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Crystal structure and magnetic properties of the compound CoN

K. Suzuki [a], T. Kaneko [b], H. Yoshida [b], H. Morita [c], H. Fujimori [b]

[a] *Tsuruoka National College of Technology, Tsuruoka 997, Japan*
[b] *Institute for Materials Research, Tohoku University, Sendai 980, Japan*
[c] *Faculty of Engineering, Yamagata University, Yonezawa 992, Japan*

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Abstract

The compound CoN was prepared as a single phase by the d.c. reactive sputtering. Its crystal structure determined by X-ray diffraction measurements is the zinc blende type f.c.c. structure. The compound CoN is stable up to 504 K and decomposes into $CoN+\delta-Co_2N$ above 509 K. This compound exhibits a Pauli paramagnetic character.

Keywords: CoN; Crystal structure; Magnetic properties

1. Introduction

There are several types of compounds in the Co–N system [1–4]. Particularly Co_3N_2 is well known to be a stable compound. This compound was obtained from cobalt cyanide $Co(CN)_2$ and cobalt oxide CoO by heating at 2000 °C [1] and by the thermal decomposition of cobalt amide $Co(NH_2)_2$ [2]. Dumont et al. prepared a cobalt nitride containing more nitrogen than these compounds by the thermal decomposition of the cobalt(III) amide $Co(NH_2)_3$. They reported that this compound was CoN with the NaCl type structure with lattice constant of $a=4.27$ Å [5]. They also mentioned that the exact stoichiometric composition could not be realized, since the decomposition of ammonia and the emission of a little nitrogen were occurring in parallel with the thermal decomposition of $Co(NH_2)_3$. In many cases of their experiment, the compositions of the prepared compound were $CoN_{0.8}\sim CoN_{0.9}$. Taylor et al. prepared the compound CoN by the thermal decomposition of cobalt ammine azide; they performed X-ray diffraction experiments for powder samples and reported that its crystal structure was a cubic one having the lattice constant of $a=4.28$ Å [6].

It has been known that the AB type nitrides, as the 3d transition metal nitrides MN (M = Sc, Ti, V, Cr), have the NaCl type structure [7–9]. However, we have recently reported that the compound FeN can be prepared as a single phase by d.c. reactive sputtering and its crystal structure is not the NaCl type structure but the zinc blende type [10]. Furthermore, we have reported that the magnetic properties of FeN are antiferromagnetic [10,11].

In this paper, the cobalt nitride was prepared by the same method described in Refs. [10,11]. Then the crystal structure and thermal stability of the prepared CoN compound were examined by the powder X-ray diffraction method and the thermomagnetic curve measurement. The magnetic properties at low temperatures were also investigated.

2. Experimental procedure

The Co–N sample was prepared by a high rate-type triode d.c. reactive sputtering [10] in a mixture of $Ar+N_2$ gas. The sputtering conditions were as follows: target voltage, 0.22 kV; target current, 50 mA; total gas pressure, 3.0×10^{-2} Torr; N_2 partial gas pressure, 0.76×10^{-2} Torr; residual gas pressure, 1.20×10^{-7} Torr; and target–substrate distance, 23 mm. A cobalt disk of 99.9% purity was used as a target, and water-cooled Cu plate was used as a substrate. The thickness of the deposited Co–N film was about 122 μm and it was stripped from the substrate mechanically. This stripped film was powdered and processed with a dilute solution of nitric acid for 60 min. Then, it was washed sufficiently with distilled water and dried in air. Finally, the powder sample was stress relieved by annealing in vacuum at 410 K for 6 h.

The nitrogen concentration in the powder sample was analyzed by the helium carrier fusion thermal

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conductivity method (He-CFC). The crystal structure was examined by X-ray diffraction method using Cu Kα radiation. In order to examine the thermal stability of the CoN compound, powder samples were annealed at successively higher temperatures for 2 h. After each annealing, the crystal structure was examined at room temperature. For a study of phase transitions by heating, thermomagnetic curves of the stress relieved powder sample were also measured with a magnetic balance in a magnetic field of 10 kOe. The magnetic properties of the powder sample at low temperatures were measured with a SQID magnetometer.

