

GROWTH AND OPTICAL ABSORPTION OF SINGLE
CRYSTALS OF NICKEL SULFATE HEXAHYDRATE

by

Hsuchiao Yeh

Submitted in Partial Fulfillment of the Requirements
for the Degree of
Master of Science in Engineering
in the
Electrical Engineering
Program

Alan J. Zuckerwar August 15, 1972
Advisor Date

Karl E. Kite August 15, 1972
Dean of the Graduate School Date

YOUNGSTOWN STATE UNIVERSITY

August, 1972

ABSTRACT

GROWTH AND OPTICAL ABSORPTION OF SINGLE
CRYSTALS OF NICKEL SULFATE HEXAHYDRATE

Hsuchiao Yeh

Master of Science in Engineering

Youngstown State University, 1972

The crystalline alpha-hexahydrate of nickel sulfate was obtained by growing crystals from solution by utilizing Holden's Rotary Crystallizer within the temperature limits of 35 deg C and 50 deg C. The crystals were then cut in two different directions, one in parallel with and the other perpendicular to the optic axis, and polished on abrasive papers and powders to a thickness of 2.53 ± 0.01 mm. The dichroism was then studied with Perkin-Elmer Spectrophotometers in ultraviolet, visible, and infrared regions. The ranges of wavelength under study are from 190 to 700 millimicrons in UV-VIS region and from 2.5 to 40 microns in IR region. It is found that in the IR region, the material has nearly total absorption, and in the UV-VIS region the material has total absorption in the wavelength ranges of 190 to 195 millimicrons, 350 to 430 millimicrons, and 590 to 700 millimicrons, while the maximum transmittance occurs at 310 millimicrons and 490 millimicrons. It is also found that

there is neither a detectable linear dichroism existing in the alpha-hexahydrate of nickel sulfate crystals within the UV, VIS, and IR wavelength regions, nor a shift in the edge of the absorption bands with regard to changes in the crystallographic direction.

ACKNOWLEDGEMENTS

I would like to express my gratitude to Dr. Allan J. Zuckerwar for his valuable suggestions and advisement. Also I would like to express my appreciation to Prof. Raymond E. Kramer, the department chairman, and Prof. Samuel J. Skarote for their valuable time in reviewing my thesis.

TABLE OF CONTENTS

	PAGE
ABSTRACT	ii
ACKNOWLEDGEMENTS	iv
TABLE OF CONTENTS	v
CHAPTER	
I. INTRODUCTION	1
II. THE CRYSTALLIZATION PROCESS	4
III. GROWING CRYSTALS	9
Preparing a Saturated Solution	10
Growing Crystal Seeds	15
Seeding the Solution in the Tank	18
Growing Crystals	20
Harvesting Crystals	23
IV. OPTICAL ABSORPTION MEASUREMENTS	28
Preparing the Sample	28
Optical Measurements	31
V. SUMMARY AND DISCUSSION	38
BIBLIOGRAPHY	42
REFERENCES	43

CHAPTER I

INTRODUCTION

The purpose of this study is to grow, from liquid solution, very pure crystals and seek linear dichroism in the alpha-hexahydrate of nickel sulfate crystals in ultraviolet, visible, and infrared regions.

There are many kinds of crystals been grown by various industrial companies. But most of these crystals are contaminated by some other chemicals, while those which are really pure are often very expensive. So we decided that we would grow the pure crystals which we needed ourselves. Since our intention is to find the dichroism of a crystal, we found that the alpha-hexahydrate of nickel sulfate crystals are very suitable for our purpose.

Nickel sulfate hexahydrate, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, forms tetragonal crystals. Their unit, containing four molecules, has the dimensions: $a = 6.80 \text{ \AA}$, $c = 18.3 \text{ \AA}$. The space group can be one or the other of the enantiomorphic pair D_4^4 or D_4^8 . The stacking of the atoms is an equal number of $\text{Ni}(\text{H}_2\text{O})_6$ octahedra and SO_4 tetrahedra; their shapes are, however, so different one from the other that the resultant grouping does not approximate a simple structure. Within the $\text{Ni}(\text{H}_2\text{O})_6$ octahedra $\text{Ni}-\text{H}_2\text{O} = 2.02$ and 2.04 \AA , the sulfate tetrahedra have their usual shape with $\text{S}-\text{O} = 1.52 \text{ \AA}$. Contact between

the two groups is through O-H₂O separations that range from 2.69 Å upwards. Also nickel (Ni) is in a lower symmetry site with only two-fold symmetry while nickel sulfate hexahydrate has a four-fold crystal symmetry. Thus it is expected that when the nickel sulfate hexahydrate crystal is exposed to the light sources from two orthogonal directions, of which one of them is along the optic axis of the crystal, the nickel ions located at a low symmetry site, after absorbing some light energy, may alter the light transmitting characteristics of the crystal in the ultraviolet and visible wavelength ranges.^{1,2} Furthermore, it is found that crystalline nickel sulfate hexahydrate can be grown very easily from liquid solution³ by utilizing Holden's Rotary Crystallizer.⁴

Nickel sulfate crystallizes from solution at room temperature (30 deg C) as NiSO₄·7H₂O in the orthorhombic system. At about 35 deg C it crystallizes as NiSO₄·6H₂O in

¹ R. Trehin. "Etude Esperimentale de la Bande d'Absorption de l'Ion Ni⁺⁺ Dans le Proche Ultra-Violet pour les Solutions Aqueuses de Sulfate de Nickel Pleochroisme des Cristaux SO₄Ni, 6OH² (Quadratique) et SO₄Ni, 7OH² (Orthorhombique)," Annalen Der Physik, XX (1945), 372-90.

² C. Furlani, "Absorptionsspektren Magnetisch Normaler Ni (II)-Komplexe," Zeitschrift Fur Physikalisch-Chemie (Frankfurter), X (1957), 291-305.

³ Alan Holden and Phylis Singer, Crystals and Crystal Growing (Garden City, N. Y.: Anchor Books Doubleday & Company, Inc., 1960) p. 112.

⁴ R. A. Laudise, The Growth of Single Crystals (Englewood Cliffs, N. J.: Prentice-Hall, Inc., 1970), p. 264.

the tetragonal system, while at about 60 deg C it crystallizes as $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ but in the monoclinic system. So far circular dichroism and absorption of crystalline nickel sulfate have been studied.^{5,6} This thesis is to report the details of an investigation with the tetragonal crystals using Perkin-Elmer Model 202 Ultraviolet-Visible and Model 457 Infrared Spectrophotometers.

⁵ L. R. Ingersoll, P. Rudnick, F. G. Slack, and N. Underwood, "Optical Activity, Circular Dichroism, and Absorption of Crystalline Nickel Sulfate," Physical Review, LVII (1940), 1145-53.

⁶ C. Furlani, "Absorptionsspektren Magnetisch Normaler Ni (II)-Complexe," Zeitschrift Fur Physikalisch-Chemie (Frankfurter), X (1957), 291-305.

- - - - -

CHAPTER II

THE CRYSTALLIZATION PROCESS

Some salts grow from water solution into large crystals relatively easily; others tend to form many small crystals. The paperback book, Crystals and Crystal Growing describes two simple methods for growing, without specialized equipment, single crystals of some salts that readily form large crystals.⁷

In one of those methods, the salt to be crystallized is dissolved in water in an amount sufficient to saturate the water at a temperature higher than that of the room. A small seed crystal is hung in the solution, the container is sealed, and the solution is allowed to cool to room temperature. Since the solution was saturated at a higher temperature, it is holding at room temperature more salt than it can stably retain. In other words, the solution that was saturated with salt at the higher temperature becomes supersaturated at the lower temperature. The extra salt slowly deposits on the seed, growing it into a larger crystal.

