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X-Ray Study of the Structural Phase Transition in Nickel Hexammine Perchlorate

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An X-ray study is made of the high-temperature and low-temperature phases of $\text{Ni}(\text{NH}_3)_6(\text{ClO}_4)_2$. At room temperature, the unit cell is regular, of the CaF_2 type, with lattice constant $a_c = 11.44 \text{ \AA}$. The monoclinic cell of the low-temperature phase has, at $T = 100 \text{ K}$, the constants $a_m = (8.19 \pm 0.01) \text{ \AA}$, $b_m = (11.76 \pm 0.01) \text{ \AA}$ and $c_m = (15.08 \pm 0.01) \text{ \AA}$ with $\beta = (93.9 \pm 0.2)^\circ$. The total change in volume amounts to 3.2%, that related with the change in structure amounting to 0.7%. The structural phase transition is found to be of a diffusional nature.

Es wird eine Röntgenstrahlanalyse der Hochtemperatur- und der Niedertemperaturphasen von $\text{Ni}(\text{NH}_3)_6(\text{ClO}_4)_2$ durchgeführt. Bei Zimmertemperatur ist die Elementarzelle regulär vom CaF_2 -Typ und die Gitterkonstante $a_c = 11,44 \text{ \AA}$. Die monokline Zelle der Niedertemperaturphase besitzt bei $T = 100 \text{ K}$ die Konstanten $a_m = (8,19 \pm 0,01) \text{ \AA}$, $b_m = (11,76 \pm 0,01) \text{ \AA}$ und $c_m = (15,08 \pm 0,01) \text{ \AA}$ mit $\beta = (93,9 \pm 0,2)^\circ$. Die Gesamtänderung des Volumens beträgt 3,2%, die mit der Strukturänderung verknüpfte 0,7%. Es wird gefunden, daß der strukturelle Phasenübergang vom Diffusionstyp ist.

1. Introduction

At certain characteristic temperatures T_c , compounds of the type $[\text{Me}(\text{NH}_3)_6]\text{X}_2$ (where Me is a bivalent metal ion and X a monovalent anion) exhibit anomalies of their physical properties. In particular, for the nickel compounds $[\text{Ni}(\text{NH}_3)_6](\text{BF}_4)_2$ and $[\text{Ni}(\text{NH}_3)_6](\text{ClO}_4)_2$ at certain temperatures T_c a drastic broadening of the EPR lines [1, 2] and an anomaly of the specific heat [3, 4] have been reported. For $[\text{Ni}(\text{NH}_3)_6](\text{ClO}_4)_2$ the Raman spectra also point to a phase transition at $T_c = 173 \text{ K}$ [5].

The earliest theoretical attempts at explaining the anomalies were based on considerations of the motions of the ammonia molecules in the $\text{Ni}(\text{NH}_3)_6$ complex [6]. However, high pressure results for ammoniacates with simple anions, I^- , Br^- , Cl^- [7], and composite anions NO_3^- , ClO_4^- [8, 9] suggest a structural transition. According to the new approach, the transition involves a re-construction of the crystal structure with a change in mutual disposition of the anions and cations [10], whereas the transition energy is related with a change in the crystal potential. This is best supported by the $T_c(a_c)$ diagram given in the present paper.

In search for a final proof, X-ray studies were performed throughout a wide range of temperatures, for $[\text{Ni}(\text{NH}_3)_6](\text{BF}_4)_2$ in the first place. This work proved the transition to be of the structural type and to be diffuse with respect to temperature [11]. Next, an investigation was performed aimed at determining the structure of the low-temperature phase of $[\text{Ni}(\text{NH}_3)_6](\text{ClO}_4)_2$ [12] applying Chojnacki's method [13] for indexing the powder patterns. The latter method, however, because of the hardly avoidable subjective approach of those using it, can easily lead to erroneous results. In the present work, we preferred to apply a numerical procedure of indexing [14] for the same purpose, and the results appear to provide a more plausible solution of the problem.

2. Experimental

In the case of $[\text{Ni}(\text{NH}_3)_6](\text{ClO}_4)_2$ and the majority of related compounds the choice of the apparatus for the structural studies has to take into account the fact that only polycrystalline material is available and that the work has to be done at low temperatures. This considerably complicates the problem, regarding both experiment and interpretation.

