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THE X-RAY INVESTIGATION OF THE PHASE TRANSITIONS IN $[Ni(NH_3)_6](BF_4)_2$

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The X-ray powder diffraction study was carried out on $[Ni(NH_3)_6](BF_4)_2$ for the temperature range 293 – 80 K. It was found that the compound undergoes an enantiomorphic transition at 140 K: the cubic form changes to the monoclinic one. At 115 K further ordering of the monoclinic structures seems to take place.

1. *Introduction*

The nickel compounds $[Ni(NH_3)_6]X_2$, where $X = ClO_4$ or BF_4, are known to have two specific heat anomalies [1, 2]. For $X = ClO_4$ one anomaly occurs at 143 K and the other at 173 K. For $X = BF_4$ the corresponding temperatures are 115 and 140 K. It was of interest to examine whether the above mentioned anomalies are accompanied by polymorphic transitions. For this purpose these compounds were investigated by X-ray techniques.

The X-ray investigations of $[Ni(NH_3)_6](ClO_4)_2$ was described in our previous paper [3]. It was found that this compound exists in two crystallographic modifications in the temperature ranges shown schematically below:

$$\begin{array}{ccccccc} & & & \text{refl. (120) absent} & & \text{refl. (120) present} & \\ 293\,\text{K} & \rightleftharpoons & 173\,\text{K} & \rightleftharpoons & 143\,\text{K} & \rightleftharpoons & 80\,\text{K} \\ & \text{cubic} & & & \text{monoclinic} & & \\ & \text{space group } Fm3m & & & \text{space group } P2_1/n & & \end{array}$$

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In the case of $[Ni(NH_3)_6](BF_4)_2$ the X-ray investigation was performed by Dynowska [4], who concluded that above 135 K the compound has cubic structure and at temperatures lower than 135 K a structure of lower symmetry.

The aim of this paper was to determine the crystallographic modification of this low temperature phase.

2. *Experiment*

The investigations were carried out with an X-ray diffractometer DRON-1 connected to a goniometer GUR-5 and a modified low temperature device [3], in the temperature range 293 — 80 K controlled with an accuracy of 0.1 deg. The sample was lowered to the required temperature gradually from room temperature, without thermic shock, by automatic regulation of the flow of liquid nitrogen vapour. The sample was kept at the given temperature for about 15 minutes before starting to record the diffraction pattern.

3. *Results and discussion*

The X-ray diffraction patterns recorded at different temperatures were analysed. Above $T = 140$ K the compound has a cubic face centered structure with lattice constant $a = 11.22$ Å which is in agreement with previous data [5]. At temperatures lower than

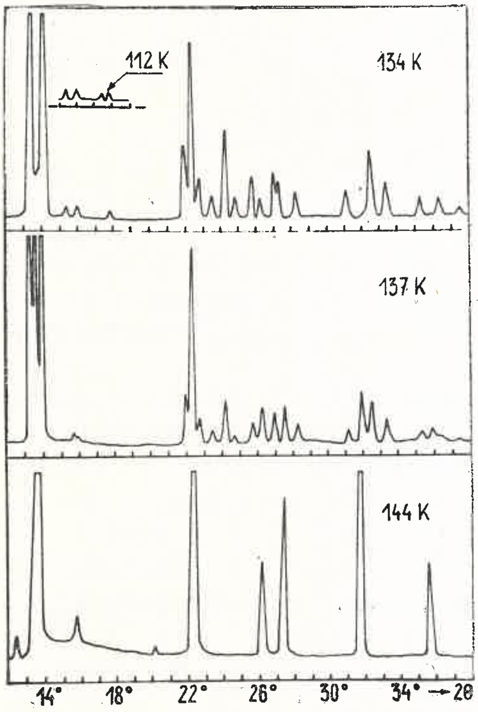

Fig. 1. Changes in the X-ray diffraction pattern of $[Ni(NH_3)_6](BF_4)_2$ in the course of sample cooling

140 K some of the diffraction maxima split giving rise to the new ones. New maxima increase in intensity on further cooling while the old ones gradually disappear. This is illustrated in the Figure. The diffraction pattern established at 134 K remained unchanged on cooling down to 115 K. At this temperature only one new maximum appeared. Further cooling down to 80 K did not cause any changes in the diffraction pattern. When the sample was heated up to room temperature the reverse changes in the diffraction patterns look place.