In the other simple method, the solution is made saturated at room temperature instead of at a higher temperature. A seed is hung in it, and the solution, instead of

⁷Holden and Singer, Crystal Growing, pp. 93-107.

being sealed, is left open to the surrounding atmosphere and allowed to evaporate. Evaporation slowly reduces the amount of solvent that is holding the salt, and the solution again becomes supersaturated and deposits salt on the seed.

Notice that both methods provide the indispensable condition for growing a crystal from solution: supersaturation. In the first case, the supersaturation is provided abruptly, when the solution is cooled; in the second case, the supersaturation is provided gradually, as the solvent evaporates. Clearly, the second method offers the advantage that the material for crystallization is made available at a rate more nearly approximating the rate at which the growing crystal withdraws that material. But evaporation takes place at the surface of the solution, and thus the supersaturation is highest where spurious seeds, entering from outside, may gain a foothold.

Furthermore, both methods suffer from two other difficulties: (1) Unless these methods are used in a room whose temperature is controlled, variations in the temperature of the solution will cause uncontrolled variations in its supersaturation. (2) Both methods leave the solution uncirculated, and differences in supersaturation can accumulate in it that disturb the regular growth of the crystal more and more as the crystal becomes larger.

The crystal-growing apparatus used in this experiment, the Rotary Crystallizer, avoids these two difficulties by controlling the temperature of the solution directly, and

by moving the crystals through the solution continuously. Furthermore, it combines the advantages of both of the simpler methods, sealing the solution against evaporation and the entry of spurious seeds, and by cooling the solution slowly so that material for crystallization is made available gradually.

As shown in Figure 1,⁸ if one plants a crystal seed in the nickel sulfate solution before it is supersaturated as shown at point A, salt will be deposited on the seed as soon as the temperature of the solution is reduced to point B so that the solution becomes supersaturated. This deposit will continue until all excess salt is evenly deposited on the seed and the solution again reaches its more stable state of saturation. The seed, or crystal, will have grown from the added deposit of salt upon its surface; the solution will have lost excess solute and assumed the state of saturation at point C. Reducing the temperature further to point D will again bring the solution to supersaturation, and again the crystal will grow from the deposit of excess solute by the supersaturated solution.

This process may be sustained until the solution reaches 35 deg C. This, as shown in Figure 1, will avoid growth of the heptahydrate, which takes place more easily at temperature below 35 deg C.

⁸Artherton Seidell, Solubilities of Inorganic and Metal-Organic Compounds (4th ed.: Princeton, N. J. Van Nostrand, 1958), p. 453.

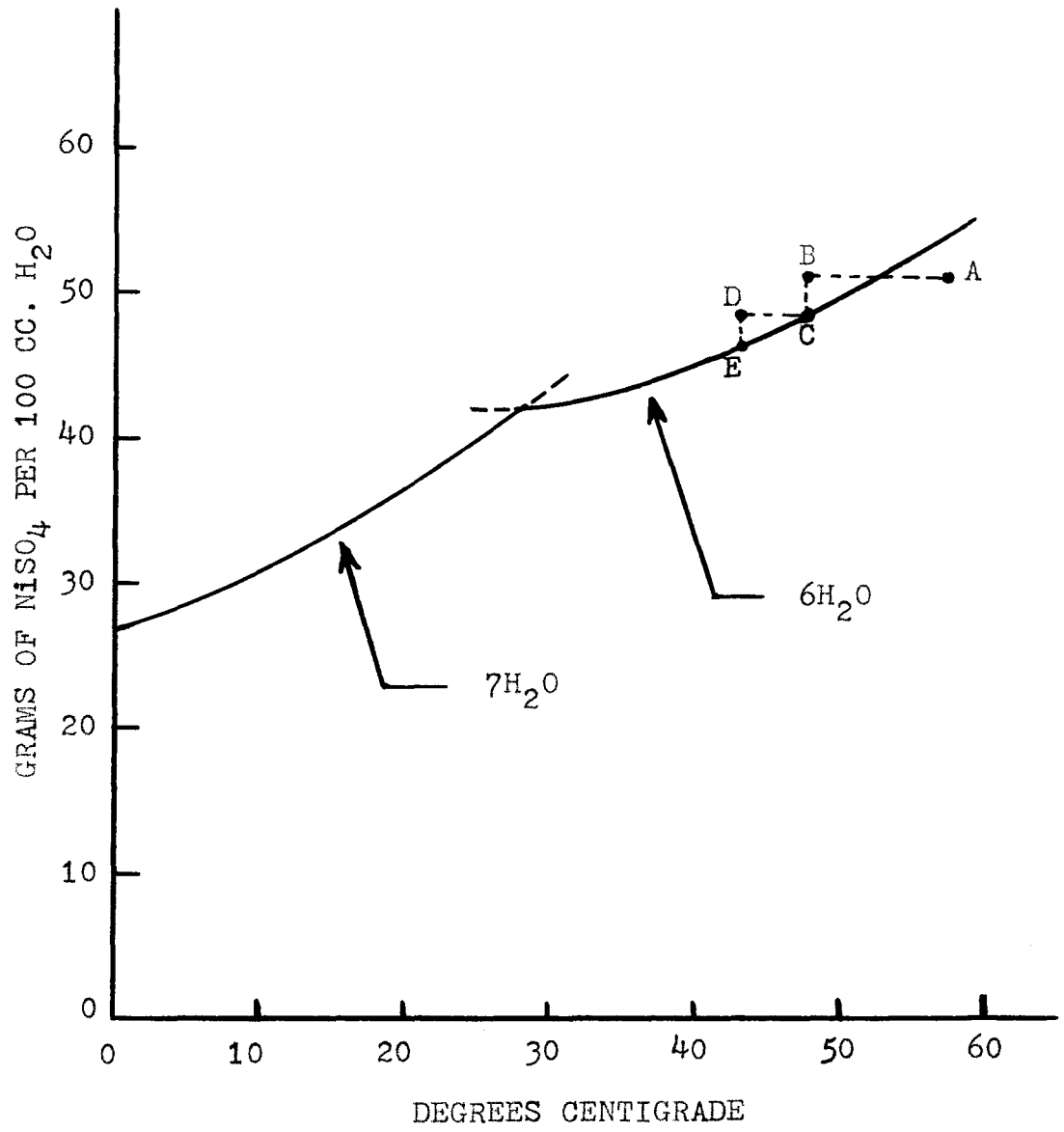


Fig. 1.--Solubility of nickel sulfate.

The rate of crystal growth depends upon the rate at which the temperature of the solution is reduced. To grow nearly perfect crystals the growth rate should be very slow. After the crystal has grown to the desired size, it can be removed from the apparatus for use in further experiments or display. The solution may be reseeded for the growing of more crystals, or stored for future use.

- - - - -

CHAPTER III

GROWING CRYSTALS

The crystalline process is carried out in such a way that the point on the solubility curve, which is temperature dependent, moves into the metastable solution region, when the temperature is lowered, near the saturation curve in the direction of lower solubility as shown in Figure 1. The apparatus is Holden's Rotary Crystallizer which can be purchased, completely assembled, from the Dependable Printed Circuit Corp., Wayne, N. J. The chemical is fine crystals reagent of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, A. C. S. grade, whose maximum impurities are shown in Table 1, and can be purchased from Matheson Coleman & Bell Manufacturing Chemists, Norwood (Cincinnati), Ohio.

