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OPTICAL PROPERTIES AND UNIT CELL PARAMETERS OF NICKEL NITRATE HEXAHYDRATE

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1. INTRODUCTION

NICKEL nitrate is known to form three hydrates with three, six and nine molecules of water at 55° C., — 16° C. and — 27° C. respectively. Very little is known regarding the structure and physical properties of these hydrates. Groth in his *Chemische Crystallographie* reports some measurements of interfacial angles, axial ratios, density and melting point of nickel nitrate hexahydrate. The hexahydrate is reported to occur as green deliquescent crystals having a density of 2·05 gm./c.c. in the monoclinic prismatic class with axial ratios $a:b:c = 1\cdot164:1:1\cdot905$ and $\beta = 101°26'$. In the literature as far as the author could find, the structure and optical properties of this substance has not been reported. Further it would be of particular interest to study the magnetic properties of single crystals of this substance. It should however be borne in mind that the material is of a highly hygroscopic nature and hence needs special technique of study. It was with a view to understand the structure and optical properties of this substance, that the present investigation was undertaken and the results of study are reported in the present communication. It would be in place to mention here that the crystals of hexahydrate obtained by the author could only be placed in the triclinic system as the optical and X-ray investigations unequivocally show this to be the case. This is in contrast to the previous report quoted earlier.

2. EXPERIMENTAL STUDY

Crystals of nickel nitrate hexahydrate for both optical and X-ray work were grown from a purified commercially available sample. The solubility of this substance is very high in water and is considerable in many organic compounds, particularly alcohol and acetone. A saturated solution in water of the substance was kept inside an airtight bell jar in a crystallising dish along with a small quantity of P_2O_5 or anhydrous calcium chloride in a separate container which served to absorb water. It was observed that crystals of

large size could be grown by this method. Since the crystals are extremely deliquescent, they were taken out of the mother liquor and transferred promptly to a bottle containing kerosene after the adhering solution was removed between blotting papers.

Needle-shaped crystals were obtained by rapid crystallisation while large elongated plates were obtained by slower crystallisation. The crystals were of a beautiful emerald green in colour and well developed crystallographic faces could be observed in it. Visual examination of the morphological characters revealed that the crystals did not possess any element of symmetry and the form was suggestive of a triclinic pinacoidal type. In very well developed crystals, many other faces could be discerned. However an optical goniometric study was not attempted as this would necessitate special immersion methods.

3. CELL PARAMETERS

Rotation and zero-layer Weissenberg X-ray photographs were taken with thin rods cut parallel to the three observed edges of the crystal form. Considerable difficulty was experienced in handling the specimens, cutting them parallel to the chosen edges, and shaping them to correct thickness owing to the extreme hygroscopic nature of the material. The rod-shaped specimen was placed in a thin-walled pyrex capillary tube, sealed at one end while the other open end was closed with wax and mounted on the goniometer head. Cu Kα radiation was employed to record the X-ray patterns. The following linear dimensions of the unit cell and its angular constants were obtained from the three single crystal and the three zero-layer Weissenberg photographs. With these six photographs cross checks of the data were possible.

$a = 5{\cdot}79$ Å.U. $\qquad \alpha = 106°{\cdot}38'$

$b = 7{\cdot}69$ Å.U. $\qquad \beta = 80°{\cdot}32'$

$c = 11{\cdot}89$ Å.U. $\qquad \gamma = 101°{\cdot}27'$

$$a : b : c = 0{\cdot}753 : 1 : 1{\cdot}546$$

The density of the material was found to be about 2 gm./c.c. and the number of molecules per unit cell when calculated came out very close to 2, revealing thereby that there are two molecules per unit cell.

In the convergent light figure observed with the cleavage plate of the crystal the brush is quite dark and very distinct while crossing the eyes, thereby indicating that the crystal is not optically active. Further, when copper radiation is used for recording the X-ray patterns, one is working very close

to the absorption edge of nickel, a favourable circumstance for the breakdown of Friedel's law if there were no centre of symmetry. No such breakdown was noticeable in the X-ray photographs and therefore it is highly probable that the crystal belongs to the centro-symmetric class of the triclinic system, the corresponding space group symobl being C_i^1 or $P\bar{1}$.

It should be remarked here that the crystal exhibits a very perfect (001) cleavage. The needle axis is found to be 5·79 A.U. while the *c*-axis is 11·89 A.U.

4. Optical Properties

The optical properties of the crystal were determined with the help of a polarising microscope. The habit plane of the crystal which is found to be the (010) face by X-ray methods exhibits straight extinction. The cleavage plate which is found to be parallel to the (001) face gives an inclined extinction, the vibration direction making an angle of 11° with the straight edge of the crystal which is parallel to the *a*-axis (100).

