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Fraunhofer-Institut fuer Chemische Technologie

**Investigation of the Phase Stabilizing Effect of  
Potassium Fluoride on Ammonium Nitrate**

R#D # 8955-CH-01 - 2  
Purchase Order DAJA45-89-M-0051  
Second Interim Report

Dr. Walter Engel

1578  
August 1988  
07570 Pfinztal-Berghausen  
W-Germany

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Investigation of the Phase Stabilizing Effect of Potassium  
Fluoride on Ammonium Nitrate

Ref.: R&D # 5955-CH-01  
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Second Interim Report

1. INTRODUCTION

In the first interim report the preparation of the samples, DSC-measurements and preliminary series of x-ray-diffraction measurements were reported.

This report will cover 5 series of diffraction measurements with dry samples of ammonium nitrate with a content of 2% KF.

<u>series</u>	<u>temperature program</u>
KF 230288	20/ 80/-70/ 80
KF 250288	20/ 80/-70/ 80
KF 230388	20/-70/ 80/-70
KF 170388	20/150/-70/ 20
KF 290388	20/-70/150/ 20

The documentation of the great amount of information provided by the x-ray diffraction measurements has been organized by means of an appendix. It contains for each series the original diffraction patterns, where each third patterns has been plotted, together with a difference curve, the explanation of which was included in the first interim report.

Besides, informations are given about the lattice distances  $d$ , the lattice parameters and the intensities of the different phases. These informations, however, are not yet available for all series, as the evaluation has not yet been fully completed. *Keywords: Graphs, West Germany, Phase Studies, Phase transformations, Transition temperature. (10)*  
In the presentation and the discussion of the results it is referred to these informations in the appendix.

## 2. RESULTS OF THE MEASUREMENTS

### 2.1 SERIES KF 230288

20/ 80/-70/ 80

At room temperature the sample contains phase III with a small amount of Phase IV. The phase changes during the temperature program can be summarized as follows:

Heating 20 => 80:	III+IV --> III	end 40 °C
Cooling 80 =>-70:	III --> IV	begin 10 °C
	III --> V	begin 0 °C
	IV --> V	begin -32 °C
Heating -70 => 80:	V --> IV	begin -2 °C
	IV --> III	begin 35 °C

At the onset of the heating cycle the minor amount of phase IV disappears so that at 40 °C the whole sample consists of phase III. No further changes are observed on heating.

On cooling phase III changes into phase IV beginning at 10 °C. The transition III/IV not yet completed, surprisingly, the residue of III changes directly into phase V. Starting at -32 °C phase IV changes into phase V as expected. However, a small amount of the sample stays in phase IV even at the lowest temperatures indicated by a weak (111)<sub>IV</sub>-peak.

During the following heating cycle phase V changes completely into phase IV in the range of -2 to +10 °C, followed by a complete transition IV -> III between 35 and 45 °C.

The described transitions are visible in the difference curve in the appendix and can also be followed in the diffraction patterns by means of the peaks with the assigned indices.

### 2.2 SERIES KF 250288

20/ 80/-70/ 80

The sample was investigated with the same temperature program as in the series KF 230288. At the beginning the sample consists

again mainly of phase III with a small amount of phase IV. The phase changes can be summarized as follows:

Heating 20 => 80:	III+IV --> III	end	40 °C
Cooling 80 =>-70:	III --> V	begin	-10 °C
Heating-70 => 80:	V --> IV	begin	2 °C
	IV --> III	begin	37 °C

Immediately after beginning the heating cycle the minor amount of phase IV disappears as in the preceding series. On cooling, phase III changes completely into phase V starting at -10 °C. This direct and complete transition III/V had not been expected. In this detail the series distinguishes itself from the preceding one.

On heating, the complete transition V/III is followed by the complete transition IV/III.

The described transitions can again be followed in the diffraction patterns and with the difference curve. Additionally, the intensity curves of the peaks  $(220)_{111}$ ,  $(020)_{10}$  and  $(022)_{10}$  show nicely the appearing and disappearing phases. The intensity curves are rather rough. This is caused by the used monochromator, which provides high resolution on the expense of the intensities with the consequence of reduced measuring statistics.

The phase changes can also be followed by the lattice plane distances calculated from the appearing and disappearing peaks. The corresponding curves are included in the appendix. Intensive peaks appear earlier and disappear later during the observed phase transitions.

From the lattice plane distances of the different phases the lattice parameters of the elementary cell were calculated. A reasonable fit of the lattice parameters is considered a proof for the presence of the different phases. The plots are also included in the appendix. They also allow the determination of the temperature range, in which the phases are present. The parameter plots against temperature are performed with large increments of the y-axis so that the curves can be seen together

in one plot.

In three further separated plots the increments of the y-axis are smaller so that some more details are visible. The lattice parameters as well as the lattice plane distances do not show any irregular behaviour. If interest might arise to check the values in all details, still more sensitive curves and tables with the complete values can be provided.

### 2.3 SERIES KF 230388

20/-70/ 80/-70

In contrast to the preceding series the sample consists at room temperature mainly of phase IV with small amounts of phase III. The phase changes can be summarized as follows:

Cooling 20 => -70:	IV + III --> IV	end 5 - 0 °C
	IV --> V	begin -32 °C
Heating -70=> 80:	V --> IV	begin 0 °C
	IV --> III	begin 40 °C
Cooling 80 => -70:	III--> V	-15 °C

At the begin of the cooling cycle the small amount of phase III disappears followed by the transition IV/V. Again a small amount of phase IV is always present during the whole cooling cycle.

On heating the already known phase changes V/IV and IV/III are observed. Both transitions are completed in a relatively short temperature interval.

On cooling phase III changes directly into phase V in a short temperature interval, too.

There is no problem to follow the described changes in the diffraction patterns, whereas the difference curve doesn't show all changes clearly.

The appearing and disappearing phases again can be followed with the intensity curves, lattice distances and lattice parameter, as described earlier.

2.4 SERIES KF 170388

20/150/-70/ 20

At room temperature the sample consisted of mainly phase III with a minor amount of phase IV. The following phase changes were observed:

Heating 20 => 150:	III+IV --> III	end 50 °C
	III --> II	100 °C
	II --> I	130 °C
Cooling 150=> -70:	I --> II	130 °C
	II --> III	40 °C
	II --> IV	40 °C
	IV --> V	-25 °C
Heating -70=> 20:	III --> IV	-60 - 0 °C
	V --> IV	begin 0 °C

On heating the peaks of phase IV are detectable until 50 °C, before it changes completely into phase III. The transition III/II begins at 100 °C before the transition II/I at 130 °C.

On cooling, after the change I/II a simultaneous transition II/III and II/IV occurs, which was unexpected after the former measurements. At -25 °C phase IV changes into phase V, which is considered as a normal phase behaviour. Unexpectedly, phase III is present during the whole cooling cycle. It stays on, until it decreases during the heating cycle up to 0 °C, when the change V/IV begins.

The described phase changes can be followed in the diffraction patterns and in the difference curve. The intensity and lattice parameter curves were not yet available at the time of the report.



The samples had been stored for more than one week at room temperature before the measurements. They consist of a mixture of the phases IV and III. In different samples both phases can prevail.

The existence of phase III is due to the incorporation of potassium ions. The potassium concentration is not yet high enough to make phase III the only stable phase at room temperature. Phase changes on heating

To get a more comprehensive view of the results, the phase changes have been summarized in table 1. It can be seen that on cooling from  $-70^{\circ}\text{C}$  phase V changes in all cases at about  $0^{\circ}\text{C}$  into phase IV, which changes into phase III between  $35$  and  $40^{\circ}\text{C}$ . The latter transition occurs in the same temperature range, when the heating starts at room temperature.

Heating up to  $80^{\circ}\text{C}$  no further transition is observed. With a temperature program up to  $150^{\circ}\text{C}$  phase III changes into phase II at about  $100^{\circ}\text{C}$ . The transition temperature is increased compared to pure humid ammonium nitrate due to the presence of the potassium ions.

Further heating changes the sample into phase I as expected. Eventually the transition temperature might be slightly higher than in pure ammonium nitrate, however, the resolution of our measurements with  $2.5^{\circ}\text{C}$  measuring intervals is not high enough to answer this question.

#### Phase changes on cooling

Cooling down from  $150^{\circ}\text{C}$  causes the samples to change at  $130^{\circ}\text{C}$  into phase II as expected. Surprisingly no hysteresis of the transition temperature on heating and cooling is observed. In pure ammonium nitrate transition temperatures of about  $120^{\circ}\text{C}$  are normally observed.

The following phase change II/III occurs at essentially lower temperatures compared to heating at  $55 - 40^{\circ}\text{C}$ . The transition temperature is low enough to allow occasionally the direct phase change II/IV, which is observed in pure, absolutely dry ammonium

nitrate.

The further cooling again includes more than one transition path. The expected path consists of the phase change III/IV in an observed temperature interval from -10 to +10 °C. At these temperatures, however, the direct transition III/V at 0 to -15 °C is already possible.

In case of changing into phase IV the transition IV/V follows at temperatures from -25 to -40 °C, which is rather sluggish. This transition is not complete. Weak peaks of phase IV are detectable during the whole cooling cycle down to -70 °C. This phase change corresponds to the change in pure ammonium nitrate. Obviously, it was not influenced by the incorporated potassium ions.

#### Summary

A summary is given in table 2, which contains the different transitions paths, which were found, together with all observed transition temperatures. The table shows that the transitions II/III, III/IV and IV/V occur with strong hysteresis on heating and cooling.

The decreased transition temperatures on cooling obviously come so close to the stability ranges of the deep temperature phases that even direct phase changes II --> IV and III --> V are possible.

The measurements show, that the concentration of 2% of the incorporated potassium ions is not yet sufficient to exclude phase changes under storage conditions.



**Appendix**

**A Peaklist**

**B Series KF230288**

**C Series Kf250288**

**D Series Kf170388**

**E Series Kf230388**

**F Series Kf290388**

**Peak List**

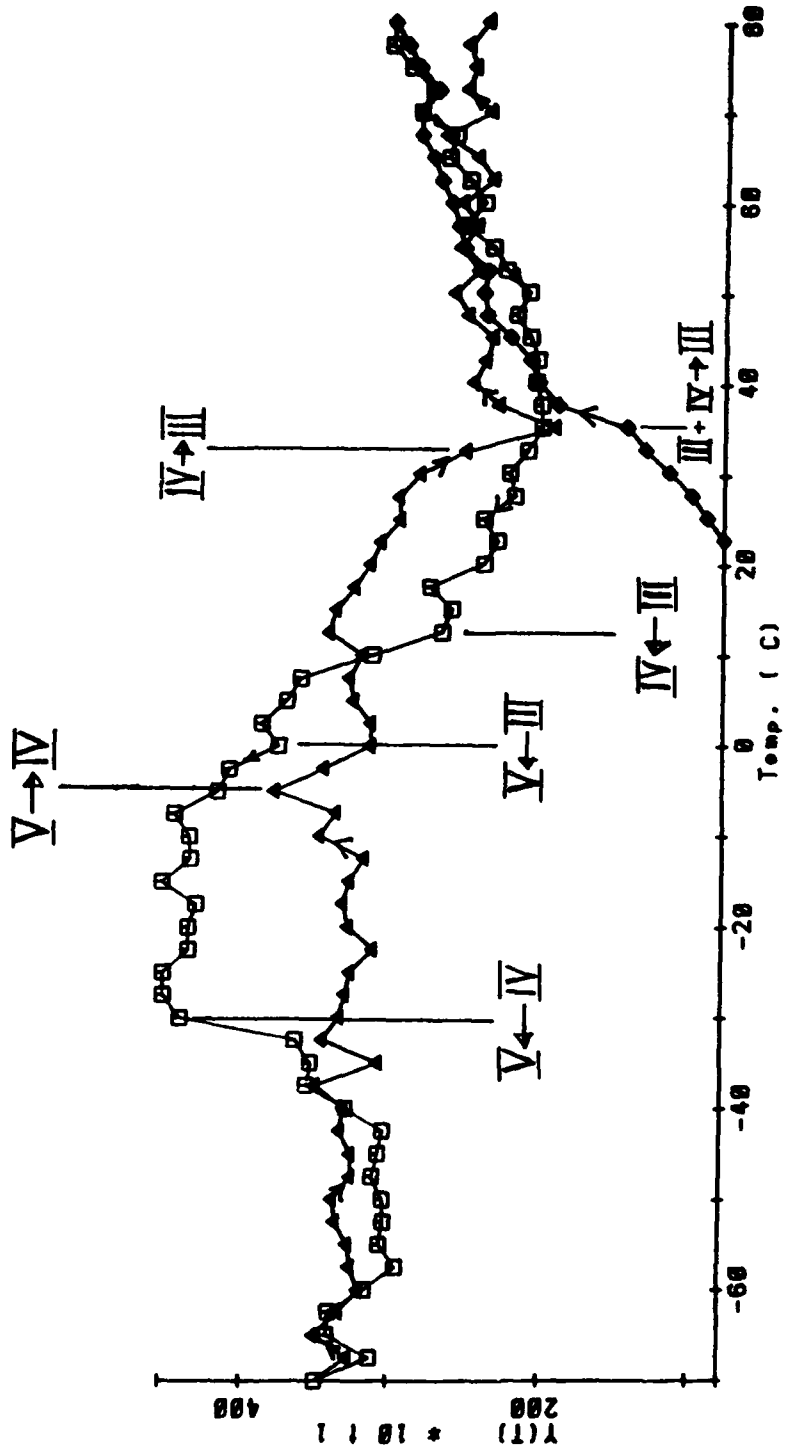
Diffraction Angles of the Ammonium Nitrat Phases I, II, III, IV, V  
with Chromium Radiation.