Since nickel sulfate will grow into crystals of two distinctly different forms, nickel sulfate heptahydrate ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$) and nickel sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), certain precautions must be taken to insure the growth of the hexahydrate desired. These are: (1) The solution must be saturated at the starting temperature for the hexahydrate to be produced because the solubility is different for the two hydrates. (2) The solution must be seeded with crystals of the same hydrate as the crystals to be produced, i.e., hexahydrate crystals. (3) The temperature range through

TABLE 1
 MAXIMUM IMPURITIES OF $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ USED

Impurities	Maximum Contents
Chloride (as Cl)	0.001 %
Cobalt & Manganese (as Co)	0.003 %
Copper	0.005 %
Insoluble Matter	0.005 %
Iron (Fe)	0.001 %
Nitrogen Compounds (as N)	0.002 %
Substances not pptd by $(\text{NH}_4)_2\text{S}$	0.100 %

which crystal growth of the hexahydrate takes place should be confined to the limits of 35 deg C and 50 deg C. This will help avoid growth of the heptahydrate, which takes place more easily at temperature lower than 35 deg C.

Crystals of two types can be identified by their shape, color, and properties. Nickel sulfate hexahydrate belongs to the tetragonal system, is blue-green in color, does not dehydrate easily, and has excellent cleavage properties. The plane of cleavage is perpendicular to its axis of four-fold symmetry. Nickel sulfate heptahydrate belongs to the orthorhombic system. It is yellow-green in color, and dehydrates readily.

Preparing a Saturated Solution

The first step of growing crystals is to make a solution that is saturated at the temperature at which the crystals will be growing. To prepare a solution for the crystallization of nickel sulfate hexahydrate use a propor-

tion of 257 grams (9 ounces) of nickel sulfate hexahydrate for each cup (237 cc.) of distilled water. The saturation temperature of a solution made from these quantities will be approximately 45 deg C.

Heat three liters of distilled water in a 4-liter beaker (or equivalent mixing container), which is covered with a lid, over a hot plate or a burner to a temperature of about 60 deg C. After the water has come to the temperature specified, add, a little at a time, 3255.4 grams (approximately 7.2 pounds) of nickel sulfate hexahydrate. Agitate the solute constantly with a stirring rod until all solute has dissolved to prevent a temperature stress which will occur at the walls of the tank and, consequently, to prevent the container from breaking. Meanwhile keep the lid on the beaker between stirrings to reduce loss of water by evaporation from the solution.

After all the salt has dissolved in the water, the solution is an unsaturated solution. As this solution cools, it will become saturated and then supersaturated because of the change of salt solubility that accompanies the change in temperature. The temperature at which the solution is saturated is then determined; it is near this point that seeds will be planted in the solution and crystals will start to grow. Errors in the published data on the saturation temperature, as well as errors in weighing and measuring the amount of the solvent, the loss of the solvent during heating are all factors which may alter the sa-

turation temperature of the solution at the moment of pouring into the crystallizer from the expected value. It can be tested if a solution is unsaturated, saturated, or supersaturated by hanging a test crystal in the solution and observing whether it dissolves or grows. Test crystals are obtained by allowing some of the solution to cool and crystallize in a separate container. In this case, imperfections are not important.

If the test crystal dissolves, it loses material to the solution immediately surrounding it, thus indicating that the solution is unsaturated. The part of solution that gains this salt is made more dense than the remaining solution, and it therefore flows downward from the crystal toward the bottom of the container. The density current can be seen if it is looked into the region within the tank at the lower edges of the crystal against some source of light. It looks as though a heavy viscous fluid were flowing from the crystal through the solution to the bottom of the tank. If this density current is not seen, it probably means the solution is saturated, since the test crystal will neither dissolve nor grow in a solution at this state. And, if the density current is rising from the crystal, it means the solution is supersaturated. When the solution is in this state, the test crystal will grow, because of deposits of excess salt from the solution onto its surfaces. The part of the solution thus depleted at the surface of the crystal is less dense than the remainder of the solution in the

tank and will rise visibly from the crystal.

The color of the salt solution of nickel sulfate hexahydrate is deep blue-green in which these density currents are not so readily seen. In this case, the state of the solution may be approximated if a test crystal is hung in the solution and any change in its shape is observed. Inspecting the corners of this crystal will be able to tell whether it is dissolving or growing. If it is dissolving, the corners will quickly get round; if it is growing, the corners of the crystal will become very sharp.

After the saturation temperature has been determined (in our case, it is found to be about 45 deg C), warm the solution to a few degrees above the assumed point of saturation and pour it into the growing tank of the Rotary Crystallizer, filling the tank to an inch or two below the brim. Pour some of the remainder of the solution into the seed-growing bowls or small glasses, and allow it to cool slowly for the production of seed crystals. Place the tank on its base support of the Rotary Crystallizer and cover it with the lid. The thermoregulator is then electrically connected to the temperature control circuit of the Rotary Crystallizer. Next, turn on the apparatus, bring the solution to its saturation temperature and set the thermoregulator, with the control magnet, to the point at which the incandescent heater of the Rotary Crystallizer just goes off, then lock the thermoregulator in place. The motor of the Rotary Crystallizer should not be turned on at this

stage.

The solution is left in the growing tank under temperature control for a few days and observed whether or not crystals form and grow in the bottom of the tank. If no crystals form, add a few grains of the salt to the solution and reduce the solution temperature a degree or so with the thermoregulator. By letting the solution stand in this way, it can be assured that the solution will reach saturation exactly at the starting temperature set on the thermoregulator. Scrap crystals that grow in the tank during this period will take salt from solution only if the solution is supersaturated; as they grow, the solution is reduced to saturation. Once the solution becomes saturated, scrap crystals will stop growing and the solution can be stored under temperature control in its starting state.

As a precaution one should not let the scrap crystals build up at the bottom of the growing tank to the extent that they entirely insulate the bottom surface of the tank from solution. If this should happen, the solution will not acquire the heat applied to the tank with the incandescent heater, and effective temperature control of the solution will no longer be possible. Moreover, a temperature stress will occur at the walls of the tank, which might cause it to crack. If scrap-crystal growth does become excessive, temporarily transfer the solution to another container, clean the tank of waste crystals, and then resume stabilizing the solution at saturation.

Growing Crystal Seeds

Crystal seeds are merely small single crystals. The valuable ones are those that can be harvested from a solution before they become imperfect. These seeds are used to start the formation of larger crystals in the Rotary Crystallizer. Any fragment of the solid, no matter how tiny, is a potential seed. But in order to be conveniently suspended by a thread to the crystal support rod of the Rotary Crystallizer, a seed must be $1/8$ to $1/4$ inch long. Furthermore, it must be a single crystal so that the crystal growing from it will also be single.

To grow seeds one must first start with a solution of the salt to be crystallized. The excess solution prepared in the foregoing procedure should be adequate for seed formation. However, if there is not enough left, one can make a little more in the same way.

When the solution becomes supersaturated, crystals will usually form spontaneously as excess salt comes out of solution. If these crystals are allowed to grow for a while, they will reach a size large enough for convenient handling. As the seeds are growing, they should be inspected from time to time to be sure that potentially good seeds are not being interfered with by other crystals. When useful crystal seeds have grown, about $1/8$ to $1/4$ inch long between opposite faces, they are removed from the solution with tweezers and dried carefully with facial tissue or a soft cloth.

These crystals seeds are then inspected for clarity, symmetry, singularity, and size. The best crystals are stored in a labelled and well-sealed vial.

Seeds may also be prepared by allowing a solution that is saturated at room temperature to stand exposed to the atmosphere in a small glass container. As solvent evaporation proceeds, the solution will supersaturate and seeds will form.

Since it is the tetragonal nickel sulfate crystals which we are interested in, the solution used for growing seeds must be kept in an oven, which has a thermoregulator, so that the temperature of the solution and its surrounding air can be kept between the temperature limits of 35 deg C and 50 deg C during the entire seed-growing process.

