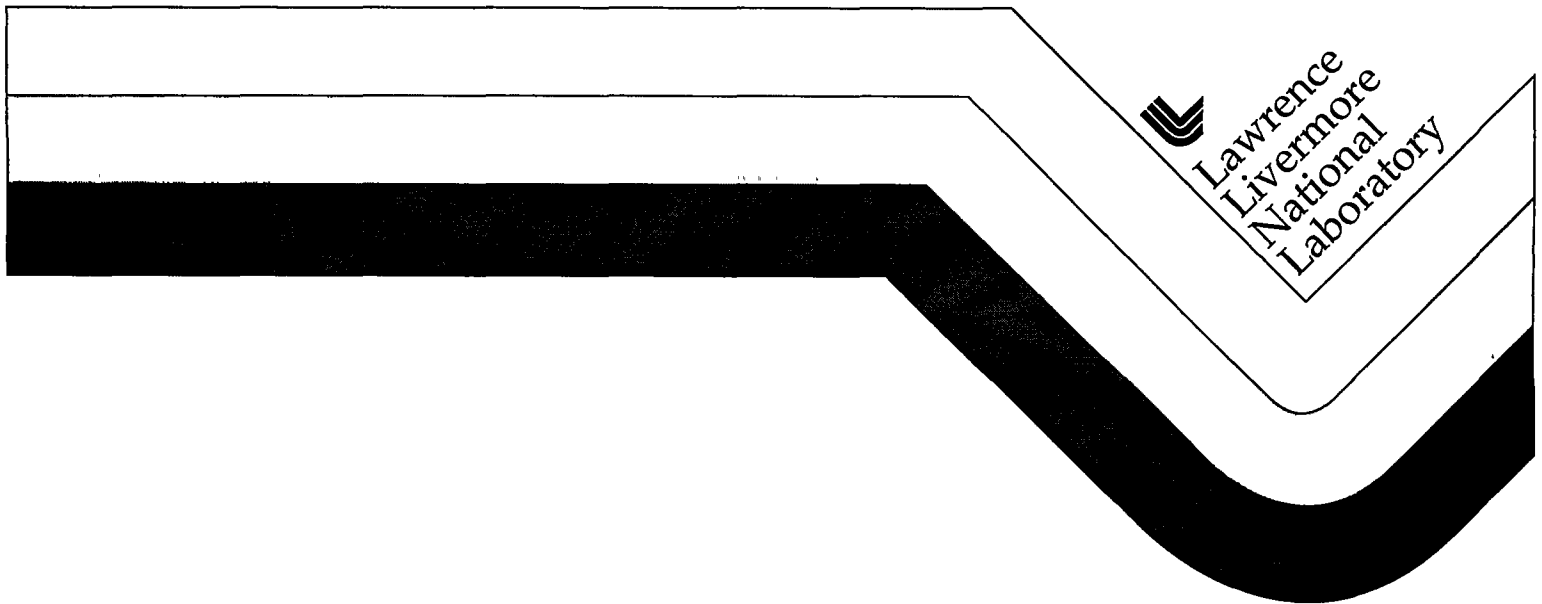


Effect of pH on the Growth of KDP

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TASK AGREEMENT NUMBER B 239783

PROJECT 4

FINAL REPORT

Project Title: Effect of pH on the growth of KDP
Lead Investigator: L.N.Rashkovich
The Technical Representatives of the University of California:
W. Howard Lowdermilk
James J. De Yoreo

Introduction.

The acidity of KDP salt solution is one of the important parameters. This parameter determines a lot of properties of solution, crystallization processes in solution, properties of grown crystals.

An alteration of the KDP salt solution acidity changes its properties such as KDP salt solubility, stability of the KDP solution, solution density, solution viscosity, solution heat capacity, etc. It also changes state of impurities in the solution and characteristics of interaction between growing faces of the crystal and solution impurities. As a result kinetics of crystallization changes, habit and physical properties of the grown crystal change too [1 - 16]. It should be mentioned that investigations in [1 - 16] were done for low rate processes of crystal growth.

Here we report the results of our investigations which have been done for high rate crystal growth processes ($R_z \approx 20$ mm/day).

The results of investigations of solution acidity influence on kinetics of crystallization of prismatic and bipyramidal faces were reported in Progress Report #1.

KDP solutions of nonstoichiometric composition.

As we reported earlier (Progress Report #2), the acidity of KDP salt solution is a function of temperature, KDP salt concentration, and ratio of K_2O/P_2O_5 in the solution. Let's consider these dependencies in detail [17].