Peak Nr.	2 $\theta$ Theta(ca.)	Phase	(hkl)
1	26.8	IV	(001) <sub>zv</sub>
	27.05	V; II	(001) <sub>zz</sub> ; (002) <sub>v</sub>
2	29.2	III	(101) <sub>zzz</sub>
3	30.5	I	(100) <sub>z</sub>
4	33.0	II; V	(020) <sub>v</sub> ; (110) <sub>zz</sub>
5	33.67	V	(200) <sub>v</sub>
6	33.8	IV	(110) <sub>zv</sub>
7	34.24	III	(111) <sub>zzz</sub>
8	39.53	III	(120) <sub>zzz</sub>
9	41.43	III	(210) <sub>zzz</sub>
10	41.78	III	(021) <sub>zzz</sub>
11	43.5	II; V	(111) <sub>zz</sub> ; (022) <sub>v</sub>
12	43.8	I; IV	(110) <sub>z</sub> ; (111) <sub>zv</sub>
13	45.7	III	(121) <sub>zzz</sub>
14	46.9	IV	(200) <sub>zv</sub>
15	46.9	V	(212) <sub>v</sub>
16	47.72	II; V	(200) <sub>zz</sub> ; (220) <sub>v</sub>
17	47.72	III	(211) <sub>zzz</sub>
18	49.8	V	(221) <sub>v</sub>
19	50.-51.	IV	(020) <sub>zv</sub>
20	51.85	III	(220) <sub>zzz</sub>
21	53.2	II	(210) <sub>zz</sub>
22	53.8	V	(130) <sub>v</sub>
23	55.0	IV	(201) <sub>zv</sub>
24	55.7	V; II	(002) <sub>zz</sub> ; (004) <sub>v</sub>
25	56.54	III	(130) <sub>zzz</sub>
26	57.4	IV	(021) <sub>zv</sub>
27	58.5	V	(014) <sub>v</sub>
28	59.02	III	(022) <sub>zzz</sub>
29	60.41	III	(310) <sub>zzz</sub>
30	60.9	III; II	(211) <sub>zz</sub> ; (202) <sub>zzz</sub>
31	60.9	IV	(221) <sub>zv</sub>
32	61.2	V	(132) <sub>v</sub> ; (312) <sub>v</sub>
33	61.8	IV	(012) <sub>zv</sub>

***Series***  
***KF 230288***

***Temperature***  
***Program***  
***20/80/-70/80***

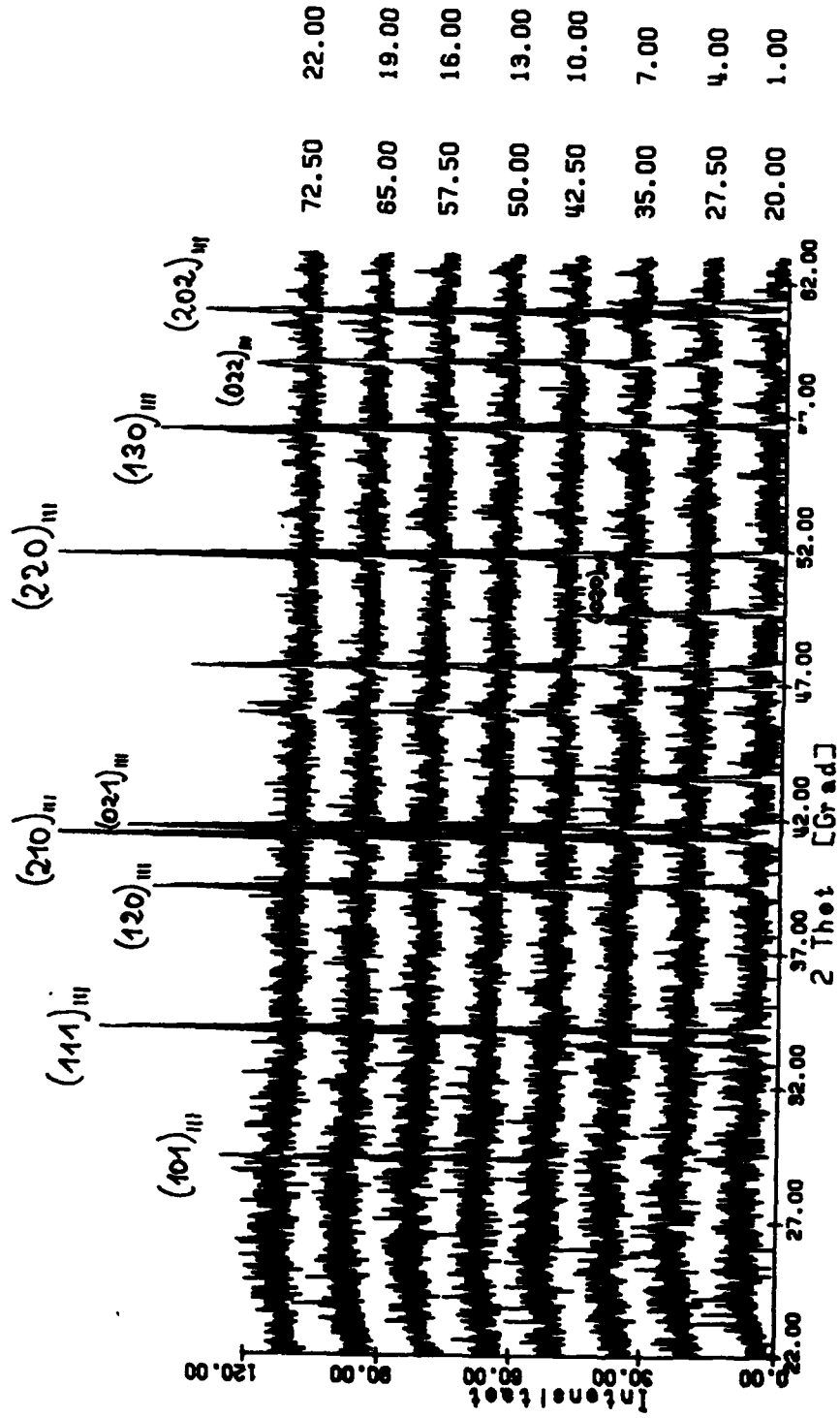
Difference Curve  
KF230288  
Y(T)