The ease with which one can grow seeds depends largely upon the material being crystallized. For example, some solutions can hold excess solute while they become more supersaturated. In this case seeds will not form spontaneously with ease. If a highly supersaturated solution of this sort is suddenly disturbed, the salt will be urged out of the solution. Solute then crystallizes so rapidly that useful seeds can not form. This may be overcome by placing a few grains of solid solute into the seed-producing liquid at the very beginning of the process. Thus the solution will not be allowed to store solute and go further and further into supersaturation. A bit of residue that remains from the evaporation of a drop of the solution may also be

used, in lieu of solute grains, to begin the growth of seeds.

The rate at which seeds grow is most important. If a solution that is saturated at a rather high temperature is allowed to cool rapidly to room temperature, crystallization may occur at a rate too rapid for good seed formation. In this case the remedy is to dilute the solution with added solvent, so that the saturation point is brought closer to room temperature.

When working with material whose crystals break apart or cleave well, such as nickel sulfate hexahydrate whose crystals cleave beautifully along the plane which is perpendicular to its axis of four-fold symmetry, seeds may be made readily from imperfect crystals by cleaving away the imperfections. A single good seed of such a material may also be sliced up and each slice used as a seed.

When the harvested seeds are examined, it may be noticed that one face of each of these little crystals is slightly concave. It is the face that rested on the bottom of the glass. Not much solution is able to get under such a face to make it grow. But slight vibrations of the glass let a tiny amount of liquid under the edges of the crystals, and those edges slowly grow until finally the hollow left at the center of the face becomes deep enough to be noticeable. But this hollow will have little effect upon the quality of the seed as a starting element for the experiments.

Seeding the Solution in the Tank

The first step in seeding the Rotary Crystallizer is to fasten the seeds to the crystal support rods that are attached to the stirring shaft. Double over a short length of white cotton thread and pass it through a piece of plastic tubing that has been cut to the length of the support rod. The thread should protrude from the tubing as a loop at one end and two tails at the other.

Slide the tubing and the thread inside it completely over one of the crystal support rods. Select a crystal seed from the supply vial and place it in the thread loop. Hold the seed in place with fingers and pull the tails of the thread until the seed is firmly secured at the end of the rod. Then cut off the loose ends of the thread with a razor blade. It will be helpful to clamp the stirring rod in some fixture while these manipulations are being performed because one must use both hands to fasten the seed crystals in place. Repeat this procedure for the other three support rods and then set the assembly aside until one is ready to plant the seeds in the solution.

Then pour the saturated solution from the tank into a 4-liter beaker so that the tank can be cleaned of all waste crystals that have formed. Immediately heat the solution to about 5 deg C above what its temperature had been in the tank. In being transferred, the solution will have cooled by giving up heat to the new container. This cooling

can result in undesired crystallization from solution. The beaker should be covered with a pyrex watch glass, or clean plastic wrap, during this operation to minimize solvent evaporation, which would upset the proportion of solvent to solute.

Remove any waste crystals from the tank and allow them to dry. They can then be stored in a clean, sealed container and later reused to prepare a new solution. Thoroughly wash the tank, lid and other parts of the apparatus that have been in contact with the solution. Affix the stirring shaft and seeded crystal-support rod assemble to the motor shaft of the Rotary Crystallizer and lock it in place.

Then, pour the solution from the beaker back into the tank. Allow it to cool, monitoring its temperature with the thermometer as it does so. When the solution reaches a temperature of from 1 deg C to 1.5 deg C above its saturation temperature, place the tank back on the heater base and set the lid on top of the tank, immersing the seeds in the solution. Turn on the temperature control system, but do not turn on the motor.

As the solution cools to its saturation temperature, all minute solute particles that might act as seeds for waste crystals will dissolve. The presence of these seeds is practically inevitable and their elimination is essential. Just as these particles dissolve in the cooling solution, so will these specially selected and planted seeds.

However, these seeds are large, and they will only be partially lost to the solution before they begin to grow. Occasionally one or two of these seeds will fall out of the thread loops holding them and drop to the bottom of the tank. This happens if the solution is too far from the state of saturation. If a seed does drop off, the solution should be reseeded.

When the solution reaches saturation, we set the thermoregulator into operation. To begin growth of the seeds into large single crystals, reduce the temperature setting on the thermoregulator 0.25 deg C by turning the control magnet. This will allow the solution to cool down from saturation and become slightly supersaturated. Turn on the motor of the Rotary Crystallizer, and the crystals will begin to circulate through the solution. The seed crystals will begin to grow, as will be most evident in one day's time. Leave the apparatus undisturbed until then.

Growing Crystals

The day after seeding the solution, the crystals should have grown partially, or completely, around the thread loops that hold them in place. If the crystals have grown much larger, either the solution saturation point was not determined correctly, or the temperature-regulation system had failed. Crystals must not grow too rapidly if they are to retain a high degree of perfection. If, on the other hand, the crystals have disappeared altogether, the solution

must have been too far into unsaturated state, and the tank will have to be seeded again.

If all has gone well, continuing the growth of the seeds to maturity requires only successive reduction of the solution temperature. Reduce the thermoregulator setting another 0.25 deg C and wait a day to see how crystal growth proceeds. Continue to reduce the temperature in such small increments each day for an over-all period of several weeks until the crystals have grown to the desired size.

This amount of daily temperature reduction is only an average figure; the optimum will vary with the material been used. The best growth rate and the best rate of temperature reduction are to encourage the crystals to grow at a more rapid rate when they are small than when they are large.

As shown in Figure 2, crystal perfection is inversely proportional to the rate of cooling. So it is very im-

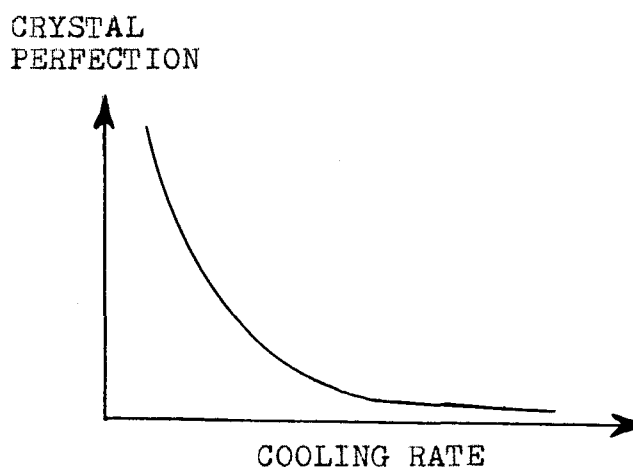


Fig. 2.--Crystal perfection as a function of cooling rate.

portant to determine the correct rate of cooling during growth. This is a difficult task and is usually approached by the trial and error method. For example, we started with a supercooling by 0.25 deg C. It was found that the growth was satisfactory. After 24 hours, the temperature was reduced by 0.25 deg C. Everything was still in order. After the next 24 hours, the temperature was reduced by a further 0.25 deg C. Everything was still all right. So another 0.25 deg C was reduced and so on until toward the end of one week, it was observed some cracks within some of the crystals. Since one of the reasons of the appearance of cracks in crystals is too great a drop in temperature, the temperature setting on the thermoregulator was reduced $1/8$ deg C at every 24 hours interval in the next run. But crystals still cracked. So the next run, the temperature setting was reduced at the rate of $1/16$ deg C per 24 hours interval. It was found that at this rate of reduction in temperature, we were able to grow better crystals. It becomes clear that the trial and error method of searching for optimum growth conditions may take months. For a crystal with a simple geometrical shape, one can use a ruler to measure externally the approximate dimensions of the crystal and weigh its weight. One can then calculate roughly the actual saturation temperature under given growth conditions. Using such a calculation, one can deduce how far one can reduce the temperature in the crystallizer.