Concentration dependencies of the KDP solution acidity at 25°C for different concentrations of phosphoric acid in the solution are shown in Fig.1. It can be seen from Fig.1 that the increase of KDP concentration by each 10g KDP/100g H_2O in interval of KDP concentrations from 15g to 50g KDP/100g H_2O results in decreasing pH by 0.1 units in stoichiometric solution and the increasing pH by 0.15 units in solutions containing 5÷15g H_3PO_4 /100g H_2O .

Temperature dependencies of the KDP solution acidity for different concentrations of KDP salt and phosphoric acid in the solution are shown in Fig.2. These dependencies show that the increase of temperature by each 10 °C in solution of constant concentrations containing 40÷50g KDP/100 g H_2O in interval of temperature 20÷60°C results in the increasing pH less than by 0.1 units in stoichiometric solution and the decreasing pH by 0.1 units in solution with 5g H_3PO_4 /100g H_2O . Similar dependence for saturated solution shows that pH decreases by ~0.07/10°C in stoichiometric solutions and by ~0.14/10°C in solutions with 5g H_3PO_4 /100g H_2O (curves 1 and 2 in Fig.2).

So it is convenient to characterize solution by quantity of acid in solvent because of the alternation of value pH at changing temperature and concentration.

In our work, solutions were prepared so that the temperature of saturating solution was 62°C in all experiments. That was the main difference from previous experiments, the results were reported earlier (Progress Report #2). To prepare solutions for crystal growth in that experiments we fixed a quantity of KDP salt and changed the ratio between quantity of phosphoric acid and quantity of water. As a result the temperature of saturating solution decreases with adding of acid.

To prepare solutions with a fixed temperature of saturation we used data which were placed at our disposal by Yu.O.Punin [17].