3. Results and discussion

3.1. X-ray diffraction

According to the result by He-CFC, the nitrogen content was 50.2at.%, that is the atomic ratio of cobalt to nitrogen was almost 1:1. Fig. 1 shows the X-ray diffraction pattern for the stress relieved powdered Co–N compound. As seen from the figure, all diffraction lines were well indexed as an f.c.c. structure. Therefore, the present sample is considered to be a single phase of the CoN compound. The lattice constant of this f.c.c. structure is 4.297 Å. This value is a little larger than 4.28 Å obtained by Taylor et al. [6].

It is known that the AB type f.c.c. compound has either the NaCl type or the zinc blende type structure (Fig. 2). The atom positions in the NaCl type and the zinc blende type structures are written respectively in summary form as:

4 Co at (0, 0, 0) + face centering translations,

4 N at (1/2, 1/2, 1/2, 1/2) + face centering translations;

and

4 Co at (0, 0, 0) + face centering translations,

4 N at (1/4, 1/4, 1/4) + face centering translations.

The difference in the atom positions between the two structures is reflected in the structure factors, and causes a large difference in the ratio of the diffraction line intensities.

In Fig. 3 the experimental diffraction line intensities were compared with the values calculated for the NaCl type and the zinc blende type CoN structure. The calculated and experimental intensities were normalized to the (111) line intensities. Here, the Debye temperature of 213 K is used in the temperature factor for the calculations. In the calculations of the structure factors, we used atomic scattering factors of neutral atoms [12].

For the NaCl type structure:

$|F|^2 = 16(f_{Co} + f_N)^2$ when $(h+k+l)$ is even
$|F|^2 = 16(f_{Co} - f_N)^2$ when $(h+k+l)$ is odd.

For the zinc blende type structure:

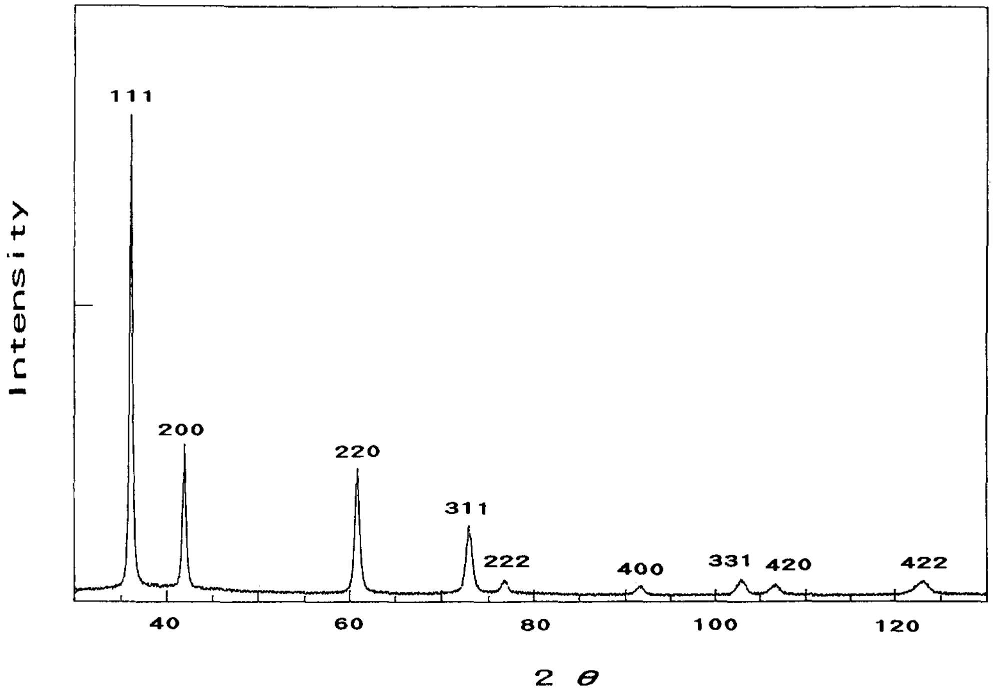

Fig. 1. X-ray diffraction pattern for the powdered CoN compound.

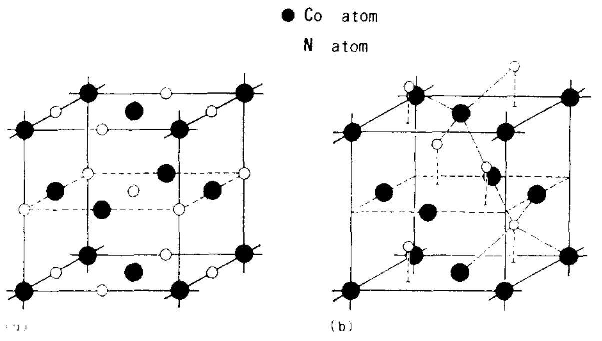

Fig. 2. Crystal structures of the NaCl (a) and zinc blend type (b).