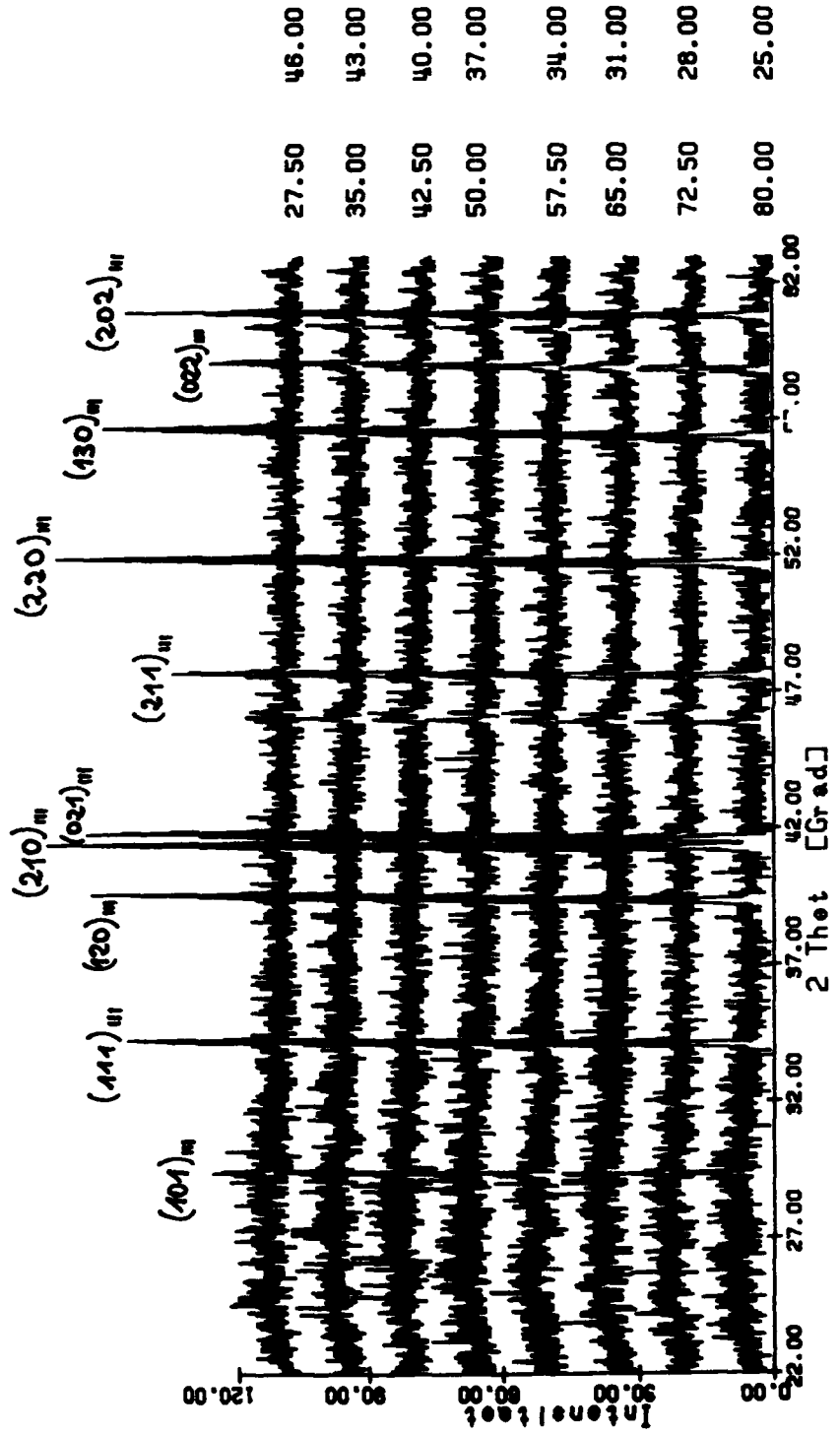
Diffraction Patterns

kf230288

20 / 80 | -70 | 80

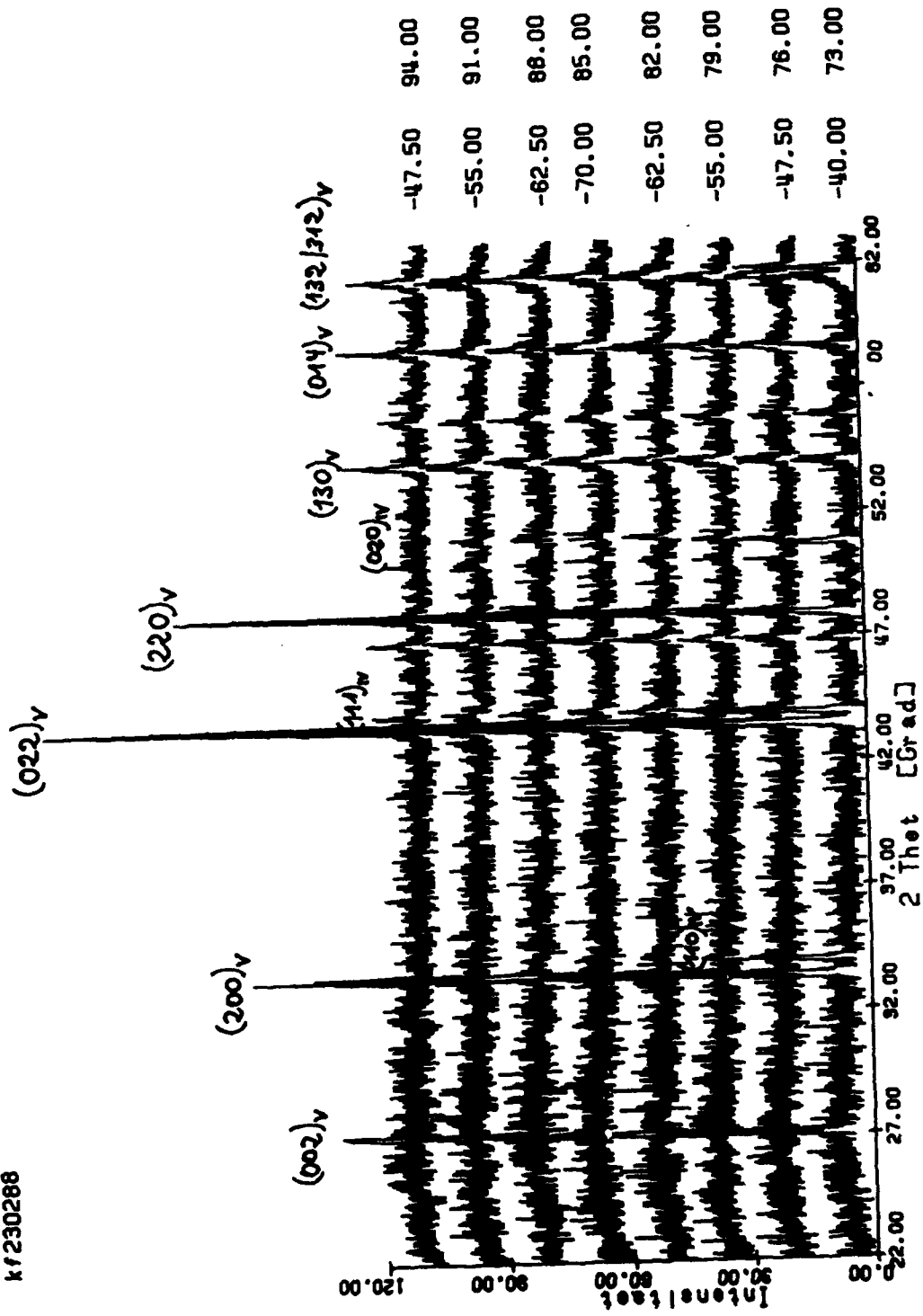


kf230288

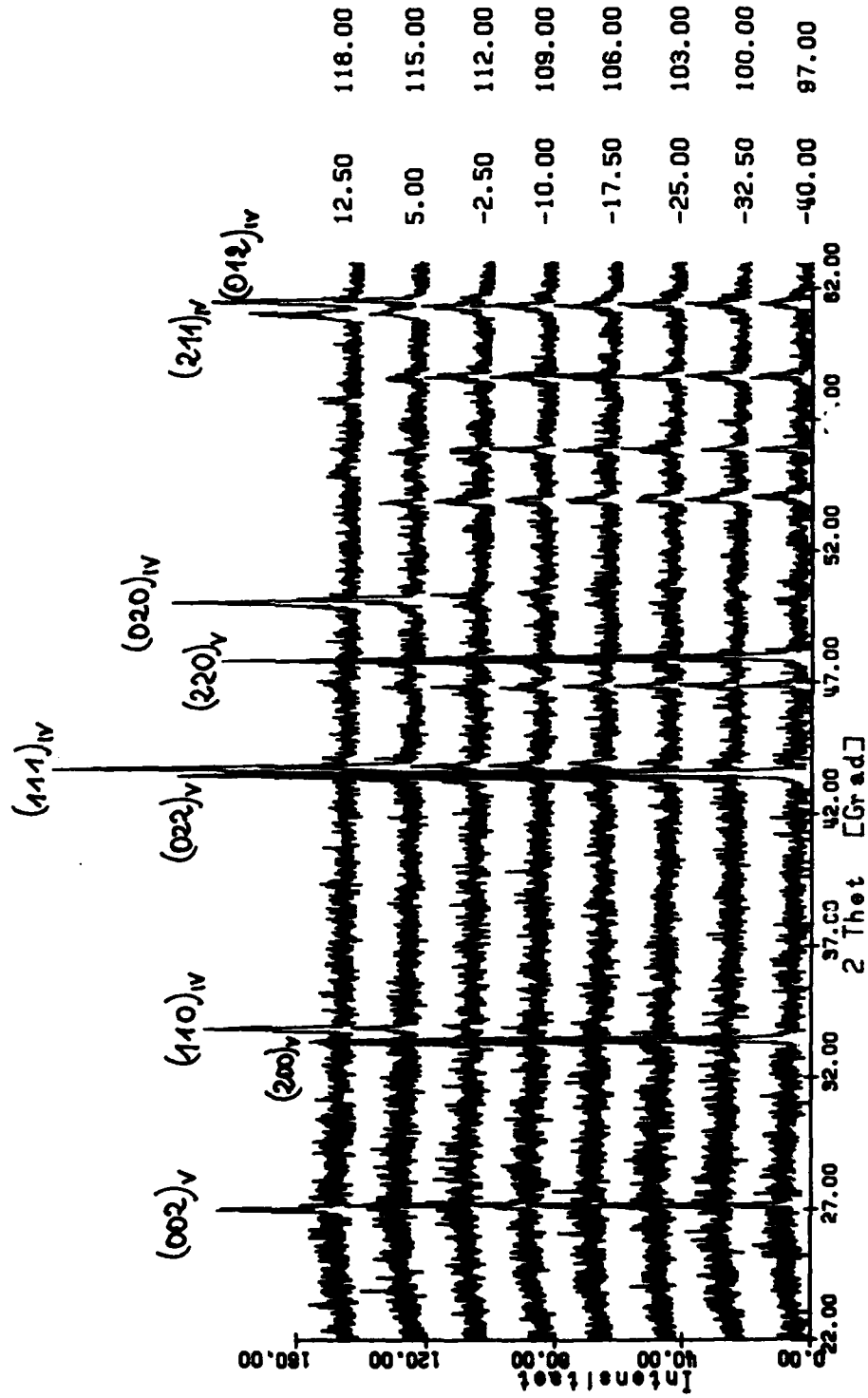




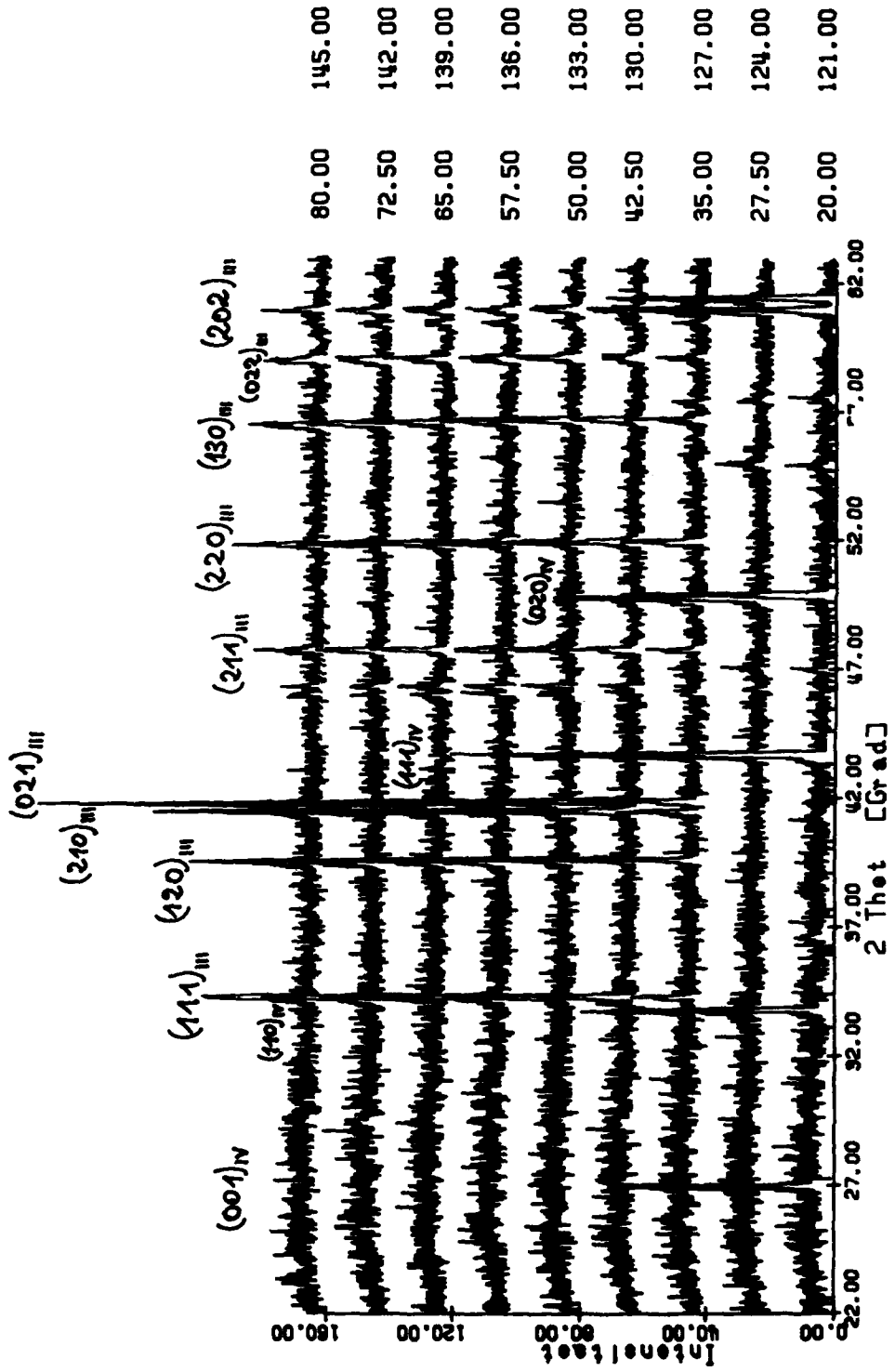
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kr230286