Harvesting Crystals

The crystallization process may be regarded as complete after 24 hours from the last reduction of temperature. Then, the crystals are extracted from the crystallizer. Certain precautions must be observed in removing crystals from the solution in which they have grown. The crystals are quite fragile and must not be suddenly exposed to a radically different temperature. If they are removed from the solution and allow to cool rapidly to room temperature, they are likely to crack. One can avoid this by transferring the crystals to an empty container that provides an environment of the same temperature as their solution bath. In this new container they can cool slowly and thus be kept from breaking.

To do this, obtain a container of the same size as the growing tank. Fill a sink with water of the same temperature as that of the growing solution. Place the new container in the water-filled sink. (One may need to put ballast at the bottom of the harvesting vessel to keep it from floating.) Turn off the Rotary Crystallizer and disconnect the motor power line. Then remove the thermoregulator from the tank lid.

Quickly transfer the tank lid and its crystal-holding assembly from the growing tank to the cooling tank in the sink. In a few hours, when the temperature of the water bath in the sink has reached room temperature, the crystals

may be taken from the cooling tank. They should then be removed from the support rods, and carefully dried immediately with a paper tissue or a soft cloth. These crystals must be handled very carefully, especially if one intends to use them in the optical experiments such as the one described later, for they are soluble in water, and their clear, plane surfaces will be easily etched and damaged by the perspiration on one's hands. The best way to store them is to wrap them in a scrap of cloth and put them in a screw-topped jar to keep them from damage in either too dry or too humid air.

The remaining solution can be used to grow more crystals, but an amount of the original substance equal to the weight of these newly grown crystals must be added to it. During long runs, the solvent losses may be considerable. Therefore, after filling the crystallizer, it is necessary to measure the level of the solution and, at the end of a run and after the addition of a new portion of the substance, solvent must be added up to the previous level of the solution. The saturation temperature is determined again and the process is repeated as described above.

Even when very pure substances are used, the repeated growth of crystals from the same solution results in an accumulation of impurities in the solution which, sooner or later, begin to affect the growth and quality of the crystals. It follows that it is necessary to change the solution from time to time.

In this method of growing crystals from solutions, the greatest difficulty is the prevention of the formation of stray crystals. Single or multiple stray crystals may appear quite quickly during the first few hours after the beginning of growth of the main crystal or they may appear in the later stages. In the former case, stray crystals are due to errors in the solution of the correct experiment conditions while in the latter case, they are due to a disturbance in the normal growth process. The main causes of the formation of stray crystals due to incorrect initial conditions are as follows:

- (1) The capture of crystalline dust particles from air during the introduction of seeds into the crystallizer.
- (2) Insufficiently careful washing of the cover, crystal holder, and seed crystals.
- (3) Defects in the seed crystals (cracks and occlusions).
- (4) Insufficient duration of the storage or too low a temperature of the solution after the determination of the saturation temperature by means of a test seed.
- (5) Too high a value of the initial supersaturation, which may be due to the evaporation of the solvent as a result of the poor sealing of the crystallizer during storage before the introduction of the seeds or due to errors in the determination of the saturation temperature.

All these faults can be remedied quite easily, but if a crystal film or floating crystals appear on the surface of the solution in spite of the measures that have been

taken to ensure the correct initial conditions, it follows that the temperature at the beginning of the process should be altered or the apparatus should be modified. If the hermetic seal is satisfactory, the appearance of floating crystals on the surface of the solution is the result of strong supercooling of the surface. This can be prevented either by additional thermal insulation of the crystallizer cover or by special heating of the cover.

Stray crystals may appear several days after the beginning of the growth of a crystal for the following reasons:

(1) The appearance of single crystals, particularly at the same points in the crystallizer in several consecutive runs, indicates cracks or scratches in which residues of the crystal phase may remain even after careful washing. This happens in a crystallizer in which a solution is permitted to dry out: such a crystallizer should be filled with a solvent and left in the filled state for several days before using in the next run.

(2) The formation of many stray crystals usually indicates that the crystallizer is not hermetically sealed.

(3) A disturbance in the normal operation of the drive from the motor, which may shake the crystal holder and fracture the growing crystals attached to it.

(4) Cracks may appear in a crystal and these may emerge on the surface.

(5) The rate of cooling may be too high, resulting in the transition of the solution to the labile state (this is al-

most always preceded by imperfections in a growing crystal, the appearance of inclusions, the skeletal growth of a crystal, etc.).

Naturally, several of these factors may be acting simultaneously and measures to prevent the effect of one of them may not give any perceptible improvement. When stray crystals are already present we can heat the solution to such an extent as to ensure a higher temperature in the lower part of the crystallizer.

- - - - -

CHAPTER IV

OPTICAL ABSORPTION MEASUREMENTS

Preparing the Sample

In a tetragonal crystal, the dielectric permittivity tensor only has two independent components. This means that the crystal has, at most, two distinct light absorption characteristics if they exist. One of them is in the direction of the optic axis of the crystal while the other one is along any of the directions which are perpendicular to the optic axis. The harvested crystal is cut along the two directions described above in the search for possible dichroism or a shift in the absorption band edges.

In nickel sulfate hexahydrate crystals, the family of cleavage planes is perpendicular to the four-fold axis of symmetry. Thus, thin square windows of quite large surface can be obtained by simple cleavage of a crystal block along the basal plane. A thin sharp knife is used for this cleavage; it is placed on in the desired cleavage direction and gently hit with a light hammer. As a rule the piece to be cleaved off should always have about the same thickness as the piece remaining; however, after a little practice this rule need not to be strictly followed. Cuts against the natural cleavage planes must be made with saws; for this fret saws or thin metallised saw blades or diamond cutting

saws are used, sometimes with alcohol or water as lubricant. The cleaved surfaces usually are very fine surfaces for optical measurements. But for those surfaces which do not cleave well or those surfaces which are cut against the natural cleavage planes, they must be polished before they can be used for optical measurements.

Nickel sulfate hexahydrate crystals are considerably soft. This property enables easier finishing and polishing compared with glass, but also causes greater sensitivity towards mechanical action by pressure and scratching, and a lower quality of the final polish. The equipment needed for finishing and polishing is quite simple: one or more glass grinding plates, which can be purchased at any optical firm; abrasive papers of various fineness, grits 2, 1, 0, 00, 000, 0000; abrasive powder of various fineness, aluminum oxide powder grit 600 and gamma micropolish 0.05 micron; a polishing powder of special fineness (jeweller's rouge); polishing clothes, metcloth and microcloth which can be found in metallurgical laboratories; and a suitable non-aqueous liquid as lubricant (kerosene). All these abrasive papers and powders and polishing clothes can be purchased from Buehler Ltd., 2120 Greenwood Avenue, Evanston, Ill. The various types of abrasive powder must be carefully elutriated and if necessary winnowed in order to obtain an even particle size. Great care must be taken that a finer type is not contaminated by a rougher type because even a single large particle will spoil all the previous work.