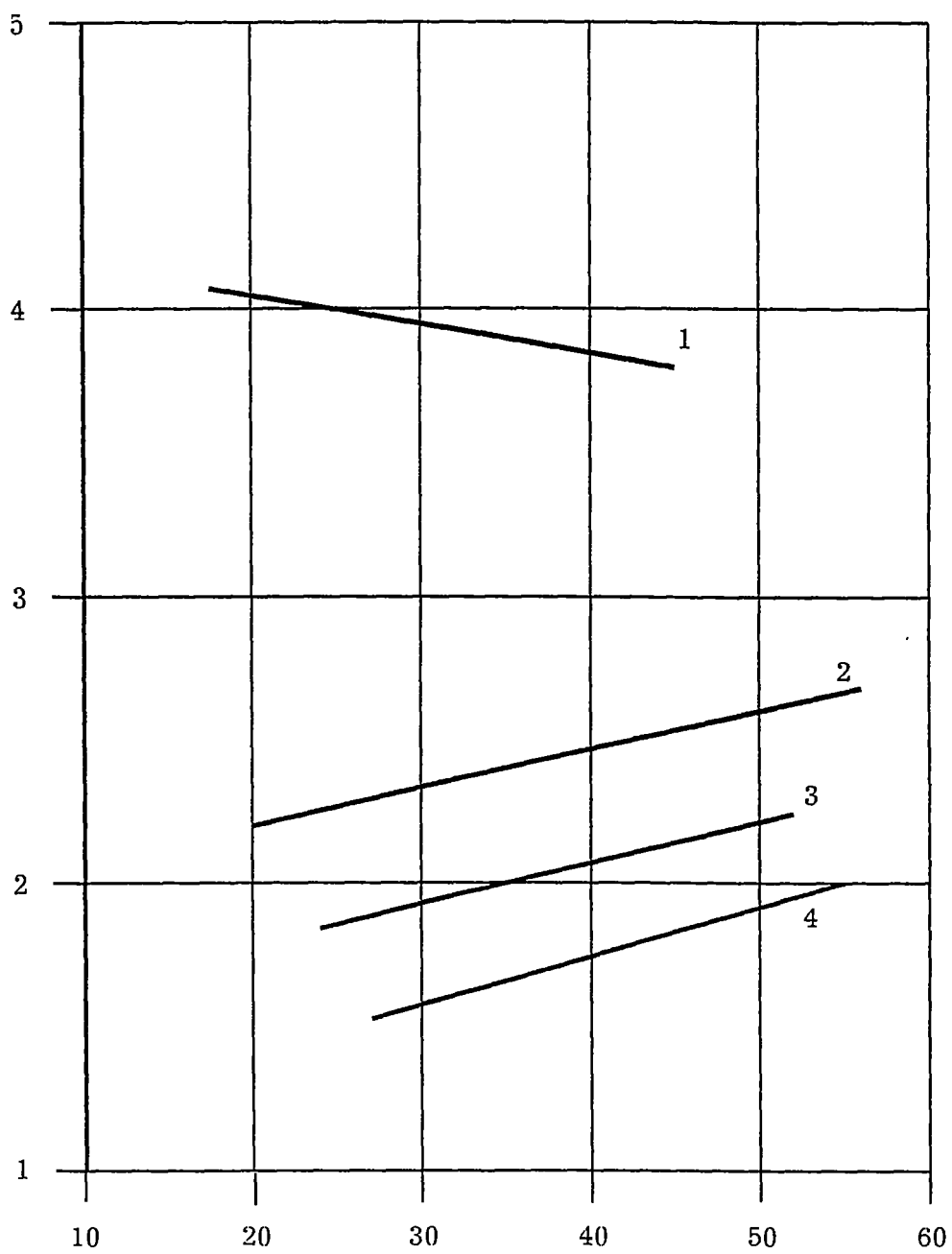


Fig. 1. Effect of KDP salt concentration on pH of KDP solution.
 Phosphoric acid concentration in the solution(g/100 g H₂O):
 1 - 0, 2 - 5, 3 - 10, 4 - 15.

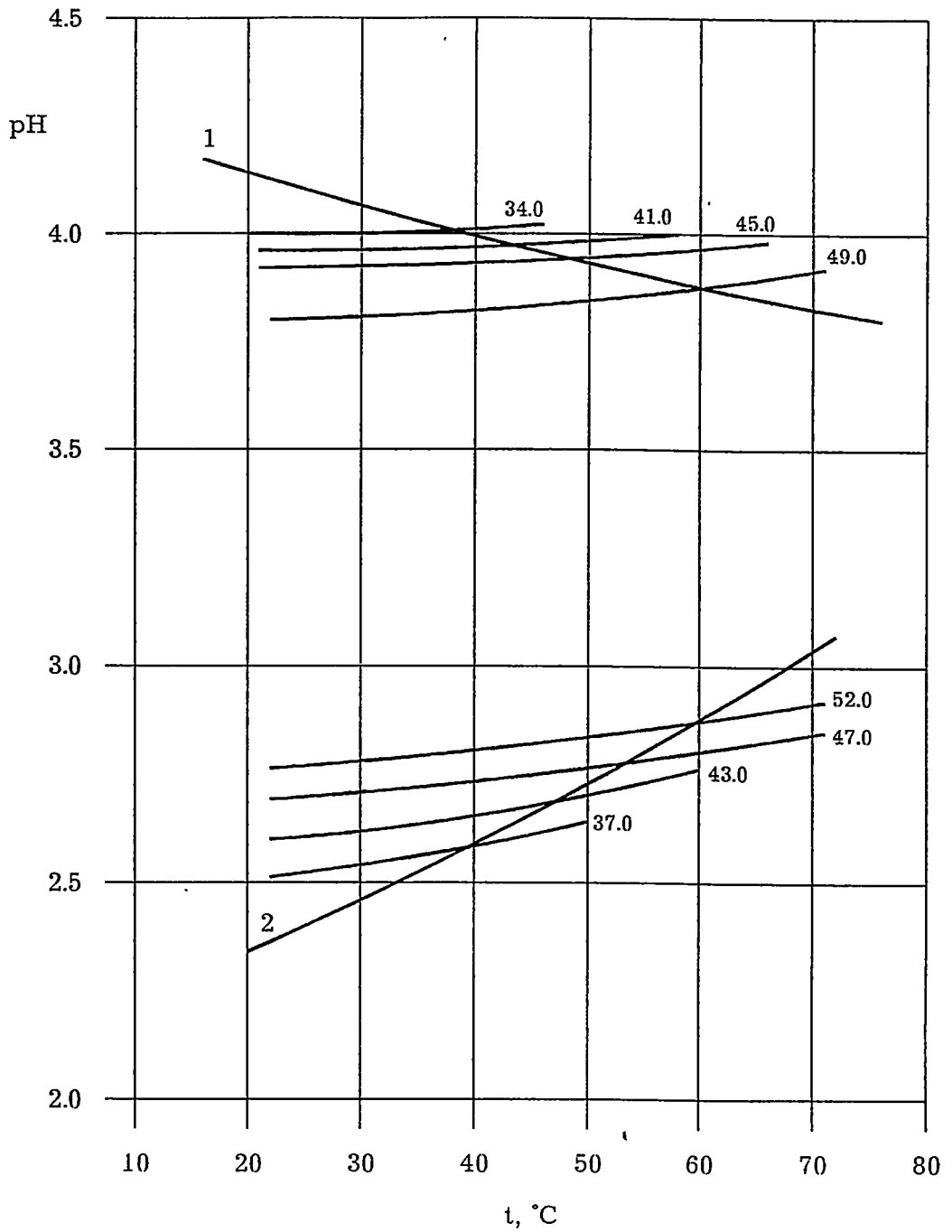


Fig. 2. Effect of temperature on pH of KDP solution.
 KDP salt concentration (g/100 g H₂O) is indicated on the right of curves.
 1 - solubility curve of stoichiometric solution,
 2 - solubility curve of solution with concentration of acid 5 g/100 g H₂O.