kf230288

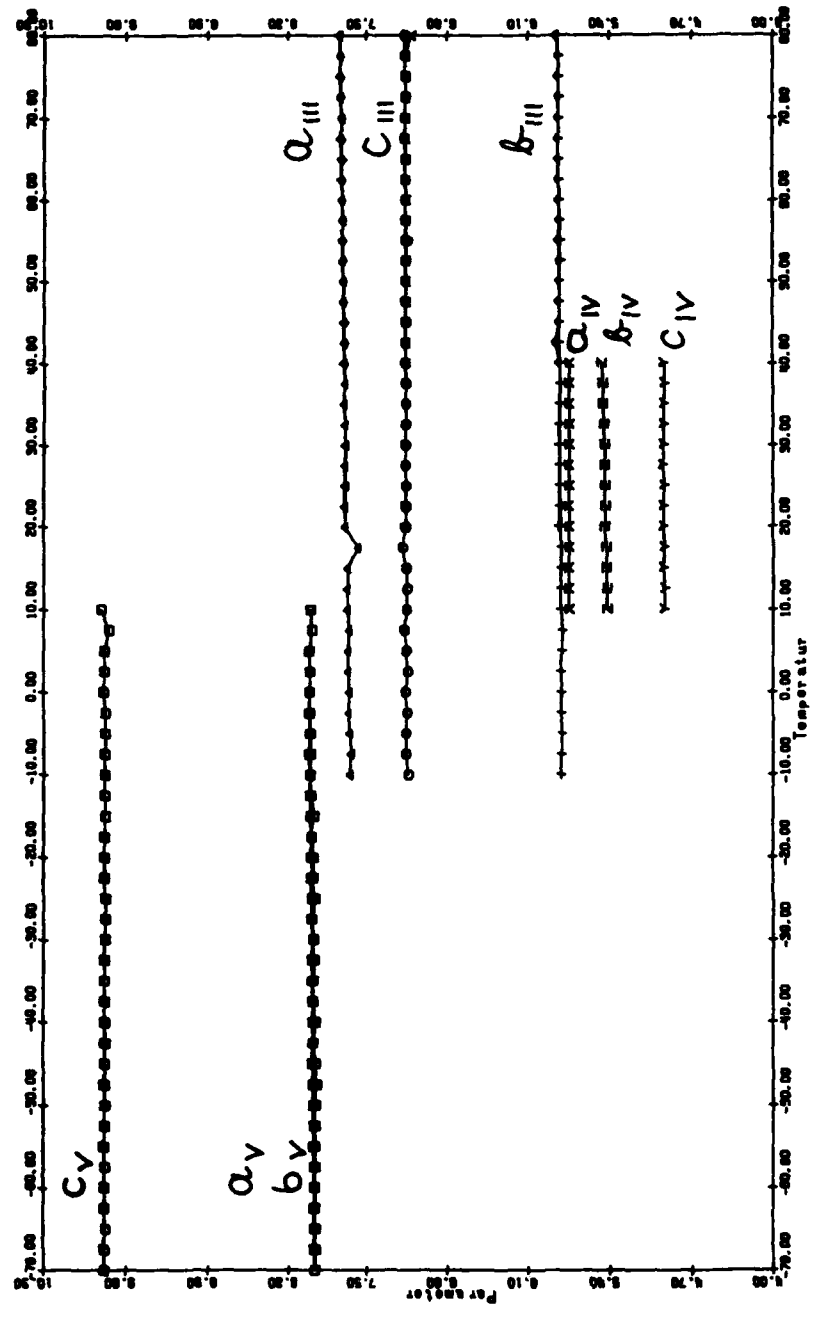


*Series*  
*KF 250288*

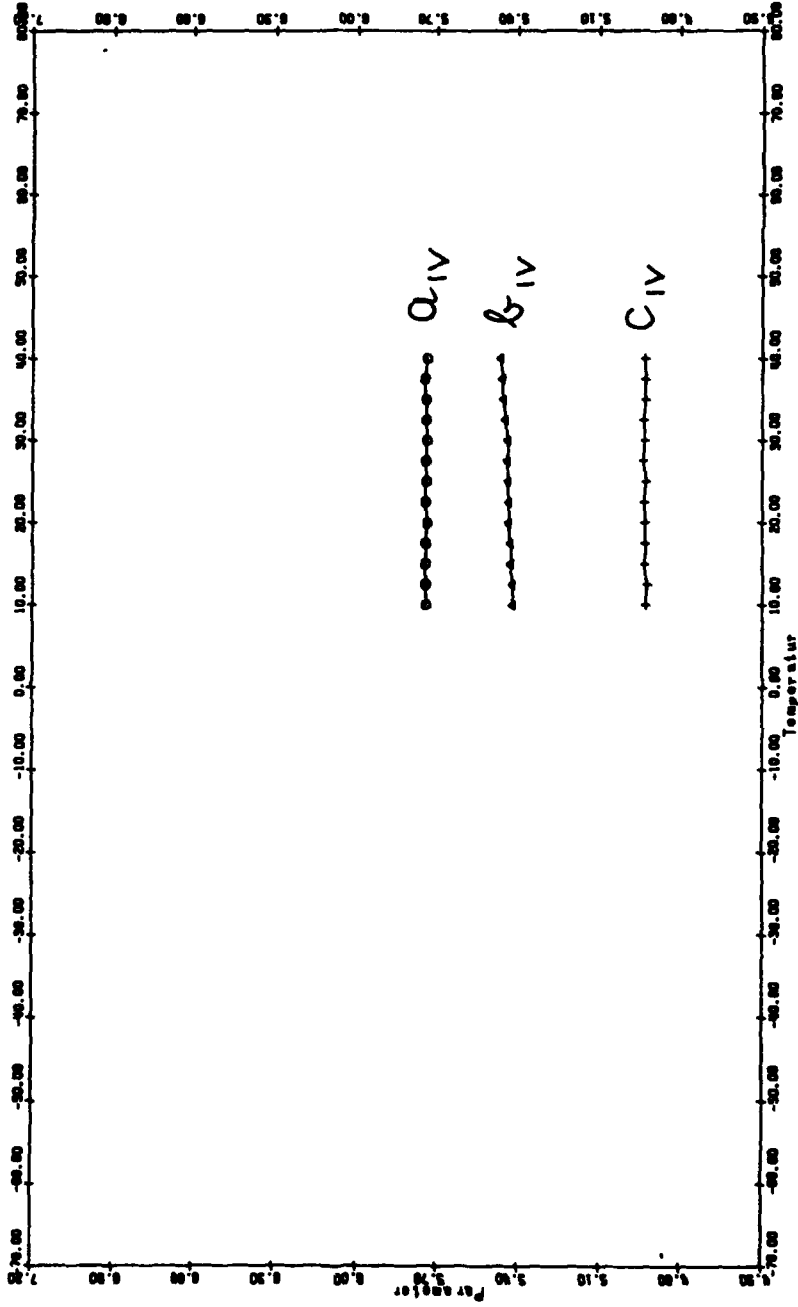
*Temperature*  
*Program*  
*20/80/-70/80*

KF 250288  
20/30/-70/80

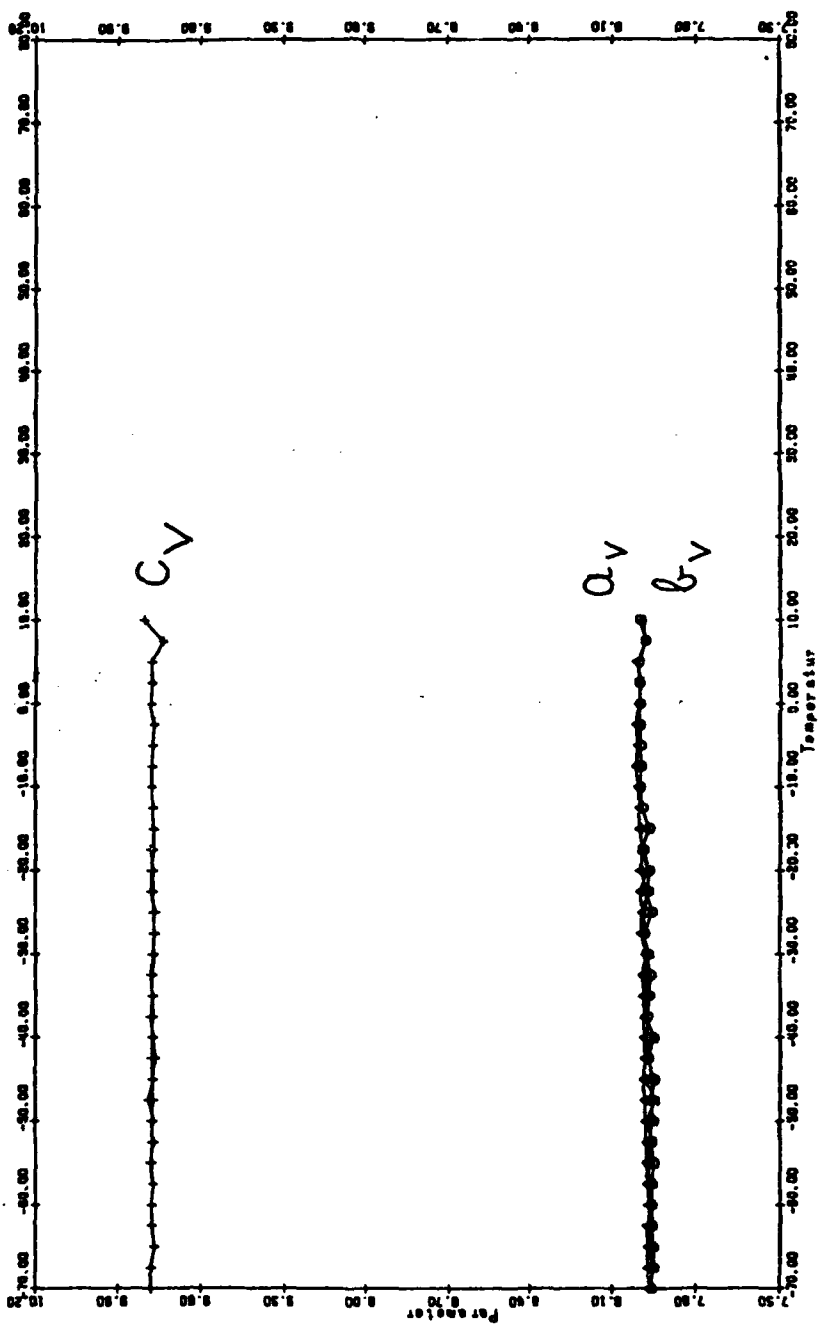
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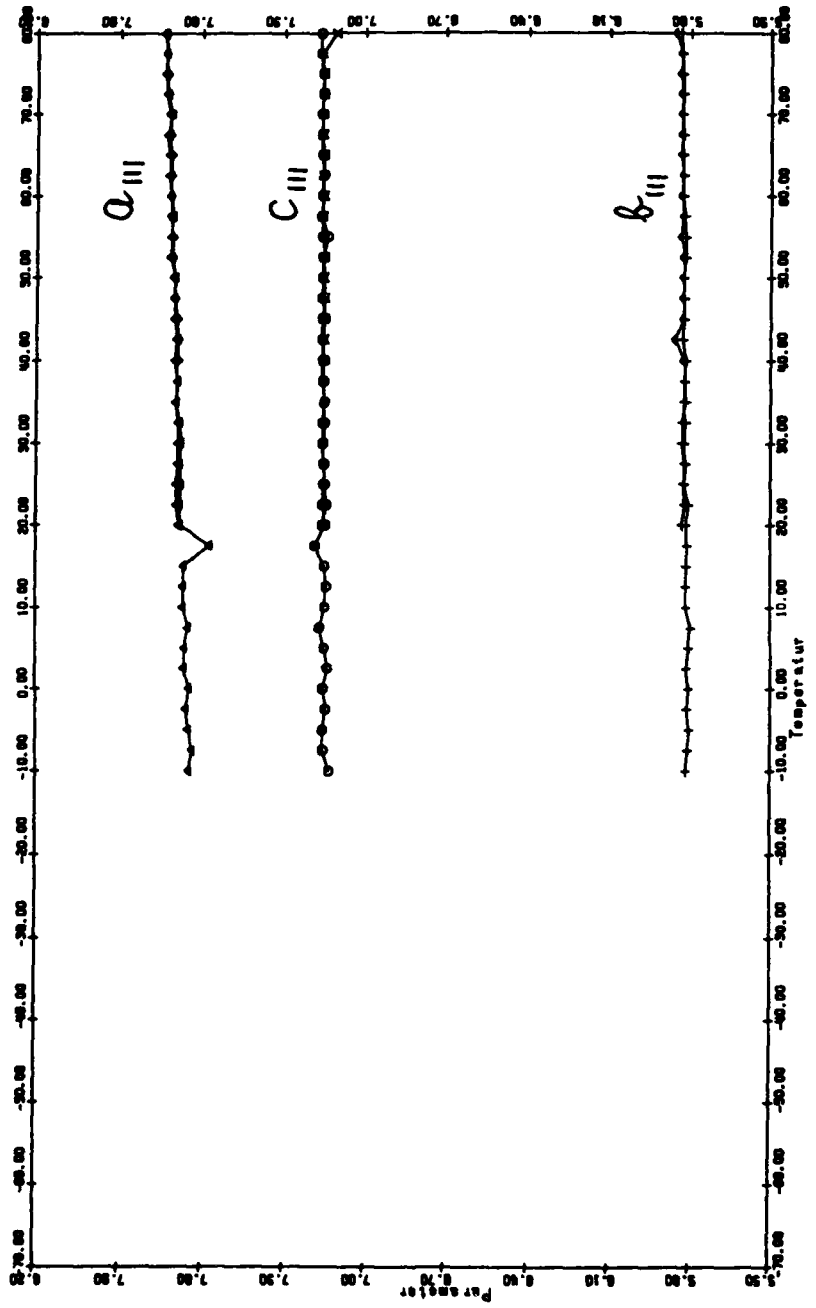
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20/80 | -70 | 80



