39, 0.43, 0.44 and 0.50 by the electron probe micro-analysis (EPMA). The X-ray diffracted intensity data for determining lattice parameters and analyzing the structure were collected at room temperature with the use of a four-circle diffractometer (Huber, 422) determining lattice parameters and analyzing the structure analysis (EPMA). The X-ray diffracted intensity data for 0.39, 0.43, 0.44 and 0.50 by the electron probe microscopy. A JEOL 2010 transmission electron microscope, operated at 200 kV equipped with a specimen-tilting device, was used and diffraction patterns were obtained.

3. Results

After analyzing the diffraction patterns, both a- and c-axis lattice parameters were determined for eight single crystals. The a-axis lattice parameter is independent of composition and given as 3.335 ± 0.005 Å for all the samples. The c-axis lattice parameters vs. compositions obtained from the EPMA experiments are shown in Fig. 1. The value of the c-axis spacing changes discontinuously at around x = 0.2 and remains constant with increasing the Co content. The increment of the spacing is about 0.07 Å in compared with the value of the mother phase.

![Fig. 1. Co concentration dependence of c-axis lattice parameters.](image)

We have measured two-dimensional intensity distributions on the (hk0) and (hk1) reciprocal lattice planes for all the specimens to search diffuse intensity maxima or superlattice reflections at special points. Typical intensity distributions are shown in Fig. 2(a)–(e) for x = 0.18, 0.23, 0.32, 0.43 and 0.50, respectively. There are several characteristics from these patterns as follows. Though no diffuse scattering intensity maxima appear for x = 0.18 as shown in Fig. 2(a), the diffuse maxima are clearly seen at 4/3, 4/3, 1 and 5/3, 5/3, 1 for x = 0.23 as shown in Fig. 2(b). The value of the full width at half maximum (FWHM) for the diffuse scattering was determined to be 0.093 a* by a Gaussian fit. The value of FWHM at the fundamental reflections was regarded as an instrumental broadening. The value of FWHM is more than twice in compared with that for instrumental broadening (0.042 a*). However, at x = 0.32, sharp intensity maxima appear at 4/3, 4/3, 0 and 5/3, 5/3, 0 in addition to 4/3, 4/3, 1 and 5/3, 5/3, 1 in Fig. 2(c). The value of FWHM for the four intensities is same as that for fundamental reflection (0.056 ± 0.003 a*). It is, therefore, understood that (√3 × √3 R30°) ordered structure exists around the stoichiometric Co content (x = 1/3). At further increasing the Co content, superlattice reflections only appear at 4/3, 4/3, 1 and 5/3, 5/3, 1 in Fig. 2(d) and (e). We have taken electron diffractions patterns for x = 0.32 and x = 0.43 to check whether the superlattice reflections appear on the (hk0) reciprocal lattice plane or not. The superlattice reflections can only been seen at 1/3, 1/3, 0, 2/3, 2/3, 0 and their equivalent positions for the sample of x = 0.32.

Fig. 3 (a)–(c) show the typical intensity distributions parallel to the [001]* direction at 4/3, 4/3, 0 and 5/3, 5/3, 0 for x = 0.23, 0.32 and 0.50, respectively. Diffuse maxima appear at L = 2n + 1 (n: integer) for x = 0.23 in Fig. 3(a). The value of FWHM for the diffuse scattering is five times larger than that for fundamental reflection. On the other hand, sharp reflections appear at L = n for x = 0.32 in Fig. 3(b) and at L = 2n + 1 for x = 0.50 in Fig. 3(c). The value of FWHM for the reflections in Fig. 3(b) and (c) is same as that for fundamental reflection. The sharp reflection is, therefore, corresponding to the superlattice ones. It is clear that reflections with having an even L number are weakening and disappear above x = 0.40.

4. Discussion

We have realized the structural characteristics for Co₃NbS₂ compounds from the X-ray diffraction patterns as shown in Figs. 2 and 3. Below x < 0.2, the Co atoms are randomly intercalated between the van der Waals gap. However, at x = 0.23, the intercalated Co atoms have √3 × √3 R30° in-plane correlation, whose length is about 40 Å. The length was estimated from the value of FWHM for the diffuse scattering along [110]* direction. On the other hand, the estimated interlayer correlation length is about 35 Å.
With increasing the Co content, the atoms have the regular arrangement three-dimensionally.