Isotherms of solubility of KDP in acid solution are shown in Fig.3. These curves are well approximated by parabolic curves. Our experimental data are in a good agreement with this dependence in the range of phosphoric acid concentrations up to 15 g H₃PO₄/100 g H₂O. But they differ from approximation curves in the solutions with concentration of acid more then 15 g H₃PO₄/100 g H₂O. It can be seen in Fig.4. In this figure dotted lines are the approximation of the "Punin's" curves up to 30 g H₃PO₄/100 g H₂O and solid curve was determined in our experiments.

Crystal growth.

The KDP crystals were grown by standard fast growth method [18,19]. For preparing of the solutions we used KDP salt (Prochem 04054 # 3100), bidistilled water and water solution of phosphoric acid. Composition of the acid is shown in table 1.

Table 1

component	wt. %	component	wt. %
H ₃ PO ₄	>85	Cd	<0.0001
Ca	<0.0015	As	<0.0001
Cr	<0.0002	chlorides	<0.001
Cu	<0.0003	fluorides	<0.0008
Ni	<0.0001	heavy metals	<0.001
Pb	<0.00005	sulfates	<0.03
Zn	<0.0001	organic carbon	<0.004

Temperature of saturation of the KDP salt solution was determined by "trial crystal" method. It was 62±0.1 °C in all experiments. The solution was filtered, overheated up to 80°C and stirred during two days.

First one KDP crystal was grown from the stochiometric solution. This crystal was cut to prepare seeds for following experiments.

In all experiments regeneration of the seed was done under the same supersaturation $\sigma \approx 3\%$. Supersaturation was determined according to the method which was described in Progress Report #2 and from figures 3,4 too. After full regeneration of the seed, temperature of the solution was linear decreased to achieve starting supersaturation and then it was decreased to maintain a rate of crystal growth about $R_z \approx 20$ mm/day (Fig.5). It should be mentioned that absolute supersaturation depends on acidity of the solution feebly (for the same overcooling), but the relative supersaturation depends on it because of strong dependence of KDP solubility from solution acidity. So the rate of temperature decreasing should be higher in acid solution to maintain the same supersaturation. When the temperature of solution decreased to $\approx 48^\circ\text{C}$ the solution was poured off and crystal was cooled to room temperature.

We have grew crystals from next solutions:

Table 2

#exp.	1	2	3	4	5	6	7	8	9
C(gH ₃ PO ₄ /100gH ₂ O)	0	1.6	5.03	10.2	15.08	20.02	22.3	25.0	29.9

An average growth rate along Z axis was 16÷18 mm/day for all crystals. The growth rate in X and Y directions was really the same in all experiments.