If the surface in question is not a good quality cleavage surface, it is first rubbed to the approximate thickness wanted with grits 2, 1, and 0 abrasive papers. The grinding process itself is then carried out by placing the component to be polished on the grit 00 abrasive paper and then rubbing the component with a gentle even pressure and small circular or in the form of figure "8" movements gradually over the whole surface of the abrasive paper. This process is repeated with grits 000 and 0000 abrasive papers of increasing fineness until a good flat surface is obtained with the appearance of a ground glass plate and so that after working on both sides the components has the desired thickness. The flatness of the surface is tested by means of mechanical precision instruments or even (after polishing) by optical methods. Further treatment, i.e., polishing, is carried out with the constant use of rubber gloves, or at least finger-stalls, in order to avoid the influence of perspiration on the surface; breathing on the component should also be avoided. For polishing, the process is carried out by placing a little aluminum oxide powder grit 600 on the polishing glass plate, which is covered by a polishing metcloth, with a few drops of kerosene as the lubricant and then rubbing the component to be polished with a gentle even pressure and small circular or in the form of figure "8" movements gradually over the whole surface of the grinding plate (which in time may become hollowed out). This process is repeated with the

gamma micropolish 0.05 micron and the jeweller's rouge until the dull surface gradually vanishes and a smooth near mirror-like surface appears. The final polishing is carried out on the microcloth by dropping a little 95% ethyl alcohol, which is being saturated with nickel sulfate hexahydrate, on it and polishing the component until it is completely dry. The component now is ready for optical measurements.

Optical Measurements

The polished crystal is then mounted in a sample support and put in the sample fixture of Perkin-Elmer Model 202 Ultraviolet-Visible and Model 457 Infrared Spectrophotometers. Its light absorption in the wavelength ranges of ultraviolet, visible, and infrared is studied. It is found that for a sample of 2.53 ± 0.01 mm. thickness, after being treated as described above, and an exposure area of 6 mm., both the A crystal component whose exposed plane is parallel to the optic axis and the C crystal component whose exposed plane is perpendicular to optic axis of the nickel sulfate hexahydrate crystal show nearly complete absorption in the infrared region while in the ultraviolet and visible regions the crystal has two transmitting bands. Since it is the differences in absorption in the "a" and "c" directions we are looking for, the investigation is then emphasized in the light transmitting characteristics of the A and the C crystal components in the ultraviolet and visible wavelength

ranges by utilizing the Ultraviolet-Visible Spectrophotometer.

The Perkin-Elmer Model 202 Ultraviolet-Visible Spectrophotometer is a double-beam instrument designed for laboratory use in quantitative analysis. This instrument, developed as an absorbance-recording spectrophotometer, performs throughout the ultraviolet and visible spectral regions with high resolution.

The Model 202 UV-VIS Spectrophotometer covers two ranges: 190 to 360 millimicrons in the ultraviolet, and 350 to 700 millimicrons in the visible. Two scanning rates, either wavelength range selected can be scanned in two or eight minutes, offer the analyst a choice of either survey or precise spectra recorded on a $8\frac{1}{2}$ x 11-in. paper.

Most ultraviolet recording spectrophotometers are electronic null instruments. That is, they are dependent upon a precision potentiometer to balance the signal produced by different light levels in the two optical channels. In such instruments, the signal is intrinsically proportional to transmittance and therefore, some type of electrical or mechanical component is required to produce the logarithmic (or absorbance) presentation that is required for the solution of most analytical problems.

In an optical null system, the light that is removed from the beam by the sample is balanced by a mechanical light attenuator wedge in the reference beam. The attenuator wedge in the Model 202 is shaped so that the light is

removed logarithmically as the wedge is moved in the beam. Motion of the attenuator is therefore directly proportional to the absorbance of the sample.

Since the taper of the attenuator wedge is logarithmic, the rate of change of transmission is not constant; in fact, it is approximately 30 times greater at one end of the range than it is at the other. Because of this 30 to 1 change in the slope of the attenuator, a similar error of the attenuator, i.e., 0.01 absorbance unit, will produce an electrical error signal 30 times larger at zero absorbance than at 1.5 absorbances. To compensate for this variation in gain, an automatic gain control keeps the output of the multiplier anode constant thereby keeping a constant pen response over a wide range of energy variation.

Two light sources are provided with Model 202: an air-cooled deuterium lamp is for the ultraviolet spectral range, and a ribbon-filament incandescent lamp for the visible range. In either range only the associated lamp is lighted. Range selection is made by rotating the drum until the metal paper holder passes the wavelength indicator. At this point, a switch is actuated which turns on the proper lamp source and control the position of a small mirror. In the VIS range, this mirror reflects radiation from the tungsten source onto the toroidal mirror; in the UV range, the small mirror is removed and the light from the deuterium source falls directly on the toroidal mirror. All the aluminum mirrors are coated with magnesium fluoride to pro-

tect them from atmospheric deterioration. The large amount of available energy results in low stray light even at 190 millimicrons.

In Model 202, the light from either source is dispersed by the monochromator and separated by a rotating chopper into two beams, each beam being interrupted at 26 cps. The sample is placed in one beam (the sample beam) and the air is used as a reference in the second beam. The beams are then recombined on the detector and the resulting signal is amplified. The main 26 cps control signal is then amplified and used to drive a servomotor which moves the attenuator wedge in the reference beam to a position where the intensity in the two beams is equalized. The pen which records the position of the attenuator is also driven by this same servomotor. A 52 cps control signal is also generated by the chopper and is used to control the loop of the servo system. This signal is amplified in the automatic gain control the high voltage across the photomultiplier in such a way as to keep the anode signal constant.

In addition to providing improved performance at short wavelengths, the end-on photomultiplier used in the Model 202 has high sensitivity in the red end of the spectrum and provides good performance out to 700 millimicrons. Furthermore, the application of the end-on photomultiplier design makes the instrument very insensitive to sample cell orientation and other effects that tend to change the beam

position on the detector.

Figure 3 and Figure 4 show that for the crystal component whose surface exposed to the light source is perpendicular to the optic axis of the crystal has total absorption bands in the wavelength ranges of 190 to 195 millimicrons, 350 to 428 millimicrons, and 585 to 700 millimicrons and transmission bands in the wavelength ranges of 195 to 350 millimicrons, 428 to 585 millimicrons with maximum transmission occurs at 310 millimicrons and 490 millimicrons, while for the crystal component whose surface exposed to the light source is parallel to the optic axis of the crystal has total absorption bands in the wavelength ranges of 190 to 195 millimicrons, 352 to 425 millimicrons, and 590 to 700 millimicrons and transmission bands in the wavelength of 195 to 352 millimicrons and 425 to 590 millimicrons with maximum transmission occurs at 305 millimicrons and 490 millimicrons. Furthermore, from these two plots, it is found that the light transmission of both A crystal component and C crystal component are the same except the magnitude of the curves. Apparently, there is no shift in the edges of the absorption bands in the alpha-hexahydrate of nickel sulfate crystals.