Paskin et al. [9] reported the $\sqrt{3} \times \sqrt{3} R30^\circ$ ordered structure at Co$_{1/3}$NbS$_2$ by single crystal neutron photographic and counting methods. The space group of the compound is $P6_322$ (No. 182) with the Co atoms occupying the 2c sites as shown in Fig. 4. The positional parameters at 2c sites are $(x, y, z) = (1/3, 2/3, 1/4)$ & $(2/3, 1/3, 3/4)$. As described above, the reflections with having an even $L$ number at 4/3, 4/3, $L$ and 5/3, 5/3, $L$ become weakening with increasing the Co content and disappear above $x = 0.40$. Here, it is interesting to understand where the excess Co atoms are distributed on the lattice sites, 2b or 2d sites in Fig. 4. The positional parameters at 2b and 2d sites are $(x, y, z) = (0, 0, 1/4) & (0, 0, 3/4)$ and $(x, y, z) = (2/3, 1/3, 1/4)$ & $(1/3, 2/3, 3/4)$, respectively. First, we have calculated the $|F(1/3, 1/3, L)|^2$ for $x = 1/3$ as the reference in Table 1(a), where the Co atoms occupy 2c sites completely. With increasing the Co atoms, there are three possibilities to distribute the atoms into following sites; (1) at 2b sites only, (2) at 2d sites only and (3) at both 2b and 2d sites. The three $|F(1/3, 1/3, L)|^2$ are calculated for $x = 0.42$ and shown in Table 1(b)–(d). From the fact that the reflections with an even $L$ number are weakening when the excess
atoms occupy at the 2b sites only, we have calculated the $|F(1/3,1/3,L)|^2$ with having null intensity at $L=2n$ with changing an occupation rate of Co atoms at 2b and 2c sites. It is confirmed that 2:1 occupation ratio of Co atoms for 2c and 2b sites, whose compositions are corresponding to $x=0.28$ and 0.14, respectively, is most probable to reduce the intensities for an even $L$ number as shown in Table 2 (a). When, at $x=0.50$, all positions at 2c sites and half positions at 2b sites are occupied by the Co atoms, $|F(1/3,1/3,L)|^2$ ($L=0$–5) are calculated and shown in Table 2 (b). It is realized that the values with $L=2n$ are almost zero. This behavior is good consistent with the observed one as shown in Fig. 3. We can, therefore, describe the structural change with increasing the intercalated Co atoms as follows. Below $x<0.2$, the Co atoms are randomly intercalated on the van der Waals gap’s layer. With increasing the Co atoms, $\sqrt{3} \times \sqrt{3}R30'$ in-plane correlation with three-dimensional nature appears. At $x=1/3$, $\sqrt{3} \times \sqrt{3}R30'$ ordered structure with the space group $P6_3\overline{2}2$ (No. 182) is confirmed to exist, where the Co atoms mainly occupy 2c sites. With increasing

![Fig. 3. Diffraction intensity distributions parallel to the [001]* direction at (4/3, 4/3, L) and (5/3, 5/3, L) for the specimens of (a) $x=0.23$, (b) $x=0.32$ and (c) $x=0.50$.](image)

![Fig. 4. The structure of the layered compound Co$_x$NbS$_2$, whose space group is $P6_3\overline{2}2$ (No. 182). The positional parameters at 2b and 2d sites are $(x, y, z)=(0, 0, 1/4) & (0, 0, 3/4)$ and $(x, y, z)=(2/3, 1/3, 1/4) & (1/3, 2/3, 3/4)$, respectively.](image)
the content, the 2:1 occupation ratio of Co atoms for 2c and 2b sites is most probable to reduce the intensities for an even L number, without introducing the new space group.

Wakihara [11] has measured the temperature dependence of the electrical conductivity for the present compounds and found that the conductivity changes from metallic into semiconducting behavior at around $x = 0.48$. They have interpreted that the $dz^2$ band of NbS$_2$ is filled with the electrons at that content by increasing Co$^{2+}$ ions from the content at $x = 1/3$. This composition is accidentally corresponding to the content for full occupancy of the Co atoms at 2c sites described above. A theoretical treatment of band structure calculations based on the space group $P6_322$ (No. 182) for Co$_{0.48}$NbS$_2$ compound will be needed to have complete interpretation of the structural characteristics.

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