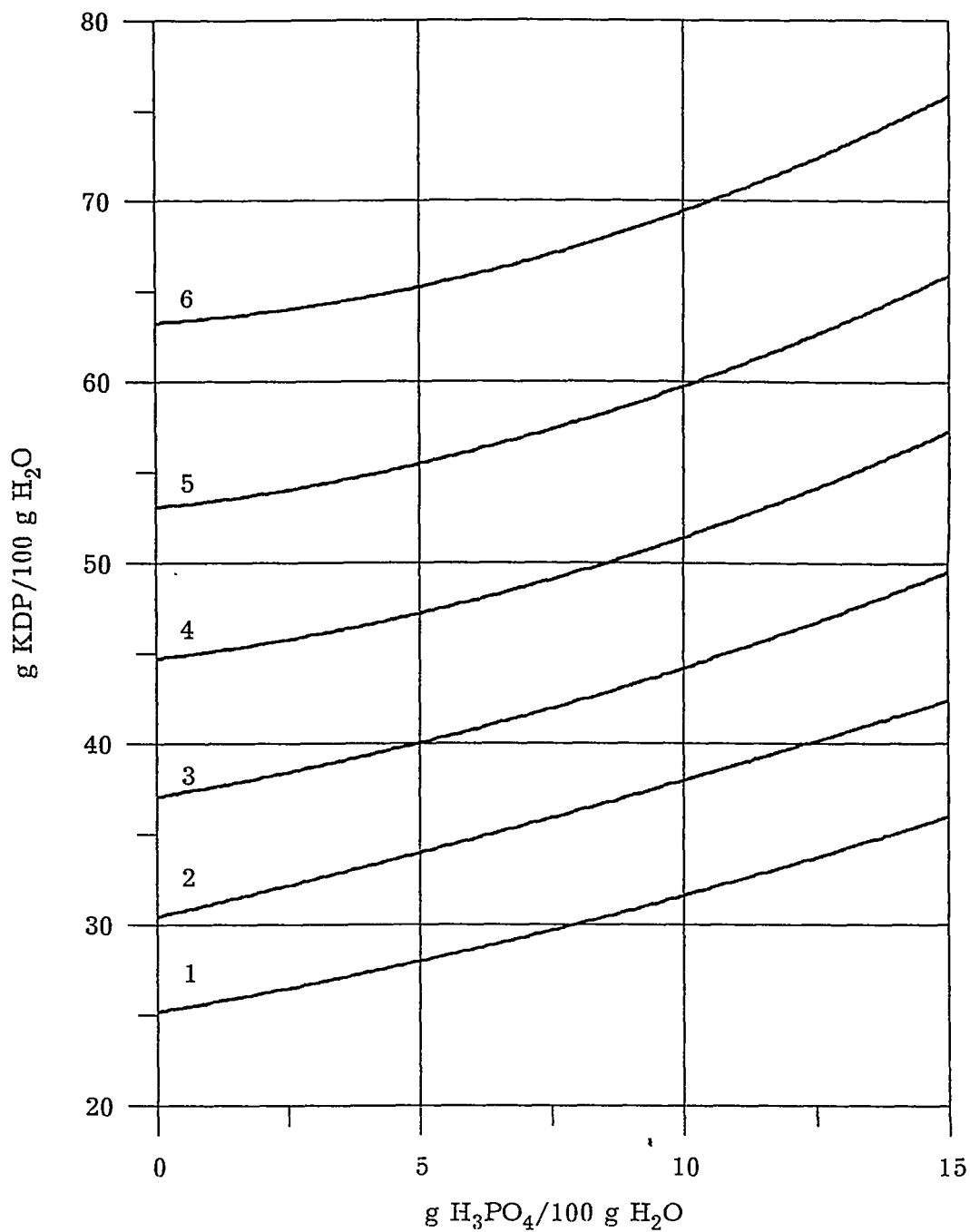


Fig. 3. KDP solubility in acid solutions.
 The temperature of solution (°C):
 1 - 25, 2 - 35, 3 - 45, 4 - 55, 5 - 65, 6 - 75.