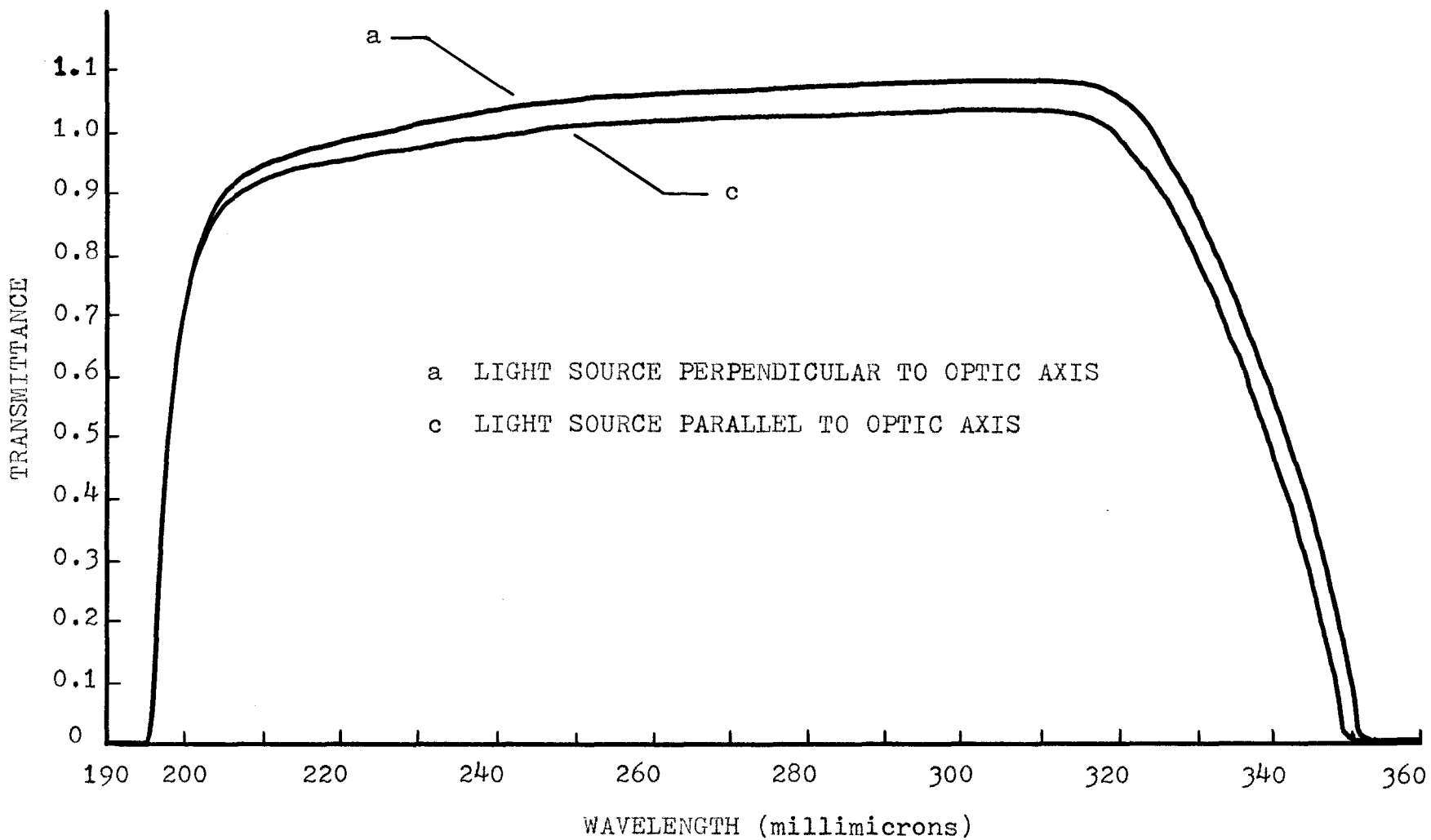


Fig. 3.--Light transmittance characteristics of $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$ crystals in the ultraviolet region. Sample thickness = 2.53 ± 0.01 mm.

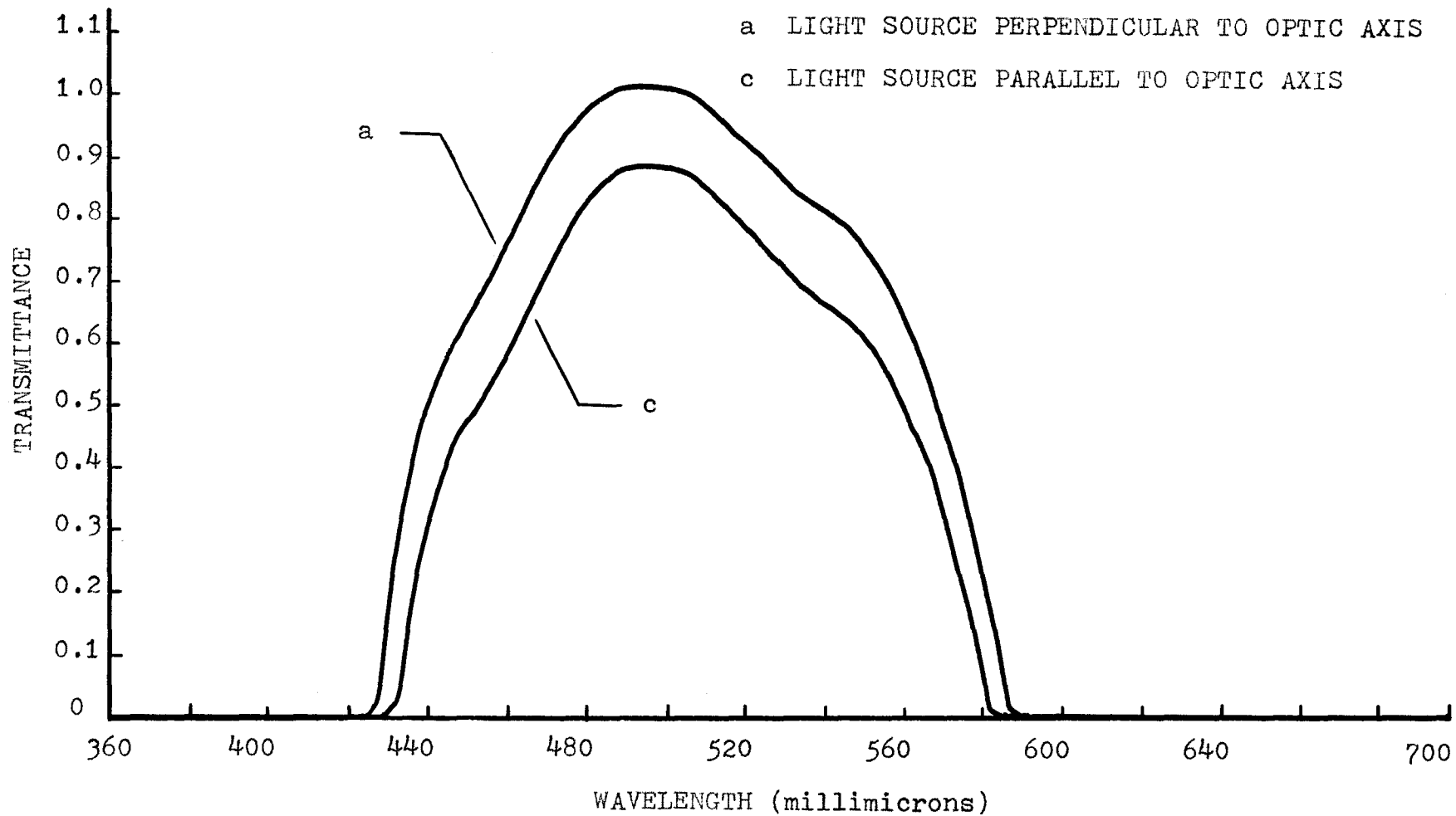


Fig. 4.--Light transmittance characteristics of $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$ crystals in the visible region. Sample thickness = 2.53 ± 0.01 mm.

CHAPTER V

SUMMARY AND DISCUSSION

By comparing this experimental data with the crystal growth data given by Holden and Singer, it is found that both data agree with each other except the saturation temperature. With the same amount of distilled water as a solvent and nickel sulfate hexahydrate as a solute, the saturation temperature of the solution, according to Holden and Singer, will be approximately 50 deg C while in this experiment it was only 45 deg C. The cause of this deviation probably is the difference in the amount of impurities contained in the nickel sulfate hexahydrate chemical used. The nickel salt used by Holden probably contained more impurities than that of used in this experiment. These impurities, in general, tend to decrease the solubility and increase the saturation temperature of the chemical.