$|F|^2 = 16(f_{Co}^2 + f_N^2)$ when $(h+k+l)$ is odd
$|F|^2 = 16(f_{Co} - f_N)^2$ when $(h+k+l)$ is an odd multiple of 2
$|F|^2 = 16(f_{Co} + f_N)^2$ when $(h+k+l)$ is an even multiple of 2.

where (hkl) are the indices of the diffraction lines, and f_{Co} and f_N are the atomic scattering factors of the Co and N atoms respectively.

The above formulas indicate that the difference in intensities between the two structures becomes distinct when the values of $(h+k+l)$ are 2 and 6. As can be seen in the figure, the calculated values for the zinc blende type structure agree well with the experimental values. However, those of the NaCl type structure are substantially larger than the experimental values, especially at the (200), (222), and (420) lines. The values of the reliability factor for the zinc blende type structure and the NaCl type one are 5.1% and 25.8% respectively. Furthermore, the present relative diffraction line intensity ratio is in good agreement with that obtained by Taylor et al. [6]. From these results, the crystal structure of the CoN compound is considered to be the zinc blende type structure, not the NaCl type.

3.2. Thermal stability

In order to investigate the thermal stability and the decomposition process of CoN, X-ray diffraction measurements were carried out for the samples annealed in vacuum for 2 h at successively higher temperatures between 494 K and 610 K. The results in Table 1 show that:

(1) the CoN phase is stable up to 504 K;

(2) the two phases of δ-Co_2N and CoN exist between 509 K and 525 K;

(3) between 531 K and 541 K the CoN disappears and instead the two phases of δ-Co_2N and γ-Co_3N exist;

(4) at 550 K the compound γ-Co_3N exists as a nearly single phase, although a few diffraction lines which cannot be indexed are observed;

(5) between 556 K and 568 K α-Co appears in addition to γ-Co_3N; and then

(6) around 573 K the sample becomes α-Co only.

The phase transitions were also examined by the magnetic measurements. Fig. 4 shows the result for the sample which initially consisted of pure CoN compound, together with the results of the X-ray diffraction measurements indicated above. The magnetization was measured in a magnetic field of 10 kOe and with a heating rate of 18 K h^{-1}. The magnetization value was calculated based on the initial sample weight. Therefore, the