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201801-70/80

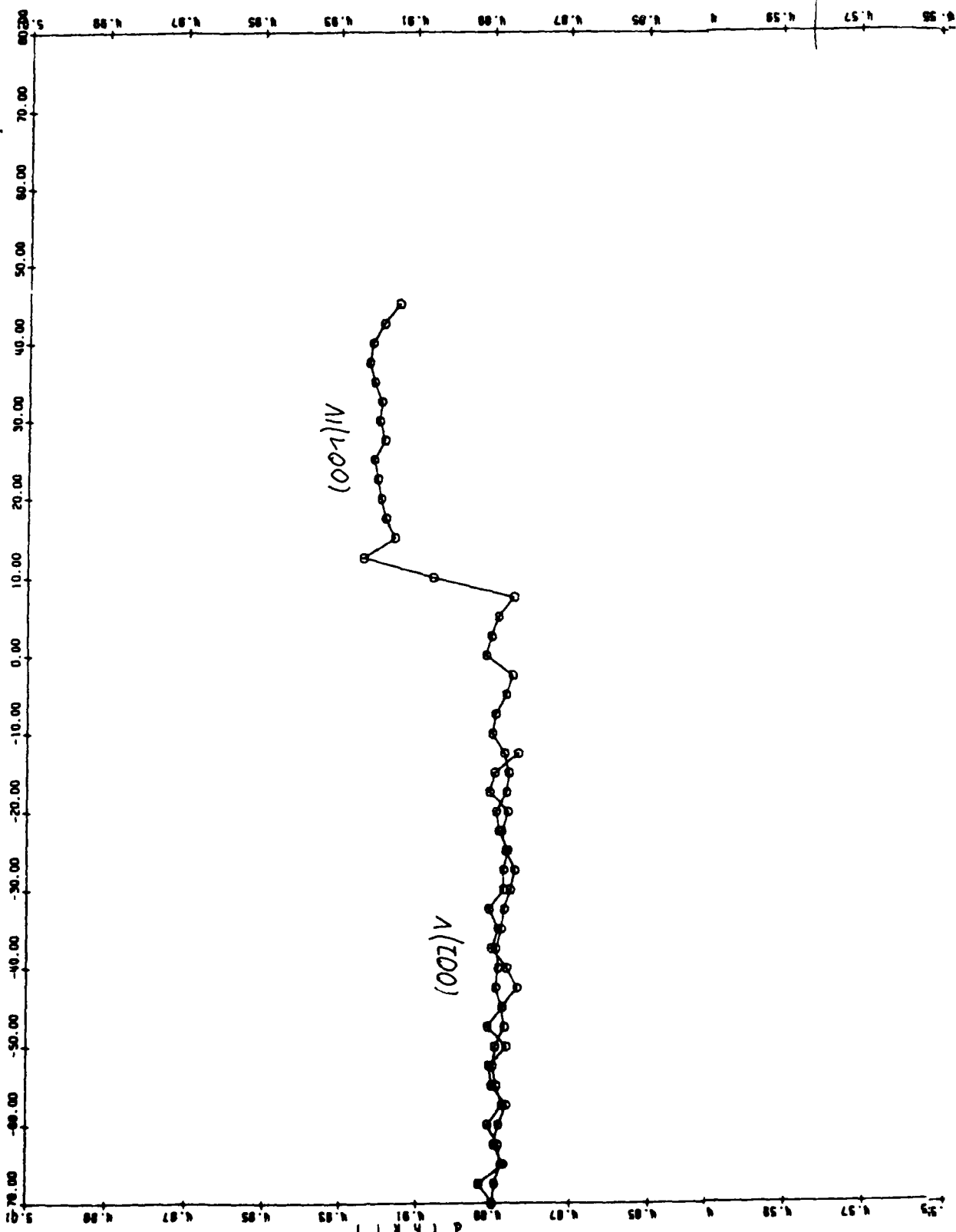


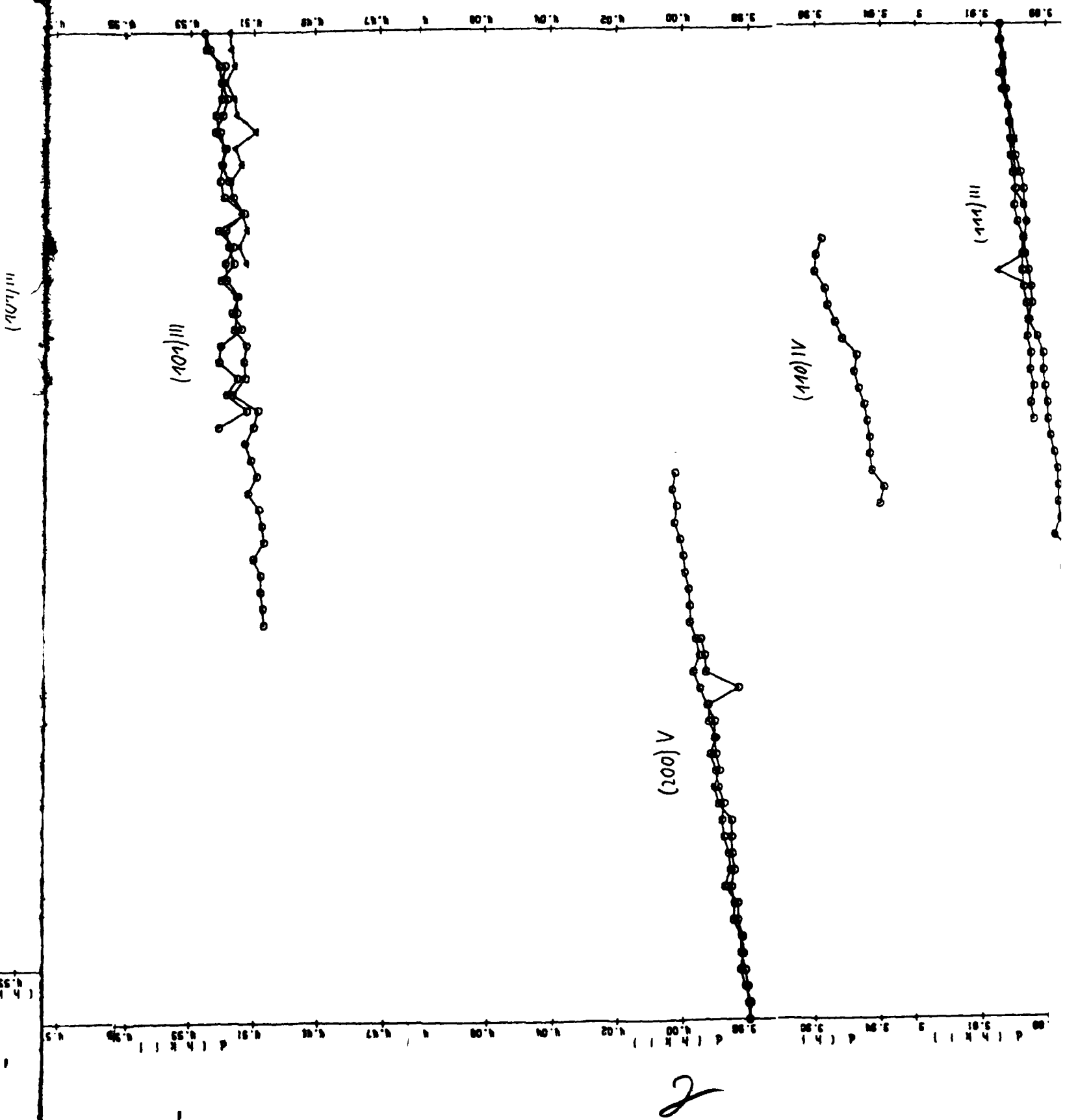
kF 250288  
20/80/-70/80



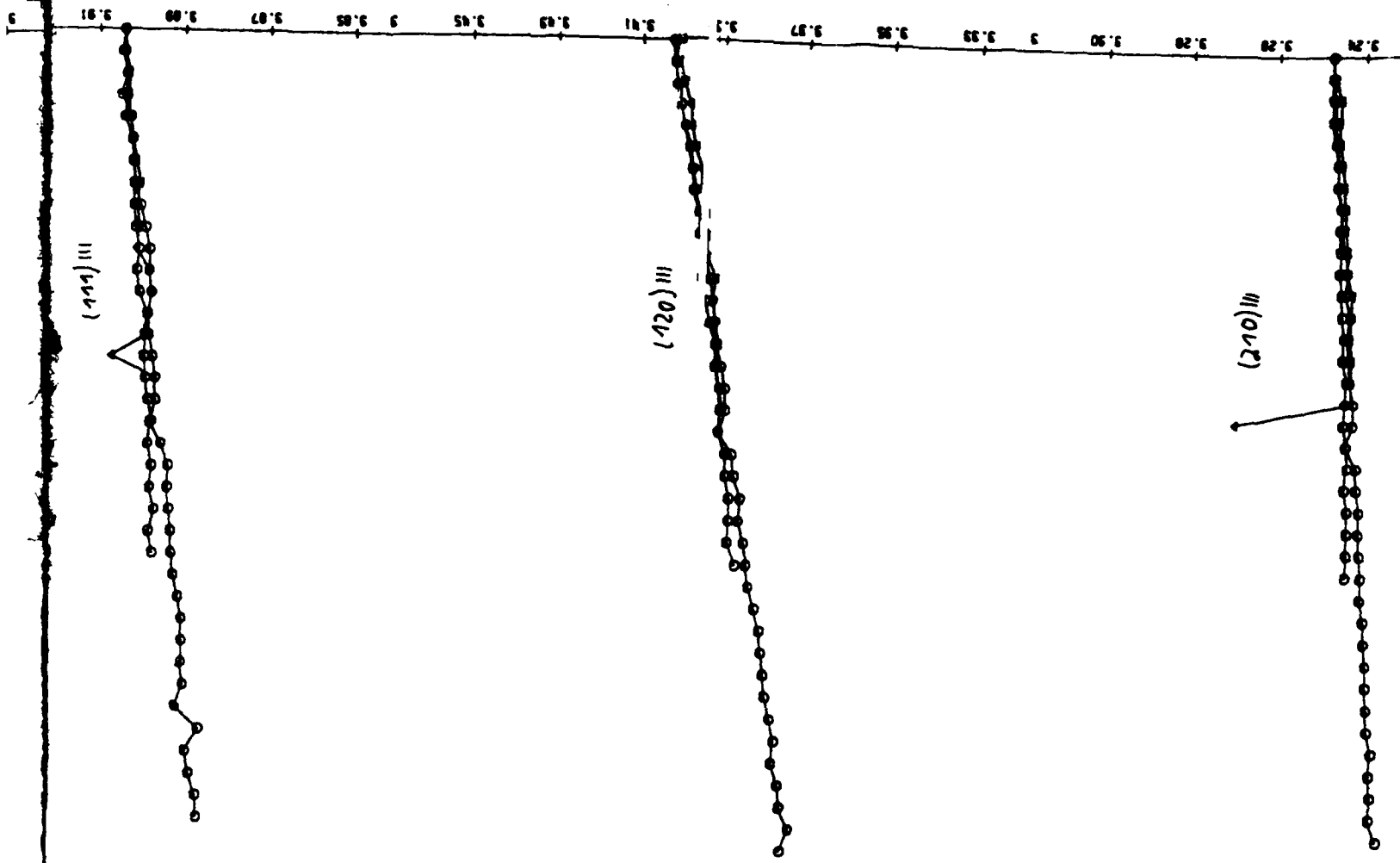
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Lattice Distances (d)