From Figure 3 and Figure 4, since the curves for the two crystal components look practically the same, it may be concluded that there is no major shift in the absorption edge in the alpha-hexahydrate of nickel sulfate crystals. Furthermore, it looks safe to conclude that the light transmittance characteristics of the A and C crystal components are exactly the same because the small magnitude difference may be caused by the differences in final polishing, actual

thickness and the spectrophotometer's machine errors.

In Model 202 Ultraviolet-Visible Spectrophotometer, the sources of machine errors are as follows: (1) A wavelength reading on the wavelength scale is different by ± 0.5 millimicron in the UV, and ± 1 millimicron in the VIS, from the wavelength actually being scanned by the instrument. (2) The wavelength readings registered on the wavelength scale are different up to ± 0.3 millimicron in the UV and ± 0.5 millimicron in the VIS from one run to the next. (3) The readings on the absorbance scale, for any fraction of full scale energy, have errors of ± 0.01 A between 0.0 and 0.1 A and $\pm 1\%$ between 1.0 and 1.5 A. (4) Absorbance readings differ by 0.005 A from one run to the next. However, during the measurements, it is found that the instrument has greater errors both in wavelength and absorbance readings than those just described above from one run to the next. Sometimes the fluctuations go as high as 10%, especially in absorbance readings.

The human errors in absorption measurements are as follows: (1) The thickness of A and C crystal components after the final polishing may differ by 0.02 mm. The thicker the sample is, the greater the absorption. (2) The difference in the fineness of the polished surfaces of the A and C crystal components. It is impossible to have exactly the same fineness of final polish on the surfaces of these two crystal components. (3) Because of the lack of enough absorption measuring instrument components,

samples have to be mounded and dismounted from the sample support every time another sample's absorption characteristic is to be measured. During these mounding and dismounting, chances of damaging the fine polished surfaces increases directly proportional to the number of measurements taken. All these human errors can be accounted for the differences in the magnitudes of the transmission curves.

The fact that A and C crystal components were not cut from the same crystal may also be accounted for the deviations.

In this experiment, a major shift in the absorption edge between A and C crystal components was not observed. Apparently, the UV or VIS absorption is not due to Ni^{++} transitions even though the Ni^{++} is located in the low symmetry site. Instead, it is believed due to the $\text{Ni}(\text{H}_2\text{O})_6$ octahedra structure and its vibration states.⁹ Furthermore, the arrangement of $\text{Ni}(\text{H}_2\text{O})_6$ octahedra and SO_4 tetrahedra within the tetragonal $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ structure is in such a way that the absorption characteristics are the same in the two orthogonal directions of which one is along the optic axis of the crystal.¹⁰

⁹C. Furlani, "Ni(II) Komplexe." Zeitschrift fur Physikalisch-Chemie (Frankfurter). X (1957), 291-305.

¹⁰R. Trehin, "Bande d'Absorption de l'ion Ni^{++} " Annalen der Physik, XX (1945), 372-90.

In this experiment, nor was the linear dichroism of nickel sulfate hexahydrate found. The reason might be the sample were too thick to show the detail absorption characteristics of the A and C crystal components. Thus thin film samples which are less than 0.5 mm. thick are recommended for future optical absorption measurements.

It is observed, from Figure 3 and Figure 4, that these transmission curves have very sharp cut off points which make nickel sulfate hexahydrate crystals very good filters in the UV-VIS regions.

BIBLIOGRAPHY

Books

- Holden, Alan and Singer, Phylis. Crystal and Crystal Growing. Garden City, N. Y.: Anchor Books Doubleday & Company, Inc., 1960.
- Laudise, R. A. The Growth of Single Crystals. Englewood Cliffs, N. J.: Prentice-Hall, Inc., 1970.
- Seidell, Artherton. Solubilities of Inorganic and Metal-Organic Compounds. Fourth Edition. Princeton, N. J.: Van Nostrand, 1958.

Articles

- Furlani, C. "Absorptionsspektren Magnetisch Normaler Ni(II) Komplexe." Zeitschrift fur Physikalisch-Chemie (Frankfurter). X (1957), 291-305.
- Ignersoll, L. R. et al. "Optical Activity, Circular Dichroism, and Absorption of Crystalline Nickel Sulfate." Physical Review. LVII (1940), 1145-53.
- Trehin, R. "Etude Esperimentale de la bande d'Absorption de l'Ion Ni⁺⁺ Dans le Proche Ultra-Violet pour les Cristaux SO⁴Ni, 6OH² (Quadratique) et SO⁴Ni, 7OH² (Orthorhombique)," Annalen der Physik, XX (1945), 372-90.

REFERENCES

Books

- Brugel, Werner. An Introduction to Infrared Spectroscopy. New York: John Wiley & Sons Inc., 1962.
- Buerger, Martin Julian. Elementary Crystallography. New York: Wiley, 1956.
- C. R. C. Handbook of Chemistry and Physics. 51st Edition. Cleveland: Chemical Rubber Publishing Company, 1970, p. B-114.
- Gmelin, Leopold. Gmelins Handbuch der Anorganischen Chemie (Ni). Weinheim: Verlag Chemie, 1963, Vol. LVII.
- International Union of Crystallography. International Tables for X-Ray Crystallography. Vol. I, Birmingham, England: Kynoch Press, 1962, p. 426.
- Landolt, Hans Heinrich. Landolt-Bornstein Physikalisch-Chemische Tabellen. Berlin: Springer, 1965.
- Lindsay, P. A. Introduction to Quantum Mechanics for Electrical Engineers. New York: McGraw-Hill Publishing Company Limited, 1967.
- National Bureau of Standards. Selected Values of Chemical Thermodynamic Properties. NBS 500. Washington: Government Printing Office, 1970, Series 1, p. 248; Series 2, p. 690.
- Nye, J. F. Physical Properties of Crystals. Oxford: Oxford University Press, 1957.
- Perkin-Elmer Corp. Perkin-Elmer Model 202 Ultraviolet-Visible Spectrophotometer Operation Manual. Norwalk, Connecticut: Perkin-Elmer Corporation, 1970.
- Wyckoff, Ralph W. G. Crystal Structures. Second Edition, Vol. II. New York: Interscience Publishers, 1963.

Articles

- Brieger, K. "Zum Optischen Verhalten des Kristallwassers," Annalen der Physik, LVII (1918), 287-320.
- Dietz, Ralph W. and Bennett, Jean M. "Bowl Feed Technique for Producing Supersmooth Optical Surfaces," Applied Optics, V (1966), 881-2.
- Hartert, E. "Uber den Einfluss der Bindung des Kristallwassers auf dessen Deformationsschwingung in Ultrarot," Naturwissenschaften, XLIII (1956), 275-6.
- Jacolson, Jacob L. and Nixon, Eugene R. "Polishing of Cesium Halide Windows," Applied Optics, VI (1967), 1583.
- Krishnamurti, D. "Raman Spectra of Nickel Sulfate Crystals," Proceedings, Indian Academy of Sciences, XLIIIA (1955), 77-80.
- Levine, M. A. "Polishing of CsI Windows for Use in the Infrared," Applied Optics, V (1966), 1957.
- Mitzner, bernard M. "Technique for Polishing Silver Chloride Plates," Journal of Optical Society of America, XLVII (1957), 328.
- Slack, F. G., et al, "Magneto-Optical Activity of Crystalline Nickel Sulfate, Alpha-Hexahydrate," Physical Review, LIV (1938), 355-7.
- Smakula, A., et al, "Optical Materials & their Preparation," Applied Optics, III (1964), 323-8.
- Vierling, J., et al, "Improving the Diffracting Properties of LiF Comparison with Graphite," Applied Spectroscopy, XXIII (1969), 342-5.