The pattern obtained at 134 K was interpreted. The character of splits suggests that the cubic lattice changes to monoclinic [6]. A method for deducing the *hkl* indices was based on the following Chojnacki's theorem [7]; if the indices *hkl* of four lattice planes fulfill the relation:

$$\begin{matrix} h_1+h_2 = h_3 & k_1+k_2 = k_3 & \text{and} & l_1+l_2 = l_3 \\ h_1-h_2 = h_4 & k_1-k_2 = k_4 & & l_1-l_2 = l_4 \end{matrix} \tag{1}$$

the experimental $\sin^2 \theta_{h_ik_il_i}$-values must fulfill the relation

$$2(\sin^2 \theta_{h_1k_1l_1}+\sin^2 \theta_{h_2k_2l_2}) = \sin^2 \theta_{h_3k_3l_3}+\sin^2 \theta_{h_4k_4l_4} \tag{2}$$

and the angle $\varphi = \sphericalangle(h_1k_1l_1), (h_2k_2l_2)$ is determined by

$$\cos \varphi = \frac{\sin^2 \theta_{h_3k_3l_3}-\sin^2 \theta_{h_4k_4l_4}}{4 \sin^2 \theta_{h_1k_1l_1} \times \sin^2 \theta_{h_2k_2l_2}}. \tag{3}$$

TABLE I

X-ray powder data for low temperature phase of $[Ni(NH_3)_6](BF_4)_2$

d_{obs} [Å]	d_{calc} [Å]	I/I_0	*hkl*
6.61	6.61	90	$1\ 1\ \bar{1}$
6.28	6.26	100	1 1 1
5.73	5.73	4	0 2 0
5.51	5.50	4	2 0 0
5.07*	5.08	3	1 2 0
4.96	4.96	3	2 1 0
4.04	4.05	22	$2\ 0\ \bar{2}$
3.96	3.96	64	2 2 0
3.85	3.82	12	$2\ 1\ \bar{2}$
3.766	3.766	6	$3\ 0\ \bar{1}$
3.660	3.664	26	2 2 1
3.573	3.571	9	3 0 1
3.453	3.455	19	$1\ 3\ \bar{1}$
3.398	3.401 and 3.403	8	1 3 1 and $3\ 1\ \bar{1}$
3.302	3.308	14	$2\ 2\ \bar{2}$
3.259	3.256	11	3 1 1
3.134	3.132	7	2 2 2
2.865	2.865	8	0 4 0
2.748	2.748	24	4 0 0

* appears at 115 K.

Ordering the observed $\sin^2 \theta_{h_i k_i l_i}$-values according to (2) permitted us to determine the *hkl* indices and the unit cell constants, which were calculated by the least-squares method using 18 reflections. The crystal data are as follows: $a = 11.02 \pm 0.01$ Å, $b = 11.45 \pm 0.01$ Å, $c = 11.02 \pm 0.01$ Å, $\beta = 94.9 \pm 0.1°$, $V_{\text{cell}} = 1390 \pm 4$ Å^3, $Z = 4$.

In the Table the experimental and calculated results are compared. The maximum which appeared at 115 K is also compatible with the monoclinic unit cell and has indices (120). Examination of the observed reflection indices shows systematic absences of $h+l = 2n+1$ for $h0l$ and $k = 2n+1$ for $0k0$ corresponding to the space group $P2_1/n$ or $P2_1/c$ in a conventional system.

4. Conclusions

The results of the investigations described lead to the conclusion that $[\mathrm{Ni(NH_3)_6}](\mathrm{BF_4})_2$, analogically to $[\mathrm{Ni(NH_3)_6}](\mathrm{ClO_4})_2$, exists in two crystallographic modifications shown schematically below:

$$293\ \mathrm{K} \rightleftharpoons 140\ \mathrm{K} \xrightleftharpoons{\text{refl. (120) absent}} 115\ \mathrm{K} \xrightleftharpoons{\text{refl. (120) present}} 80\ \mathrm{K}.$$

cubic monoclinic

The interpretation of the changes in diffraction patterns with temperature is similar, too. The main change at 140 K is related to a polymorphic transition. The small diffraction maximum, occurring at 115 K, can be interpreted as the result of further ordering of the structure and seems to correspond to the λ transition.

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REFERENCES

[1] M. Rachwalska, J. M. Janik, J. A. Janik, G. Pytasz, T. Waluga, *Phys. Status Solidi* (a) **30**, K81 (1975).

[2] T. Grzybek, J. A. Janik, M. Mayer, G. Pytasz, M. Rachwalska, T. Waluga, *Phys. Status Solidi* (a) **16**, K165 (1973).

[3] S. Hodorowicz, M. Ciechanowicz-Rutkowska, J. M. Janik, J. A. Janik, *Phys. Status Solidi*, in press.

[4] E. Dynowska, *Phys. Status Solidi* (a) **31**, K23 (1975).

[5] R. W. G. Wyckoff, *Crystal Structures*, Interscience, New York 1960, Chap. X.

[6] L. M. Kovba, V. K. Trunov, *Rentgenofazovyi analiz*, I-vo Moskovskogo Universiteta, Moskva 1969.

[7] J. Chojnacki, *A General Method for Determining of the Linear and Angular Lattice Constants from Debye-Scherrer Patterns*, Thesis, Jagellonian University, Kraków 1945 (unpublished).