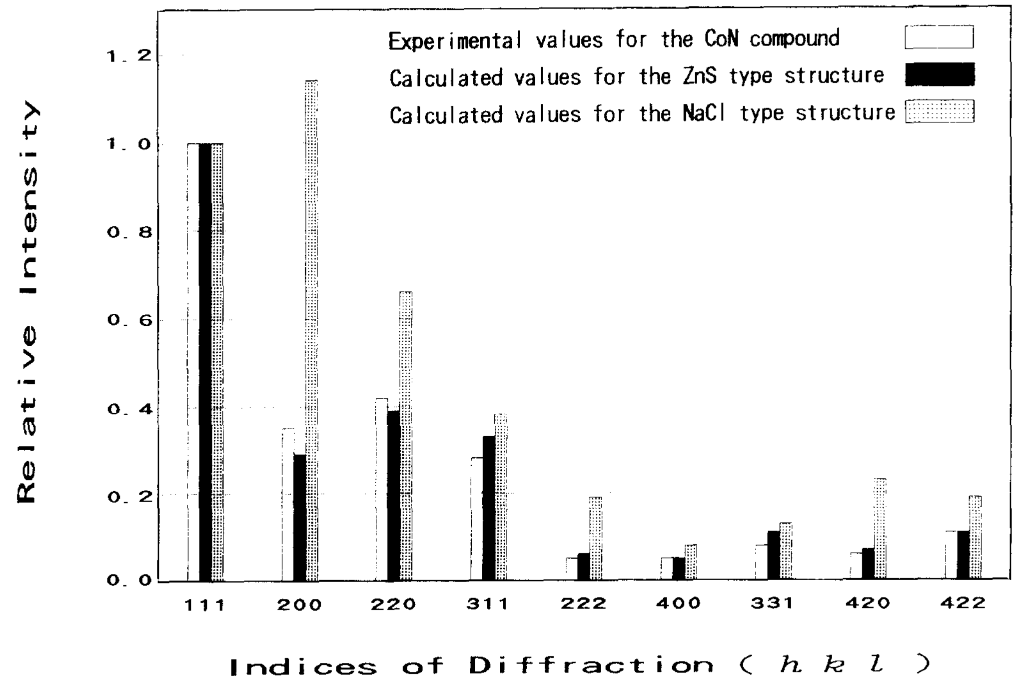

Fig. 3. Relative X-ray diffraction intensities normalized to the (111) line.

Table 1
Results of the X-ray diffraction measurements for the CoN compound annealed in vacuum for 2 h at various temperatures

Annealing temperature (K)	Phase analysis
494	CoN
504	CoN
509	δ-Co_2N+CoN
520	δ-Co_2N+CoN
525	δ-Co_2N+CoN
531	δ-Co_2N+γ-Co_3N
541	δ-Co_2N+γ-Co_3N
550	γ-Co_3N
556	Co+γ-Co_3N
563	Co+γ-Co_3N
568	Co+γ-Co_3N
573	α-Co
610	α-Co

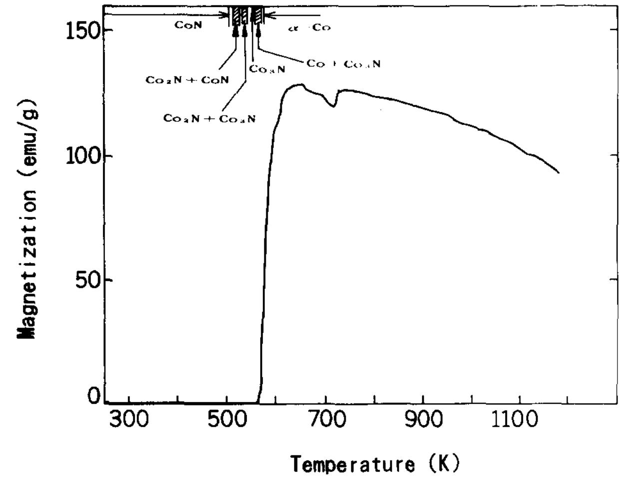

Fig. 4. Thermomagnetic curve of the prepared sample which is initially the CoN compound; the results of X-ray diffraction experiments are shown in the upper part.

magnetization shown in the figure is smaller than the actual magnetization at high temperatures, since the sample loses weight due to the evaporation of nitrogen.

The value of the magnetization is very small at temperatures below about 560 K. There are a few reports about the magnetic properties of δ-Co_2N and γ-Co_3N [13,14]. Mader et al. reported that at the room temperature the compound δ-Co_2N and γ-Co_3N exhibited a paramagnetic character and the magnetizations of these compounds were very small [14]. Therefore, the results of the present experiment are consistent with those by Mader et al. The magnetization begins to increase rapidly around 560 K with increasing temperature. This increase is considered to be due to the partial decomposition of the compound γ-Co_3N to α-Co from the result in Table 1.

The magnetization shows a maximum around 640 K, where the compound is considered to be decomposed perfectly to the α-Co. However, according to the result of Table 1 by X-ray diffraction experiment, the sample becomes pure α-Co at 573 K. The discrepancy between these decomposition temperatures is considered to be ascribed to the difference in the time of the measurements between the two experiments. The decrease in the magnetization between 650 K and 715 K is considered to be due to the temperature dependence of the magnetization of α-Co. The magnetization increases again around 720 K. This increase is considered to be caused by the transformation of α-Co (h.c.p.) to β-Co (f.c.c.) [15]. Above 725 K, the magnetization decreases monotonically. It is found that the decomposition of CoN occurs at 504 K which is lower than that of the FeN compound of 593 K [10].

3.3. Magnetic properties

Fig. 5 shows the temperature dependence of the magnetizations measured at 1 and 2 kOe by a SQID magnetometer in the temperature range from 5 K to 300 K. The lower curve (1) in the figure is the temperature dependence of magnetization at 1 kOe and the upper curve (2) at 2 kOe. The measurements were made as follows. The sample was cooled at first from 300 K to 5 K in a magnetic field of 1 kOe. Subsequently the magnetic field was set to be 2 kOe at 5 K and the sample was heated again to 300 K. As shown in the figure, the temperature dependence of both curves is almost the same. The magnetization decreases very rapidly with increasing temperature up to about 50 K and gently above about 50 K. As can be seen on the curve (2), there is a small decrease of magnetization apparently observed between 250 K and 300 K. At room temperature the value of the magnetization at 1 kOe is about 0.01 e.m.u. g^{-1}.