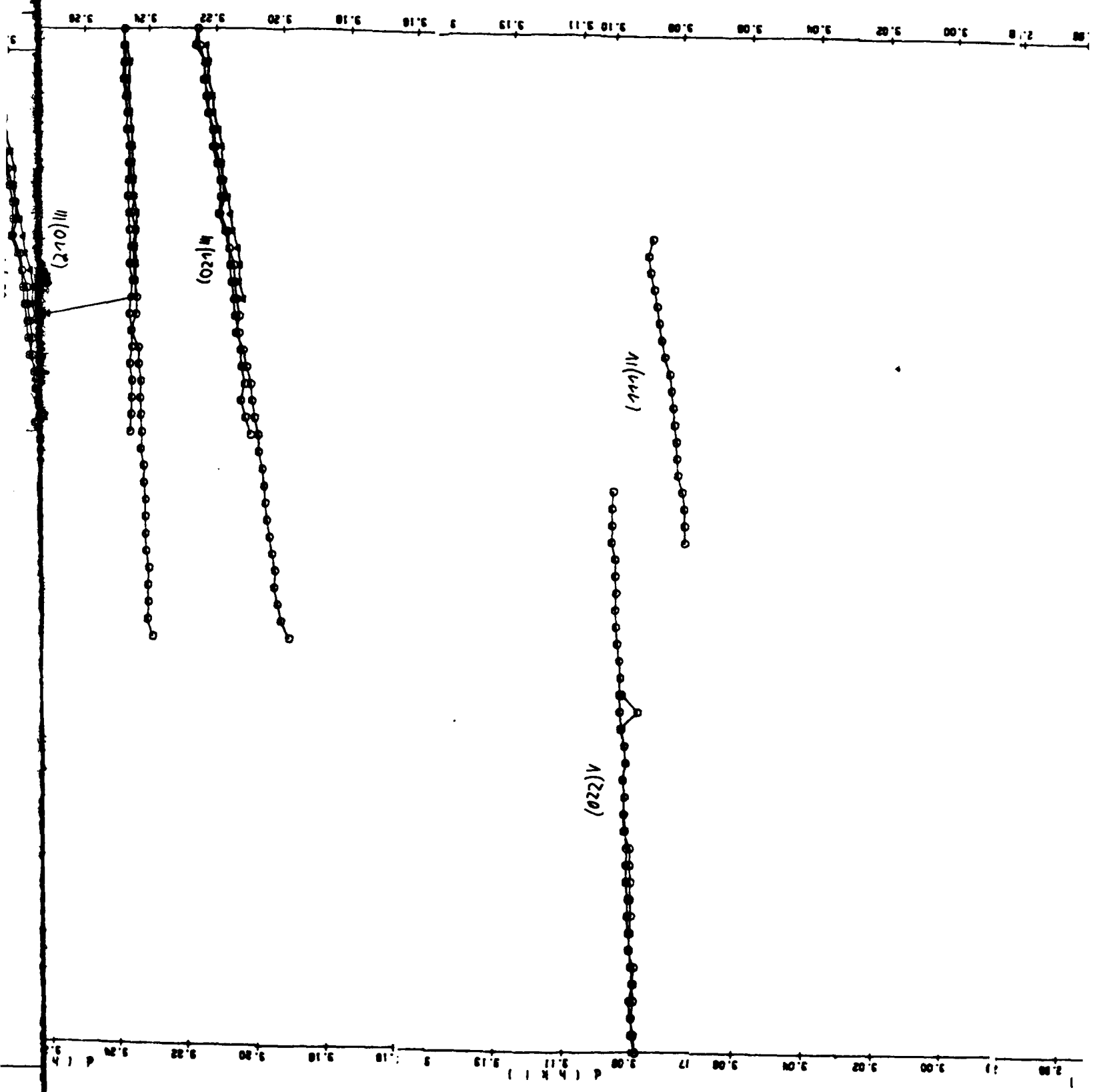




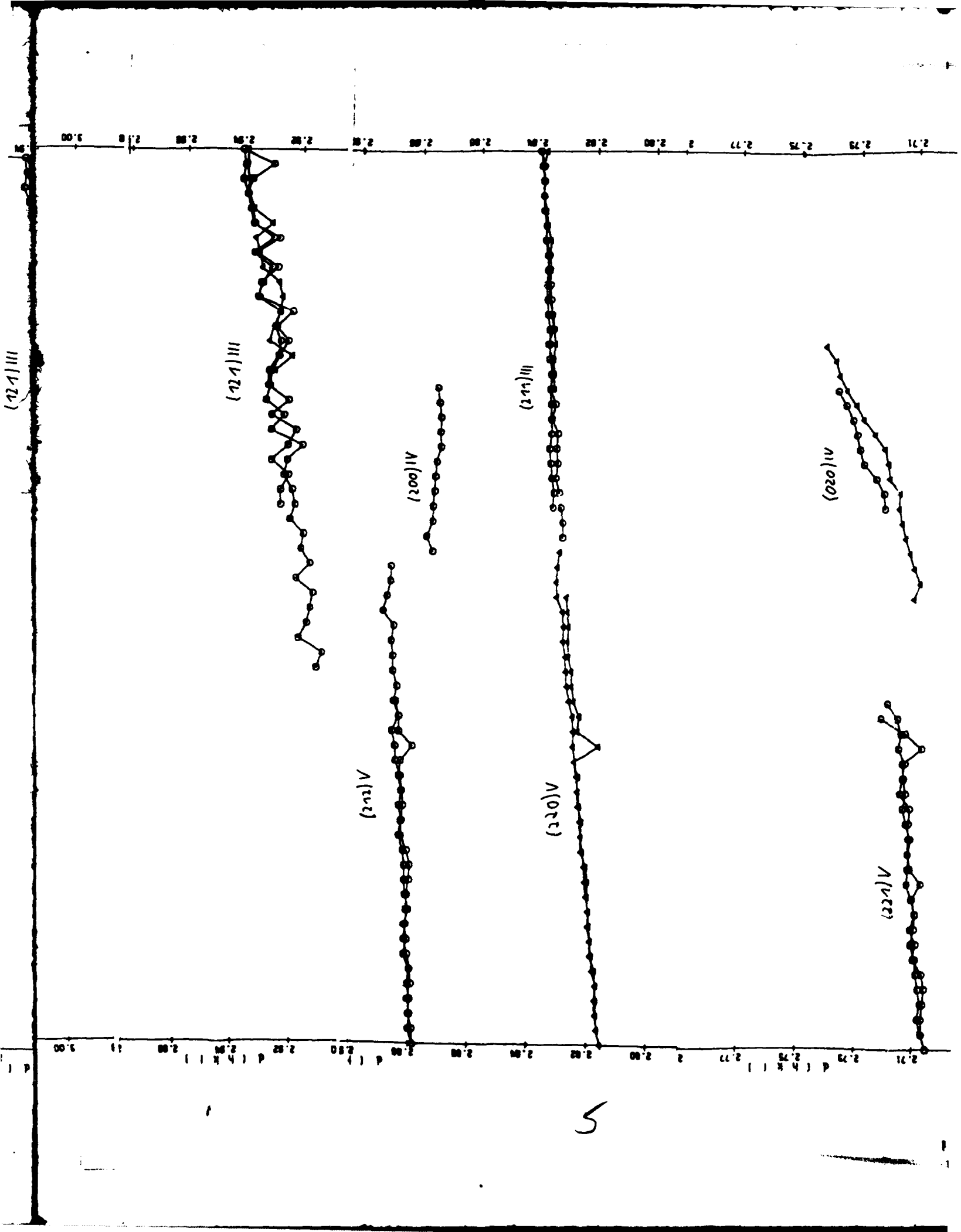
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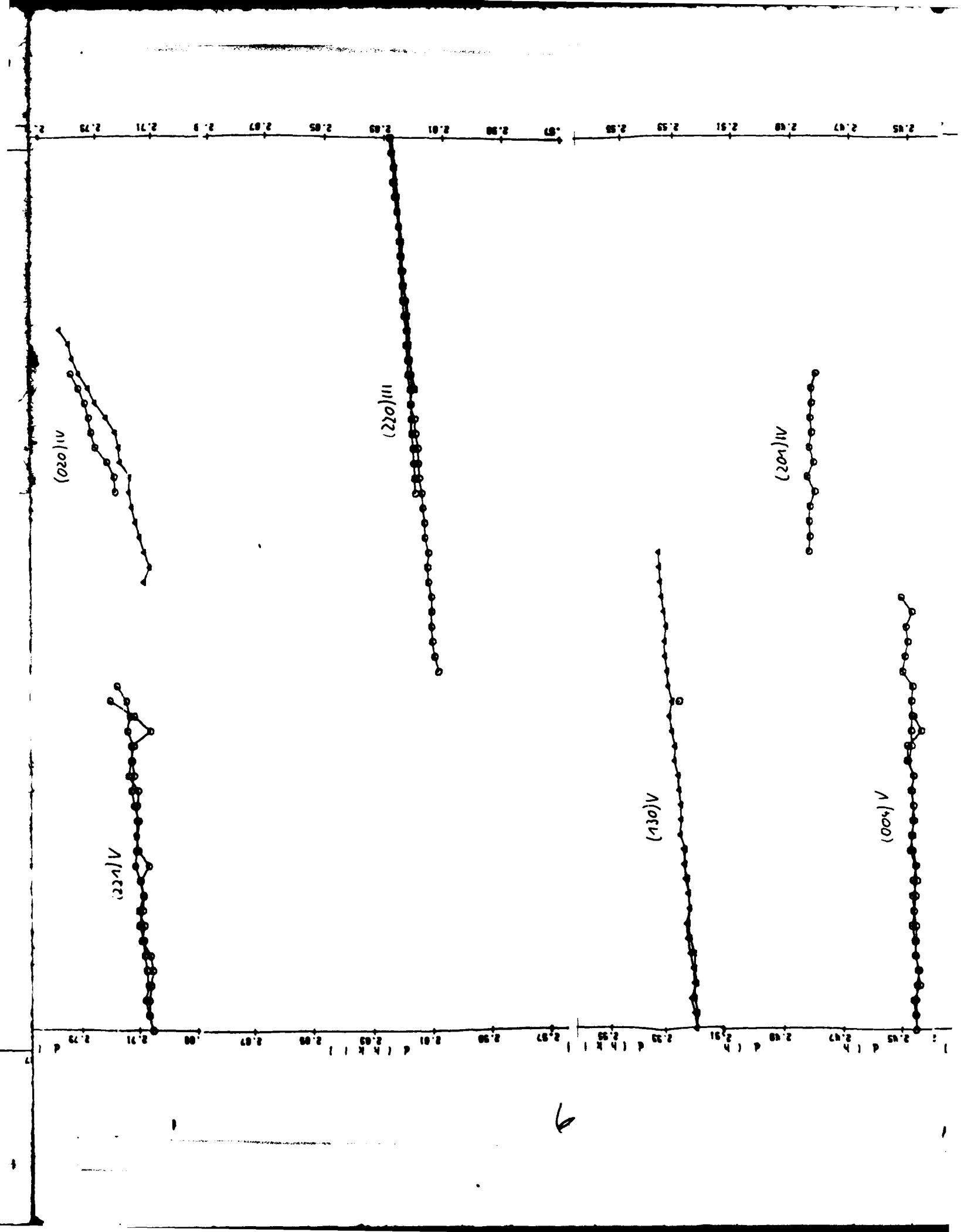


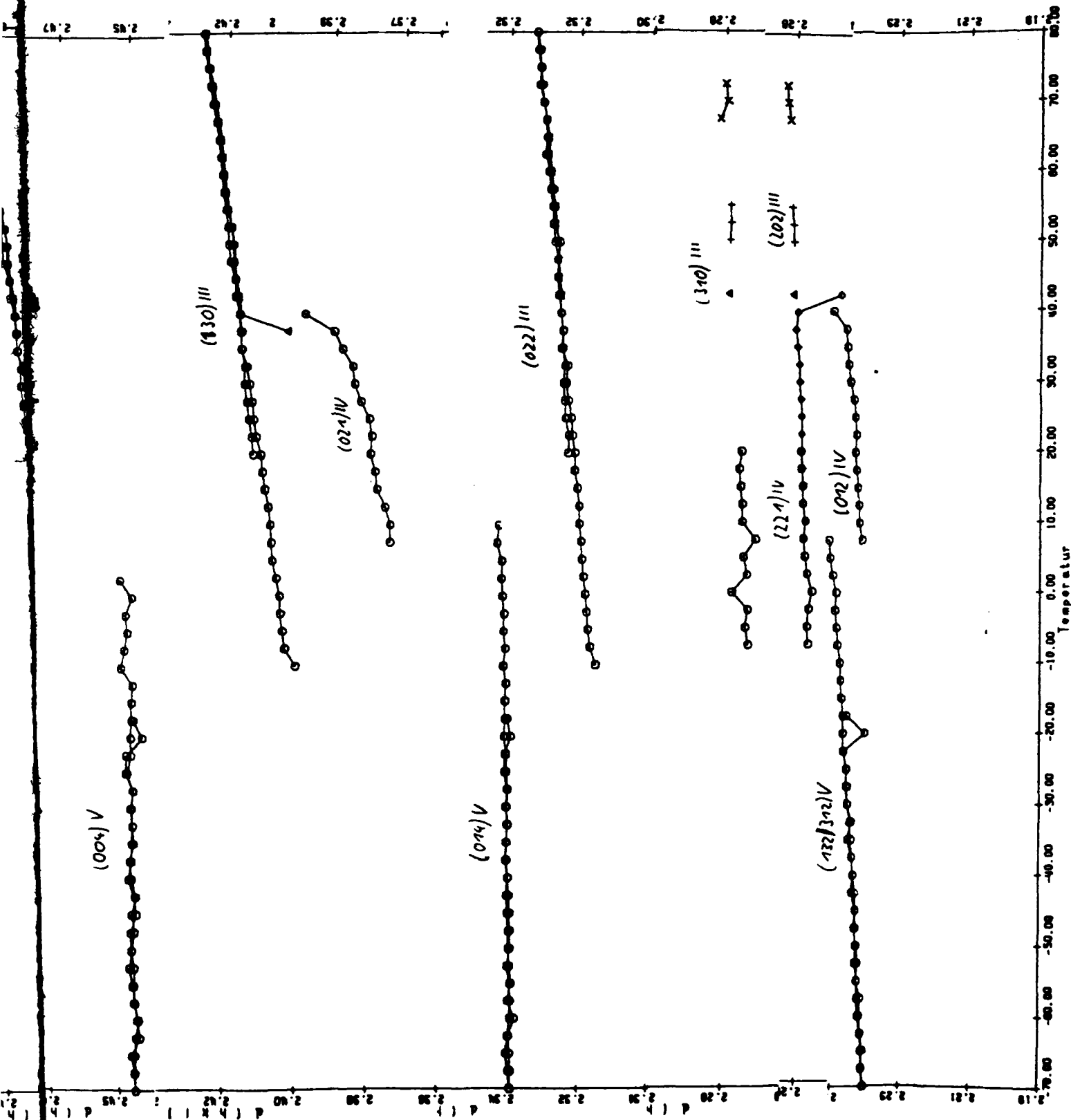
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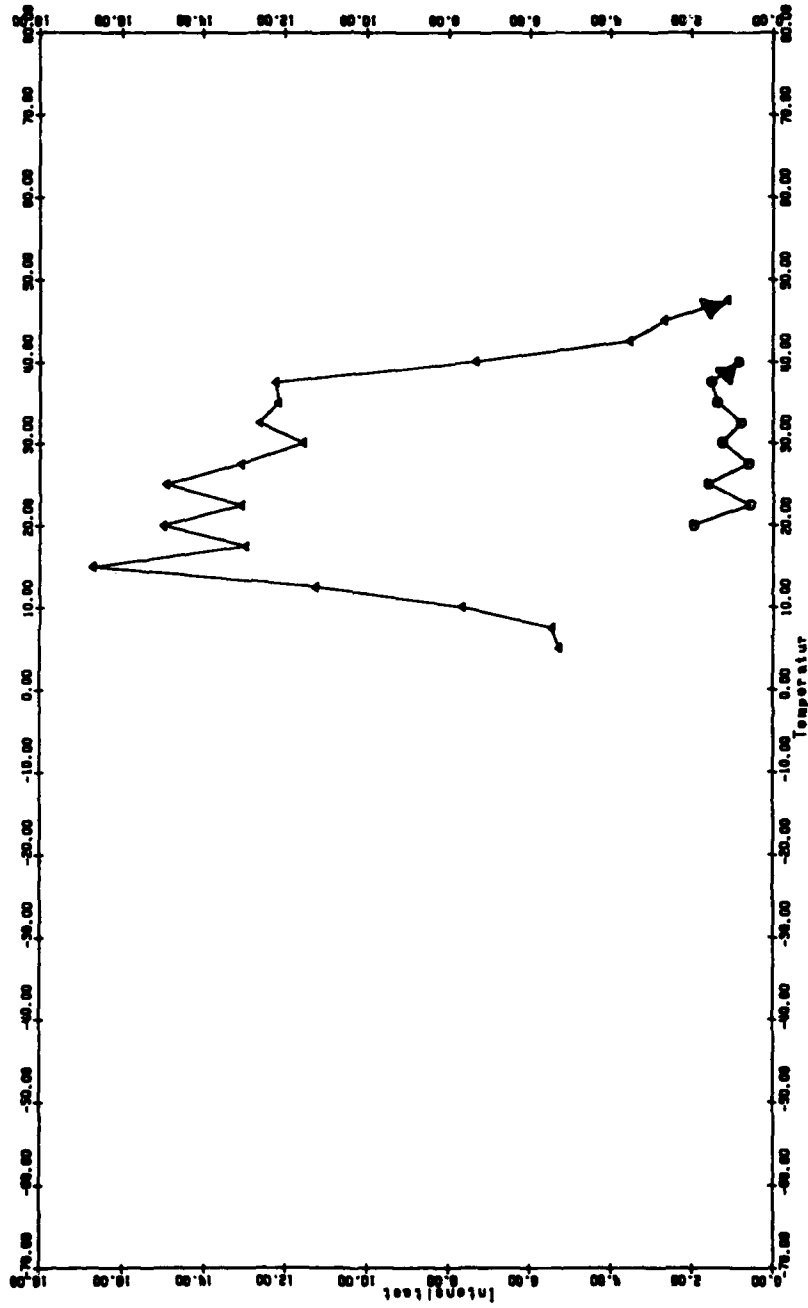