We opted for an X-ray DRON-1 diffractometer and a low-temperature chamber KRN-190, the latter well adapted for polycrystalline materials and worked at 85 to 300 K. The sample was cooled by means of a cold tube connected with a reservoir of liquid nitrogen and heated by means of a heater built-in in the sample holder. By appropriately setting the current flow through the heater, the temperature of the sample could be maintained constant to within ± 0.5 K for arbitrary periods of time, in the range from 85 to 300 K. A drawback arises from the fact that the thermocouple is fixed on the cold tube, so that a temperature gradient can arise between the point of measurement and the sample. The latter circumstance, however, was of little importance since the present work was not aimed at determining the absolute temperature of the transition but rather at establishing the transition itself and determining the structure of the low-temperature phase.

3. Results

Diffraction patterns obtained at temperatures ranging from 85 to 300 K were analyzed. In agreement with earlier results, the compounds $[\text{Ni}(\text{NH}_3)_6](\text{ClO}_4)_2$ was found to crystallize in a cubic structure of the type $\text{Fm}\bar{3}\text{m}$ (CaF_2) at room temperature. The lattice constant, after Wyckoff [15], amounts to $a_c = 11.41$ Å whereas our measurements led to $a_c = 11.44$ Å. This value was derived from powder measurements, applying extrapolation with the function $\cos^2 \theta$ to the last ten diffraction lines and, next, a least-squares procedure to draw the straight line through the set of our experimental points. The value a given by us is that at $\theta = 90^\circ$.

Successive diffraction patterns taken at lower and lower temperatures showed no changes, except for some slight shifts of the diffraction maxima towards larger angles, due to the thermal dilativity of the material.

Close to $T = 158$ K the diffraction spectrum undergoes a radical change, and an additional diffraction peak appears at about $T = 128$ K.

The proceeding observations prove beyond doubt that a structural phase transition takes place in two steps: a considerable re-structuralization occurs near $T = 158$ K, followed by a (probably slight) modification of the structure at 128 K. It should be noted that the temperature was measured on the sample holder and not on the sample, where it is surely higher. This temperature gradient, by the way, can be assessed as amounting to about 15 K from a comparison of our results with those of a c_p -study by Rachwalska et al. [4] for the same compound reporting a strong anomaly of c_p at $T = 173$ K related with a drastic re-structuralization and a slight anomaly at $T = 143$ K corresponding to a slight change in structure. None the less, all the temperatures given in this article concerning our X-ray studies were measured on the sample holder.

The nature of the diffraction spectrum subsequent to the phase transition shows the low-temperature phase to have a structure of symmetry much lower than that of the cubic phase α . We denote the phase in the immediate neighbourhood $T < T_c$ as β , whereas at 100 K the phase δ exists. The structure of the phase δ was determined from measurements made at $T = 85$ K.

In cases of unknown low-symmetry structures, the indexing of powder diffraction patterns is considerably difficult and requires complicated methods. Recently, to this

aim, recourse has been made to special numerical procedures, programmed to high-grade computers, and based on the method of trial and error. We used a method of this kind, proposed by Taupin [14], using as data the positions of the diffraction maxima [2]. The program, on successively testing all the crystallographical systems for the experimentally obtained set of data, selects the type of structure and yields the parameters of the unit cell.

In order to obtain a univocal solution, the angles 2θ have to be determined with a high degree of accuracy. According to Taupin [2], the accuracy could not be worse than 0.03° in the 2θ scale, which is very difficult to achieve in practice. In our case, chiefly because the spectra obtained were not of the very best quality and with regard to difficulties in the adjustment of the low-temperature chamber, 2θ could be determined with an accuracy of about 0.04° , i.e. less than that required, notwithstanding the fact that each 2θ value was the average of ten independently performed measurements and that all possible corrections had been taken into account. In this situation several solutions were obtained, all of them relating to a monoclinic structure, though differing as to the unit cell parameters. An analysis on the assumption of an unit cell volume decreasing at $T = T_c$ enabled us to select one solution, characterized by the required variation in volume of the cell, and according to which the low-temperature phase of $[\text{Ni}(\text{NH}_3)_6](\text{ClO}_4)_2$ at $T = 100 \text{ K}$ (on taking into consideration the correction for the temperature gradient) has a monoclinic structure of the type P, with the following parameters:

$$\begin{aligned} a &= (8.19 \pm 0.01) \text{ \AA}, \\ b &= (11.76 \pm 0.01) \text{ \AA}, \\ c &= (15.08 \pm 0.01) \text{ \AA}, \quad \beta = (93.9 \pm 0.2)^\circ, \\ V_{\text{uncell}} &= 1449 \text{ \AA}^3, \quad V/V_{\text{cub}} = 3.2\%. \end{aligned}$$

The indexing results, contained in the print for the solution, are given in Table 1.