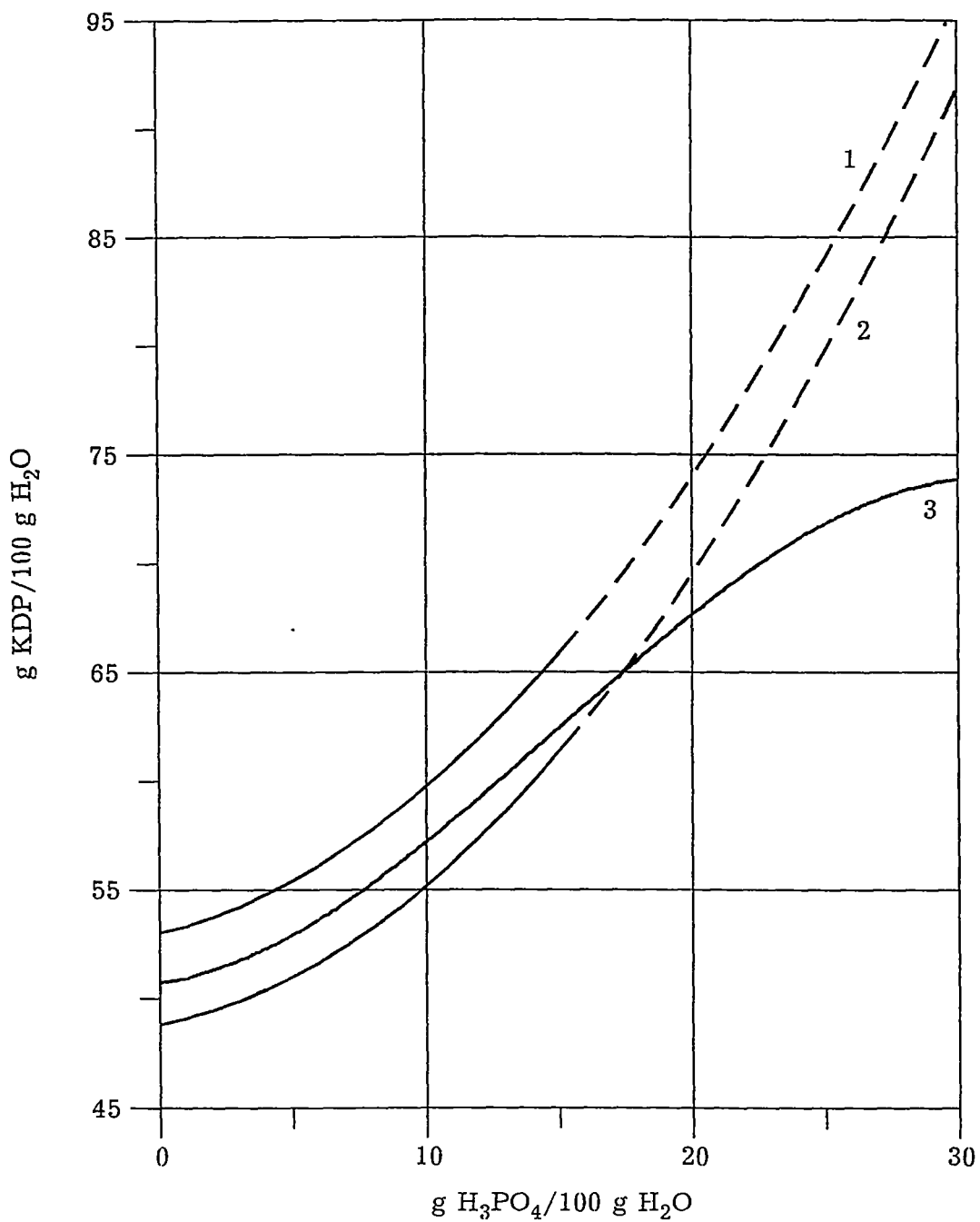


Fig. 4. KDP solubility in acid solutions.
 The temperature of solution (°C): 1 - 60, 2 - 65, 3 - 62.
 The dashed part of the curves is approximation of curves from [17].