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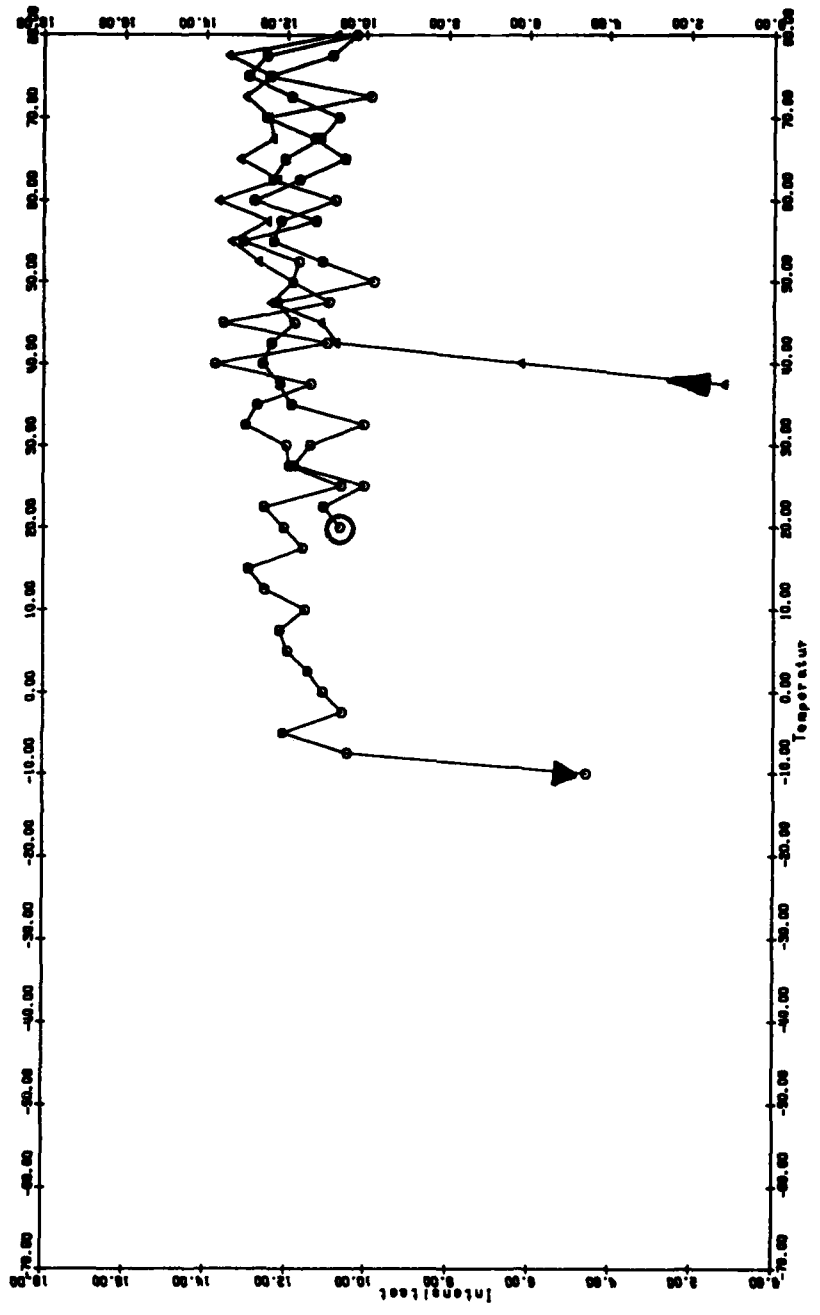
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(020) IV

Intensities



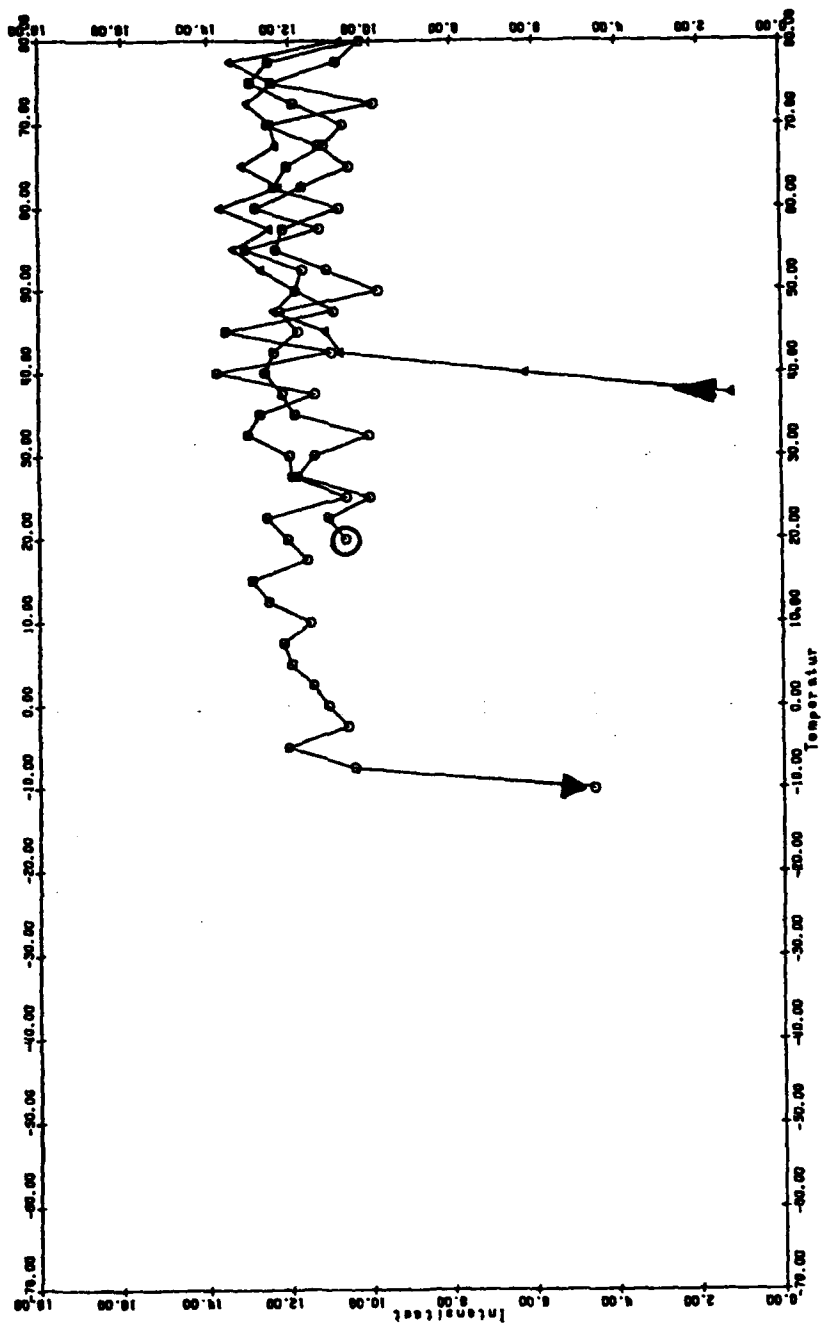
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Intensities



KF 250288  
(220) III

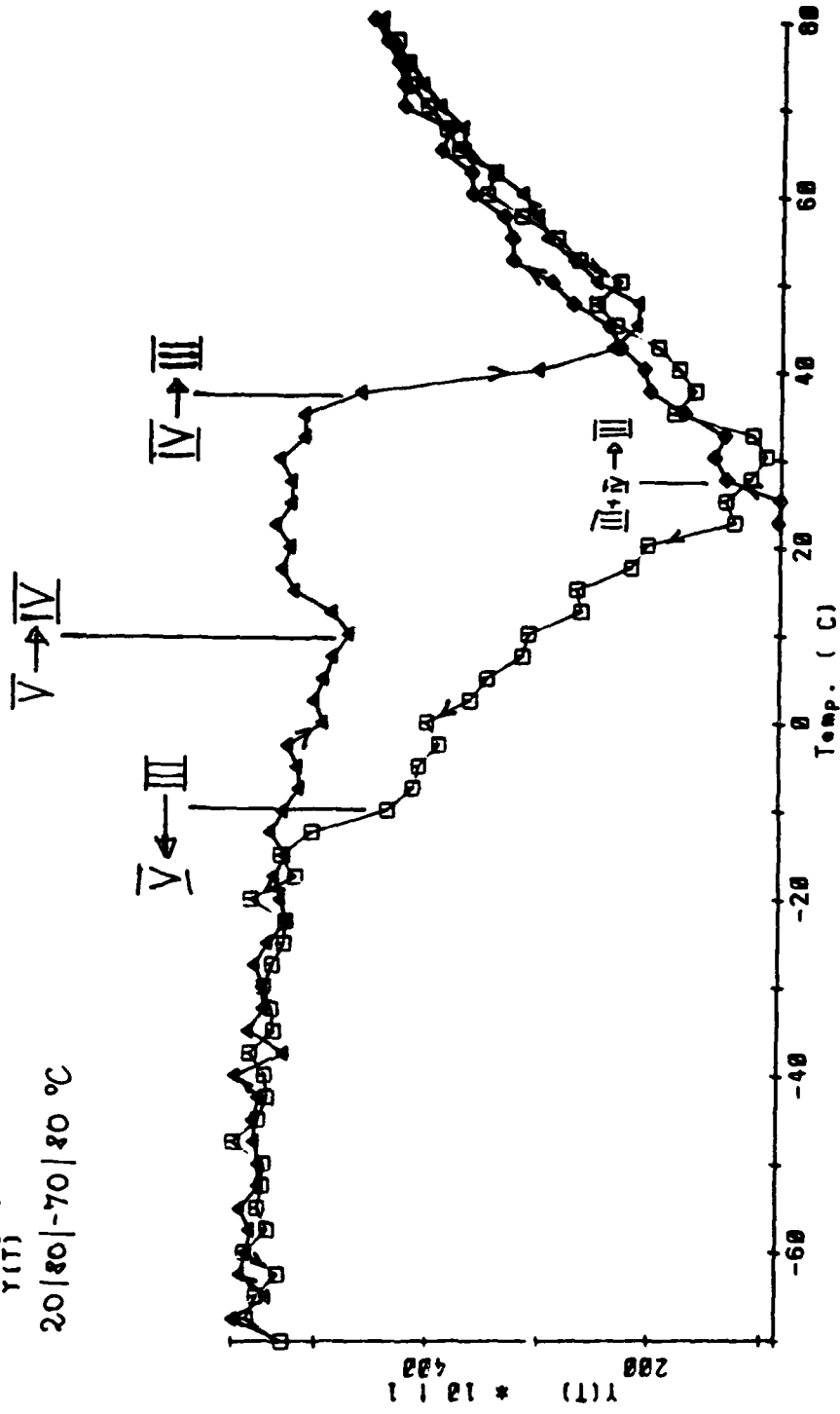
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**Difference Curve**