Likewise to the compound $[\text{Ni}(\text{NH}_3)_6](\text{BF}_4)_2$ [11], the transition does not occur at a well defined temperature but rather extends over a temperature interval ΔT . We determined the interval by measuring the intensity at the maximum of the [111] diffraction peak for the cubic phase as a function of temperature (Fig. 1). With regard to the sensitivity of the method of measurement, the interval was found from the graph to extend from 153 to 164 K. Diffraction patterns taken in this range of temperatures (shown in part in Fig. 2) point obviously to the coexistence of two phases in this transition region. Accurate studies led to the conclusion that, at a given temperature

T_i from the interval $153 < T_i < 164 \text{ K}$, the ratio of the two phases is a constant, independent of time.

The transition is reversible in that, on being brought to room temperature, the compound again goes over into the cubic structure Fm3m, also, a change in temperature between 153 and 164 causes a shift in equilibrium of the two phases α and β .

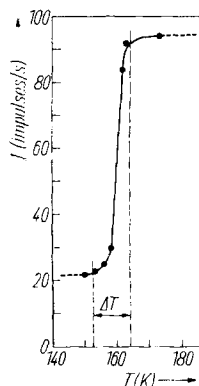


Fig. 1. Temperature dependence of the intensity of the diffracted beam at the maximum of the [111] peak for the cubic phase α of powdered $[\text{Ni}(\text{NH}_3)_6](\text{ClO}_4)_2$. $T_c = 164 \text{ K}$, $\Delta T \approx 11^\circ$

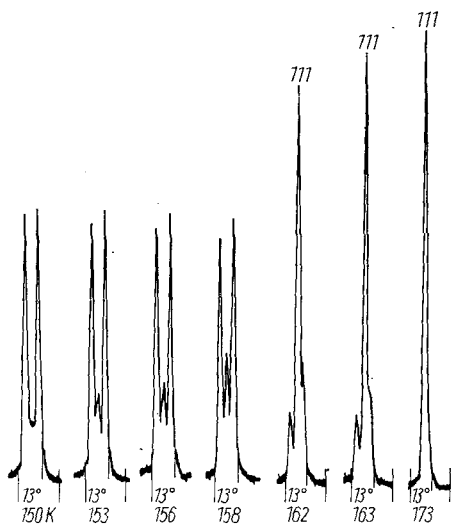


Fig. 2. Diffraction patterns showing that the transition of $[\text{Ni}(\text{NH}_3)_6](\text{ClO}_4)_2$ from the cubic phase α to the monoclinic phase is diffuse

Table 1

d_{exp}	d_{cal}	hkl	$10^{-3} \Delta(1/d^2)$
6.677	6.709	110	-0.219
6.321	6.337	012	-0.130
5.822	5.882	020	-0.592
5.537	5.478	021	0.704
5.141	5.154	112	-0.190
4.999	5.015	003	-0.247
4.076	4.084	200	-0.243
4.012	4.012	201	0.00406
3.766	3.761	004	0.199
3.585	3.582	014	0.110
3.507	3.509	104	-0.113
3.426	3.419	131	0.396
3.340	3.345	212	-0.295
3.286	3.279	203	0.356
3.165	3.163	132	0.126
3.068	3.065	203	0.218
2.912	2.915	015	-0.227
2.767	2.767	140	-0.0155
2.705	2.710	141	-0.461
2.497	2.500	125	-0.386
2.457	2.452	016	0.613
2.338	2.342	241	-0.681
2.225	2.229	151	-0.756
2.145	2.149	007	-0.813
		standard deviation:	0.411

4. Discussion and Conclusions

The unit cell proposed above results from a computer analysis of the changes in powder X-ray diffraction patterns as well as a crystallochemical analysis of the structure of $[\text{Ni}(\text{NH}_3)_6](\text{ClO}_4)_2$. In the transitions $\alpha \rightarrow \beta$ and $\beta \rightarrow \delta$ the structural reorganization is but slight, showing that the disposition of the ions in the monoclinic cell is close to that in the cubic cell. Fig. 3 shows the cells of $[\text{Ni}(\text{NH}_3)_6](\text{ClO}_4)_2$ for the two phases: the high-temperature phase α of the CaF_2 type, and the monoclinic low-temperature phase α and δ resembling the double tetragonal cell of ZrO_2 . Fig. 4 shows projections of the monoclinic cell on the axes b_m , c_m , and a_m .