Fig. 6 shows the magnetization curve at temperatures from 5 K to 200 K. The measurements are made as follows. First, the temperature is set at 5 K, the magnetic

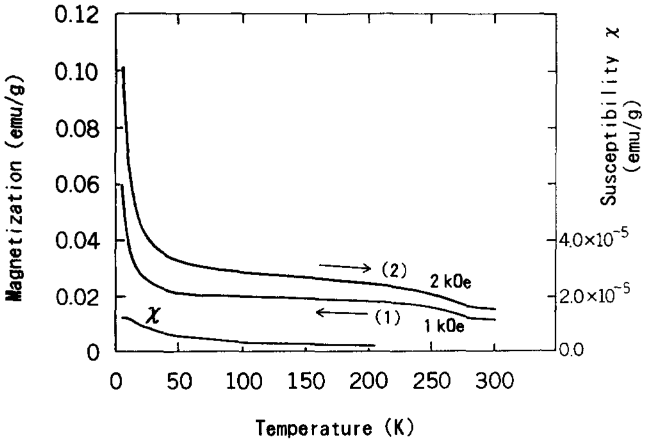

Fig. 5. Temperature dependences of the magnetization for CoN at 1 kOe and 2 kOe.

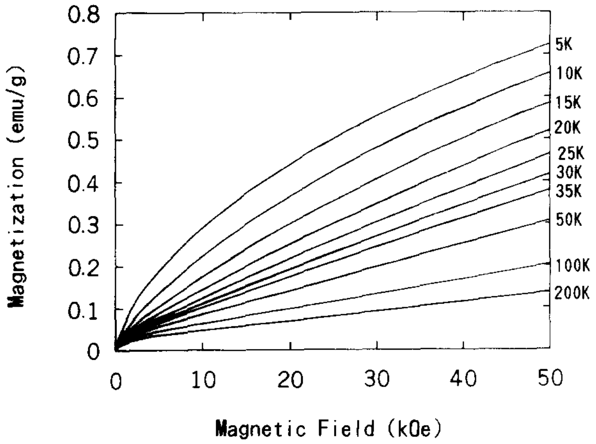

Fig. 6. Magnetization curves for the sample at 5 K, 10 K, 15 K, 20 K, 25 K, 30 K, 35 K, 50 K, 100 K and 200 K.

field is increased from 0.5 kOe to 50 kOe and then decreased again. Next, the temperature is set at 10 K, the magnetic field is changed from 0.5 kOe to 50 kOe and then decreased again. The following magnetization measurements at several temperatures are carried out in the same procedure. As seen in the figure, the magnetic hysteresis was not observed in any case of magnetization measurements. The magnetizing process at each temperature was analyzed by using the law of approach to saturation:

$$\sigma = \sigma_0(1 - b/H^2) + \chi H$$

where σ is the specific magnetization, σ_0 the spontaneous specific magnetization, b is a constant, χ the susceptibility and H the magnetic field. The value of σ_0 obtained at 5 K is 0.15 e.m.u. g^{-1}, which is very small. The estimated values of χ are plotted in Fig. 5. As seen in the figure, the temperature variation of χ is small. At temperatures above 100 K the values of χ are small (2.3×10^{-6} at 200 K) and almost constant, which shows the temperature dependence characteristic of a Pauli paramagnet.

Thus it is considered that CoN itself is a paramagnetic compound and the small σ_0 is due to a little ferromagnetic impurity such as other cobalt nitrides contained in the present sample. It is found that the magnetic properties of CoN and FeN are different from each other, although they have the same zinc blende type crystal structure.

4. Conclusions

The compound CoN was prepared by the d.c. reactive sputtering method. From the powder X-ray diffraction experiments and magnetic measurements, it is found that (1) the crystal structure of the CoN compound is of the zinc blende type, (2) the CoN compound is stable up to 504 K, above which it decomposes into δ-Co_2N, and (3) CoN has a Pauli paramagnetic character.

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