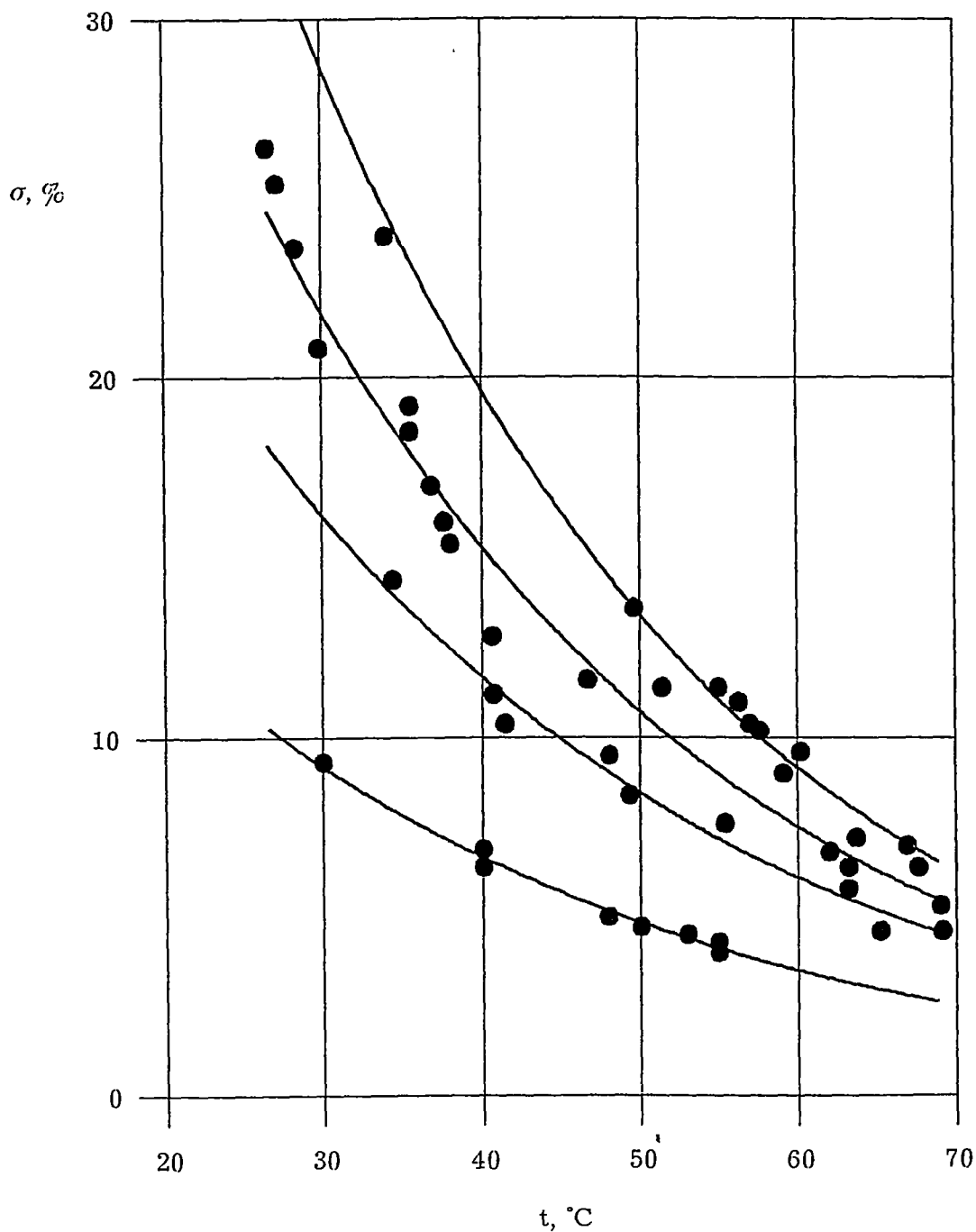


Fig. 5. Temperature dependencies of supersaturation needed for providing constant growth rates along Z-axis for KDP crystals [18].

- - experimental results,
- - approximation.
- 1 - 10 mm/day, $\sigma = 24.0778 \exp(-0.0321556 t)$
- 2 - 20 mm/day, $\sigma = 42.9267 \exp(-0.0325538 t)$
- 3 - 30 mm/day, $\sigma = 63.2394 \exp(-0.0355174 t)$
- 4 - 40 mm/day, $\sigma = 90.0688 \exp(-0.0381607 t)$.

This result differs from our results which were reported in Progress Report #3. Where the ratio $2H/(A+B)$ for grown crystals decreased when acidity of solution increased. The last experiments showed that there weren't a correlation between this ratio and acidity of the solution. This ratio was 0.71-0.77 in all our experiments. Apparently, the results from Progress Report #3 are connected with mutual influence of saturation temperature and acidity on crystal habit.

Optical properties of the crystals.

Optical properties of the grown crystals were found to be depended on acidity of solution. Crystals #1÷4 (see Table 2) were perfect and hadn't any visible inclusions. Crystals #5÷9 had some parallel to face of prism inclusions which appeared near the prism-prism boundaries and decorated them. But central part of prism faces hadn't inclusion. Inclusions didn't appear in pyramid in all experiments. Besides we grew crystal from the solution #9 with growth rate ≈ 7 mm/day. This crystal hadn't any inclusions.

We have investigated sectorial boundaries between dipyramidal and prismatic growth sectors by shadowgraph. Contrast of these boundaries was less for crystals which were grown from more acid solution. But these boundaries were observed in all grown crystals.

The UV absorption spectra of crystals were measured by spectrophotometer Shimadzu. The results are shown in Fig.6. Spectral dependence doesn't depend on solution acidity for pyramidal part of the crystal (curves 1-4). But there is a significant dependence for prismatic part (curves 5-8), these curves show that absorption at 270 nm decreases and at 200 nm increases with increasing of solution acidity. Apparently, phosphoric acid reacts with impurities which are responsible for absorption band at 270 nm, but simultaneously the solution of phosphoric acid adds to the KDP solution some impurities which are responsible for the absorption band at 200 nm.

Measurements of absorption spectra of phosphoric acid water solutions show that increase of acid concentration results in increase of absorption at 200 nm.

Perhaps, absorption at 200 nm in prismatic part of the crystal can be decreased too by using more pure acid.