The cell shape obtained enables us to draw conclusions concerning the experimentally observed vibrations of the complex ion $[\text{Ni}(\text{NH}_3)_6]^{2+}$ and the perchloric ion ClO_4^- . The decrease in dimensions of the crystal along the $[110]$ direction of the cubic cell causes the c_m -axis of the monoclinic system to be shorter than $a/\sqrt{2}$. The increase in dimensions of the cell in the plane perpendicular to this a -direction, i.e. in the directions of b_m and a_m of the monoclinic system, permits the statement that the ion $[\text{Ni}(\text{NH}_3)_6]^{2+}$ which at high temperatures performs isotropic vibrations with a large amplitude, exhibits a change in motion: vibrations still occur in the planes a_m and b_m , but the individual octahedra are strongly bonded along the c_m -axis. This causes a deformation of the $\text{Ni}(\text{NH}_3)_6$ octahedra along the C_4 -axis, two NH_3 molecules being strongly bonded in the chain running in the c_m -direction and far less strongly bonded to the anions surrounding them.

Earlier, Piślewski et al. [16] suggested that two kinds of NH_3 groups exist in the $\text{Cd}(\text{NH}_3)_6$ ion in order to interpret the values of proton relaxation times in NMR. The recent results of Krupski [17] concerning the thermal dilatativity permitted the determination of the changes in cell volume on cooling to the phase transition temperature. Taking, after Krupski [17], the volume dilatativity coefficients as $\beta_c =$

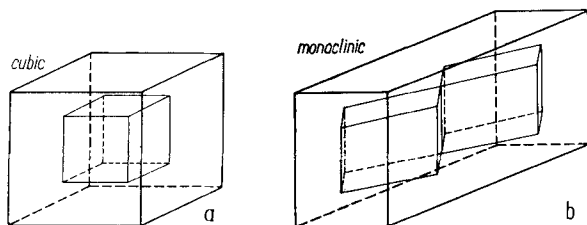


Fig. 3. Outline of the unit cell in the phase a) α and b) phases β and δ of $[\text{Ni}(\text{NH}_3)_6](\text{ClO}_4)_2$

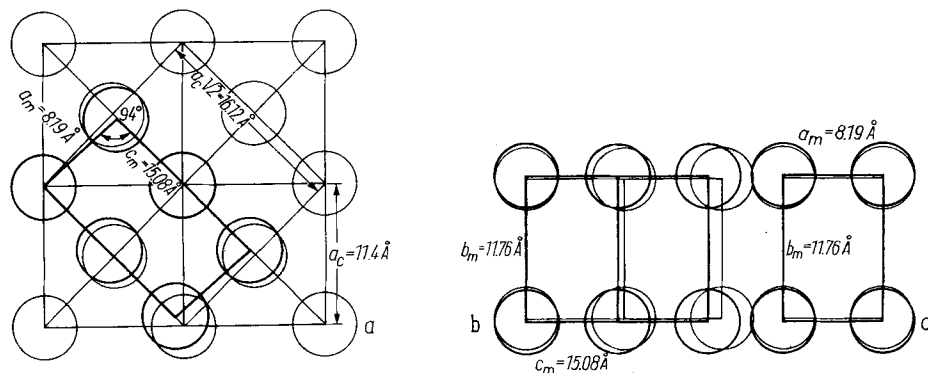


Fig. 4. Projections of the monoclinic unit cell a) along b_m , b) along the axis a_m , and c) along the axis c_m . Thin lines denote the cell of cubic $[\text{Ni}(\text{NH}_3)_6](\text{ClO}_4)_2$

$= 16.5 \times 10^{-5} \text{ K}^{-1}$ for the cubic phase, $\beta_m = 30.6 \times 10^{-5} \text{ K}^{-1}$ for the monoclinic phase, and $\Delta V/V_{T_c} = 1.56\%$ for the volume change at T_c , the total change in volume when cooling the sample to 100 K from room temperature is $\Delta V/V = -5.5\%$.