The convergent light figure is observed on the (001) face that is the cleavage plate and the β vibration direction lies on this. The optic axial angle was determined by adopting the undermentioned procedure which was found to be very convenient. The cleavage plate was mounted between a glass plate and a cover slip with a suitable immersion liquid and this was placed on a Federov stage. The stage was fixed on to a polarising microscope and a glass hemisphere belonging to the Federov stage was attached to the stage of the microscope in the aperture admitting light. This acted as a converging lens and with a low power objective and the Betrand lens one could easily observe the interference figure. The crystal could easily be set by proper adjustment of the stage such that the axial plane is brought parallel to one of the cross wires. Having obtained this setting, the axial angle is easily determinable and two principal refractive indices could also be obtained. For obtaining the latter, parallel light is needed which can be got by removing the hemispherical glass condenser and lowering the substage, while leaving the desired setting of the crystal undisturbed.

The axial angle and the two refractive indices β and γ were obtained by following the above procedure and using immersion methods to measure the refractive index. The third principal refractive index (α) was measured on the (010) face by suitably tilting the stage to get the vibration direction parallel to the cross wire. The following are the values obtained for sodium light.

$\alpha = 1 \cdot 422$

$\beta = 1 \cdot 555$ $\qquad 2V = 41° \cdot 12'$

$\gamma = 1 \cdot 577$

A diagram is reproduced below to show the orientation of the optic elements with respect to the crystallographic elements observed in the crystal. The acute bisectrix is the (α) vibration direction and the crystal is therefore biaxial negative.

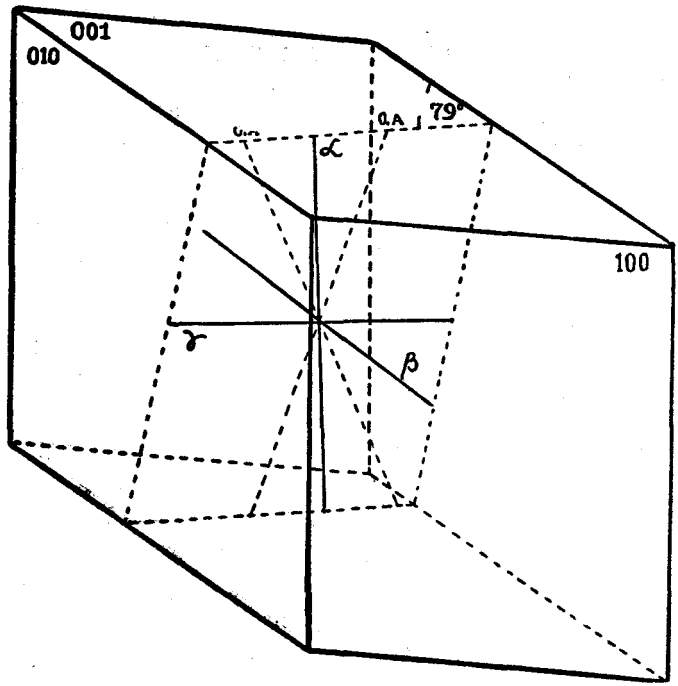

FIG. 1

As already remarked, crystals of $Ni(NO_3)_2\,6H_2O$ are emerald green in colour and exhibit pleochroism in polarised light. Pleochroism is very striking on the (010) face. For a vibration parallel to (α) the colour is bluish green while it is yellowish green for a vibration parallel to the (β) vibration direction. Pleochroism is not marked on the cleavage face and the difference in absorption is not observable for a vibration parallel to β and γ vibration directions.

5. SOME REMARKS

A study of the optical properties in relation to the observed morphological characters of the crystal by itself revealed that the crystal can only

be placed in the triclinic system. The straight extinction observed can only be an accident the possibility of which is not totally excluded for a cyrstal belonging to the triclinic system. Otherwise, the optical properties bear no symmetric relationship to the crystal edges and faces.

It would be seen from an examination of refractive index data that the maximum refractive index lies very close to the cleavage plane and the minimum index is nearly normal to it. The difference between the two indices, *i.e.*, the birefringence, is fairly high. The perfect cleavage of the (001) plane and the refractive properties indicate that the planar nitrate ions lie very close to the cleavage plane.

A complete determination of the structure and other physical properties is under progress and the results will be reported in due course.

In conclusion the author wishes to express his thanks to Sir C. V. Raman, F.R.S., N.L., for his kind interest in the work and to Dr. S. Ramaseshan for helpful criticisms.

SUMMARY

The unit cell parameters and optical properties of nickel nitrate hexahydrate are reported. It is found that the crystal belongs to the centrosymmetric class in the triclinic system. The refractive properties and the very perfect cleavage of the (001) indicate that the planar nitrate ions lie very close to the (001) face.