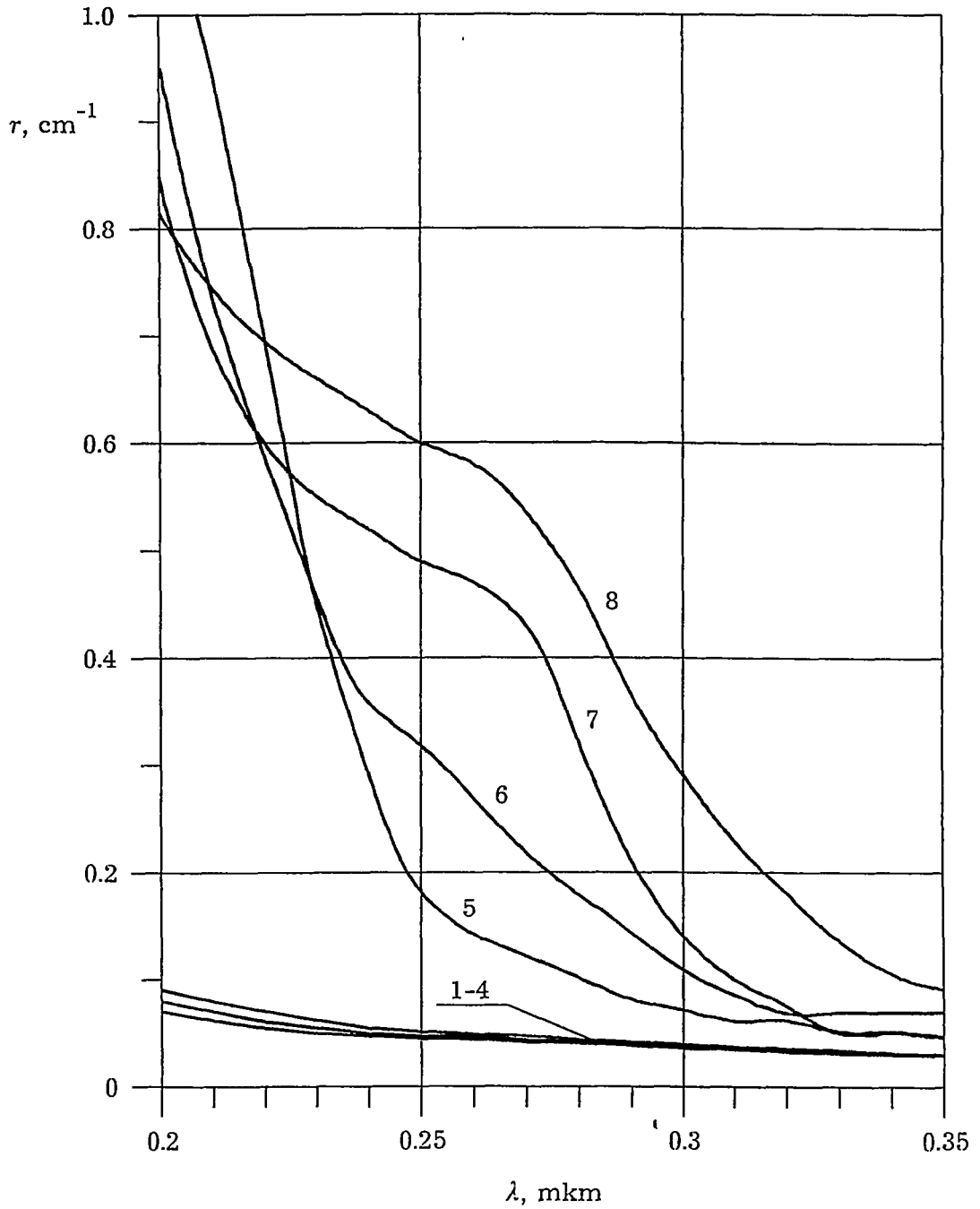


Fig. 6. UV absorption spectra of the KDP crystals.
 1-4 - pyramidal part, 5-8 - prismatic part.
 Crystals were grown from solution with concentration of acid
 ($\text{g H}_3\text{PO}_4/100 \text{ g H}_2\text{O}$):
 5 - 29.9, 6 - 20.02, 7 - 10.2, 8 - 0.

Conclusion.

The results of investigations which has been carried out in the frame of the Project #4 are the next:

The decrease of solution's pH

a) doesn't effect significantly at a habit of the crystal. It depends on regeneration regime of the seed;

b) decreases a contrast of sectorial boundaries between dipyramidal and prismatic growth sector, but disappearance of these boundaries wasn't observed in our experiments;

c) decreases absorption in prismatic part of the KDP crystal at 270 nm and increases absorption at 200 nm. At the same time absorption of pyramidal part doesn't depend on the solution acidity;

d) results in appearance of inclusions in prismatic part of the KDP crystals, when crystal growth rate is about 16÷18 mm/day, decreasing of the crystal growth rate decreases quantity of inclusions.

Effects, which were mentioned in items 2÷4 may, be connected with impurities in phosphoric acid.

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