The change in volume of $[\text{Ni}(\text{NH}_3)_6](\text{ClO}_4)_2$ at the structural phase transition previously calculated by us [18] from high-pressure measurements amounts to $\Delta V/V_{T_c} = -0.7\%$, i.e. twice smaller. The variation of $\Delta V/V = -5.5\%$ from thermal expansion is in good agreement with the X-ray data, according to which the change in volume of the unit cell $(V_{290} - V_{180})/V_{290}$ amounts to -3.2% . The results of the present study, as obtained for a powder, do not provide a final solution concerning the nature of the phase transition of $[\text{Ni}(\text{NH}_3)_6](\text{ClO}_4)_2$.

None the less, the transition is proved to be of a structural nature. Work aimed at obtaining single crystals is proceeding. The fact that the transition is diffuse, as observed in this laboratory by EPR [19, 20] by Dynowska [11] and subsequently by Hodorowicz et al. [12] applying X-rays, points to the complexity of the transition. This may be due to the strong dependence of the transition on hydrostatic pressure. On transition of some part of the crystal into the low-temperature phase, the internal pressure acting on the remaining part decreases. The positive pressure coefficient $\delta T_c/\delta p$, lowers the transition temperature of the latter part, still awaiting the transition. As a result, an interval of about 10 to 20 K exists in which the two phases are at equilibrium. Detailed studies are now proceeding on monocrystals.

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References

- [1] J. STANKOWSKI, J. M. JANIK, A. DEZOR, and P. B. SZCZANIECKI, *phys. stat. sol. (a)* **16**, K167 (1973).
- [2] P. B. SZCZANIECKI, L. LARYŚ, and U. GRUSZCZYŃSKA, *Acta phys. Polon.* **46**, 761 (1974).
- [3] T. GRZYBEK, J. A. JANIK, J. MAYER, G. PYTASZ, M. RACHWAŁSKA, and T. WALUGA, *phys. stat. sol. (a)* **16**, K165 (1973).
- [4] M. RACHWAŁSKA, J. M. JANIK, J. A. JANIK, G. PYTASZ, and T. WALUGA, *phys. stat. sol. (a)* **30**, K81 (1975).
- [5] J. A. JANIK, J. M. JANIK, G. PYTASZ, T. SARGA, and J. SOKOŁOWSKI, Report IFJ No. 926/PS; *J. Raman Spectr.*, in the press.
- [6] A. R. BATES and K. W. H. STEVENS, *J. Phys. C* **2**, 1573 (1969).
- [7] M. PAGANNONE and M. G. DRICKAMER, *J. chem. Phys.* **43**, 4064 (1965).
- [8] L. LARYŚ, J. STANKOWSKI, and M. KRUPSKI, *Acta phys. Polon.* **50**, 351 (1976).
- [9] J. STANKOWSKI and M. KRUPSKI, *Bull. Acad. Polon. Sci.*, in the press.
- [10] J. STANKOWSKI, *Proc. Conf. RAMIS 75*, Ed. Univ. A. Mickiewicz, Poznań, No. 19 (p. 243); *Mater. Sci. II* **3**, 57 (1976).
- [11] E. DYNOWSKA, *phys. stat. sol. (a)* **31**, K23 (1975).
- [12] S. HODOROWICZ, M. CIECHANOWICZ-RUTKOWSKA, J. M. JANIK, and J. A. JANIK, *phys. stat. sol. (a)* **43**, 53 (1977).
- [13] J. CHOJNACKI, Thesis, Jagiellonian University Cracow, 1945.
- [14] D. TAUPIN, *J. appl. Cryst.* **6**, 380 (1973).
- [15] R. W. G. WYCKOFF, *Crystal Structure*, Chap. X, Interscience, New York 1960.
- [16] N. PIŚLEWSKI, J. STANKOWSKI, and L. LARYŚ, *phys. stat. sol. (a)* **31**, 415 (1975).
- [17] M. KRUPSKI, to be published.
- [18] M. KRUPSKI and J. STANKOWSKI, *Acta phys. Polon.* in the press.
- [19] P. B. SZCZANIECKI and J. STANKOWSKI, *Acta phys. Polon.* **51**, 117 (1977).
- [20] M. KRUPSKI and J. STANKOWSKI, *Acta phys. Polon.* **50**, 685 (1976).

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