## *Crystallization of Amorphous Nickel Sulfate*

By Hideaki CHIHARA and Syûzô SEKI

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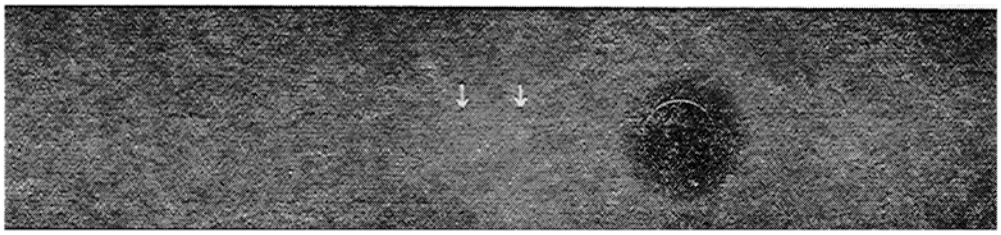
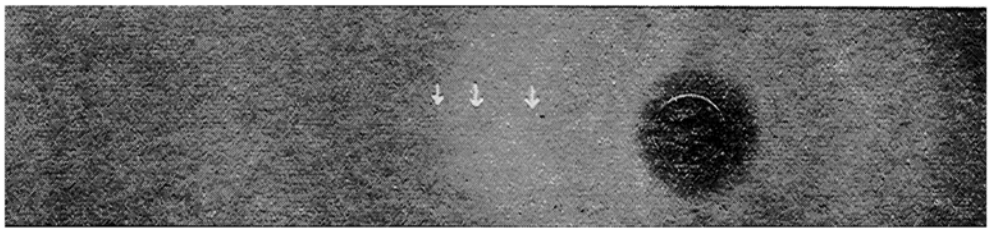
While working with the dehydration of a series of hydrates of nickel sulfate[1], crystallization of amorphous nickel sulfate was observed. Kahlbaum nickel sulfate was used to obtain the hexahydrate from aqueous solution. The hexahydrate structure[2] being identified by the X-ray powder method, the crystals were dehydrated on a quartz helical balance under vacuum less than $10^{-5}$ mm Hg, at temperatures up to 250°C until a constant weight was reached (four hours at 130° and an hour at 250°). The initial formula was calculated to be $NiSO_4 \cdot 5.98H_2O$ on the basis of complete dehydration.

The anhydrous nickel sulfate was brown in color and soluble in water (thus not nickel oxide). The X-ray pattern taken in a closed glass capillary with Cu $K_\alpha$ radiation showed that it was amorphous with two hardly discernible haloes (Fig. 1). Annealing at 100°C made the haloes progressively sharper and an additional halo appeared at a larger diffraction angle. Fig. 2 is the result obtained after four hours annealing at 100°C. Further heating at 110°C for six hours brought about sharp Debye rings as shown in Fig. 3, which remained unchanged on further heating. The observed spacings together with the relative intensities obtained by a recording microphotometer are listed in the accompanying table.

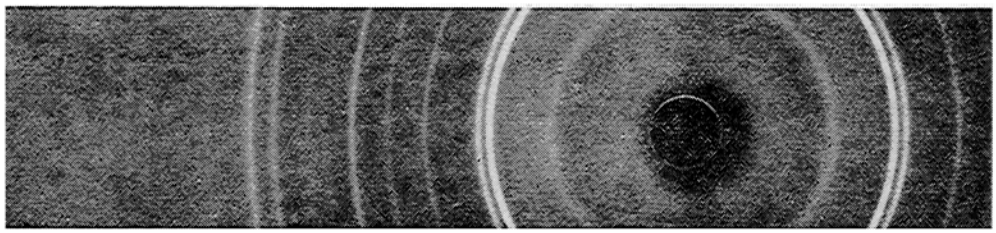
A survey of the literature revealed that F. Hammel reported[3] that the anhydrous nickel sulfate is orthorhombic with the unit cell of dimensions $a=4.6_2$, $b=6.5_1$, and $c=8.4_9$A. The present result is, however, consistent neither with this unit cell nor with the pattern given by Hammel. A



1. Anhydrous $NiSO_4$, amorphous.



2. Anhydrous $NiSO_4$, annealed at 100°C., 4 hours, amorphous.



3. Anhydrous $NiSO_4$ annealed further at 110°C., 6 hours, crystalline.

1) H. Chihara and S. Seki, This Bulletin, **26**, 88 (1953).
2) C. A. Beevers and H. Lipson, *Z. Krist.*, **83**, 123 (1932).
3) F. Hammel, *Compt. rend.*, **202**, 57 (1936).

TABLE

| Spacing in Å. | Intensity | Tentative index based on the tetragonal cell |
|---|---|---|
| 4.72 | 15 | 200 |
| 3.32 | 130 | 111 |
| 3.16 | 95 | 300 |
| 2.55 | 40 | 211 |
| 2.25 | 35 | 301 |
| 2.19 | 5 | 311 |
| 2.16 | 5 | — |
| 2.02 | 75 | 321 |
| 1.88 | 20 | 411 |
| 1.80 | 15 | — |
| 1.78 | 20 | 421 |
| 1.76 | 10 | 520 |
| 1.74 | 5 | |
| 1.66 | 50 | 440 |
| 1.63 | 10 | 550, 002, 551 |
| 1.58 | 70 | 600, 112 |
| 1.57 (shoulder) | 35 | |
| 1.45 | 15 | 222, 531 |
| 1.44 | 10 | 302, 601 |
| 1.27 | 18 | 422 |

comparison of ionic radii of bivalent cations ($Mg^{++}$ 0.65Å, $Ni^{++}$ 0.70Å, and $Zn^{++}$ 0.74Å) suggests that nickel sulfate may well be isomorphous with $MgSO_4$ and/or $ZnSO_4$. The anhydrous nickel sulfate prepared in a different manner from Hammel's may crystallize in a different way. A possibility will be open for finding other modifications of sulfate of metals of the magnesium series.

An attempt was made to assign a unit cell to the new modification which can reasonably account for the observed spacings. There are not fewer than three possibilities. The simplest one is indicated in the third column of the table. This is of simple tetragonal cell with dimensions $a=9.5_4$Å and $c=3.2_5$Å (the volume of the unit cell is 300Å$^3$). An orthorhombic unit cell with dimensions $a=6.9_3$Å, $b=6.3_1$Å, and $c=4.7_1$Å or with dimensions $a=10._0$Å, $b=7.9_3$Å, and $c=4.7_7$Å can equally well or better reproduce the observed spacings, the volume of the unit cell being 200 and 380Å$^3$, respectively. These orthombic cells are considered to be less probable in view of the too small or too great unit cell volume. A trial of finding the crystal class and the unit cell in an unarbitrary way was also made by Ito and Sadanaga's method[4], unsuccessfully, owing to lack of accuracy in the determination of the diffraction angle.

*Department of Chemistry, Faculty of Science, Osaka University, Nakanoshima, Kita-ku, Osaka*

4) T. Ito, X-ray Studies on Polymorphism, Maruzen Co Ltd., Tokyo, (1950).