KF250288  
Y(T)

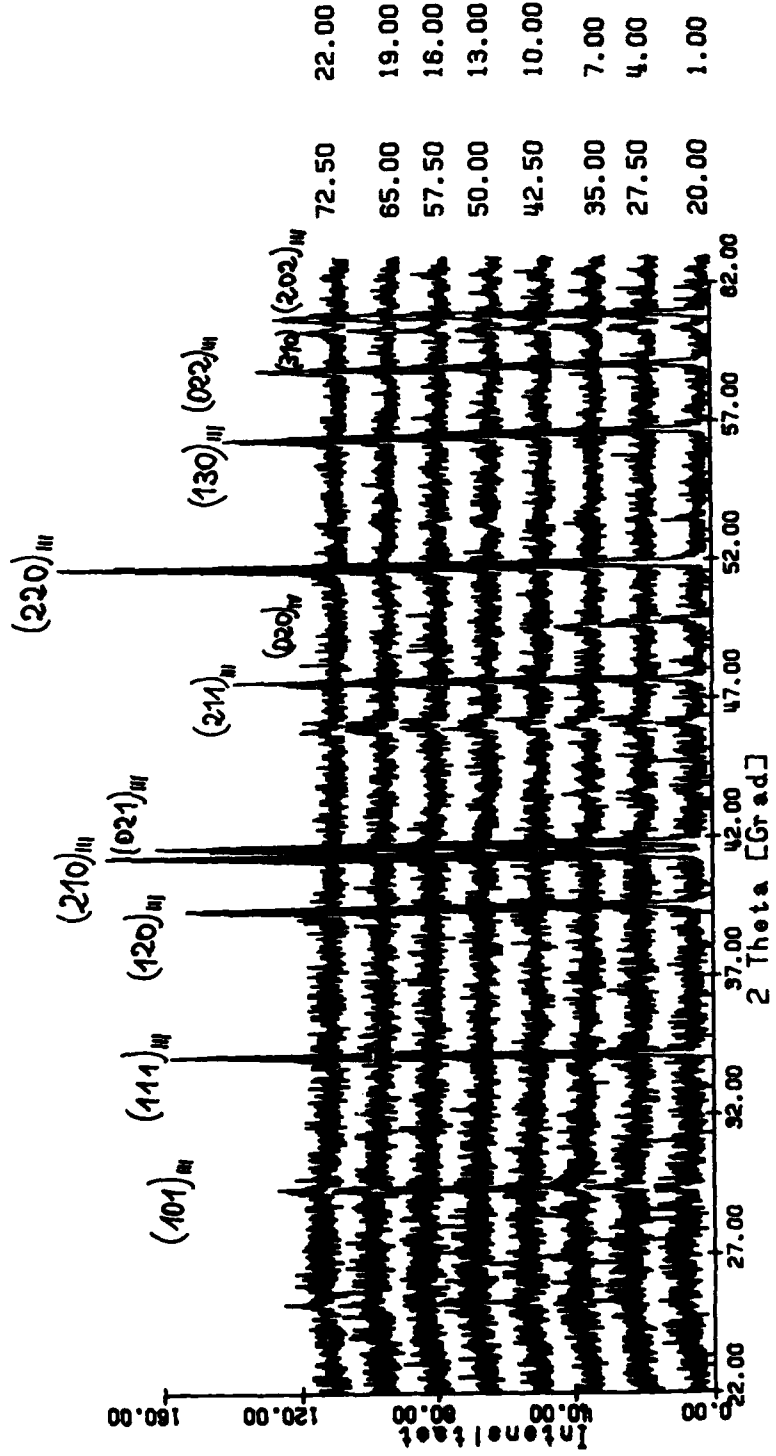
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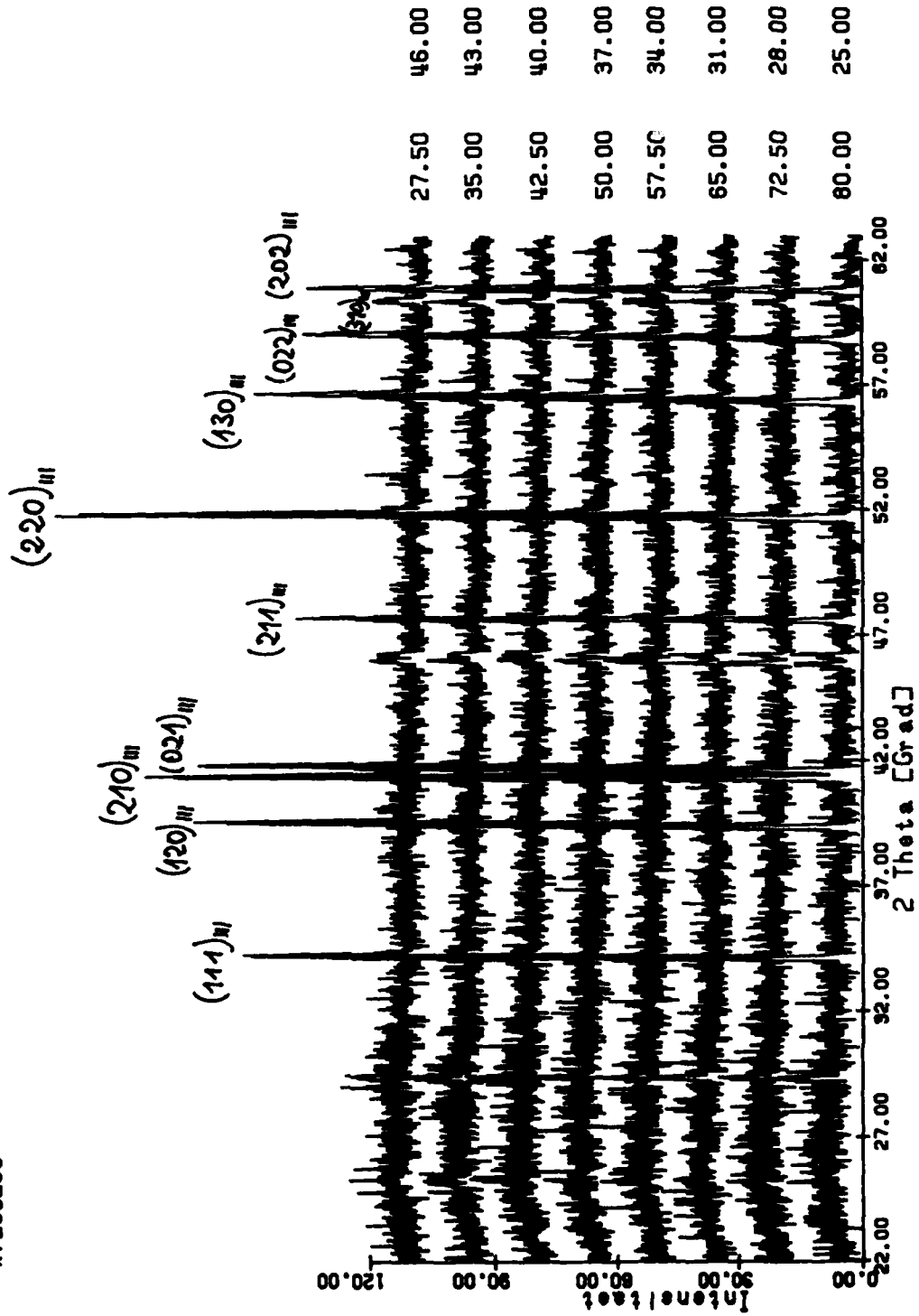
Diffraction Patterns

KF250288

20 | 80 | -70 | 80 °C



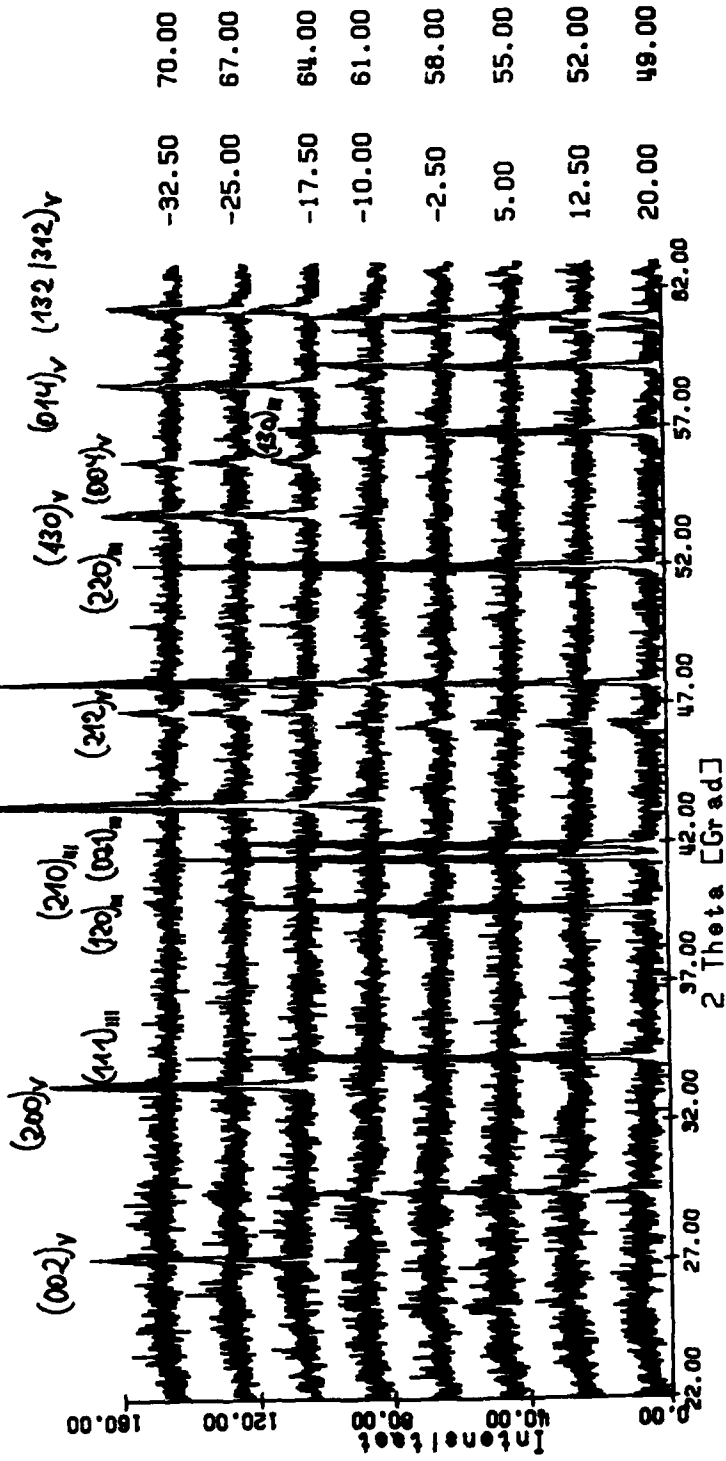
kf250288



kr250288

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(220)<sub>v</sub>



kf250288

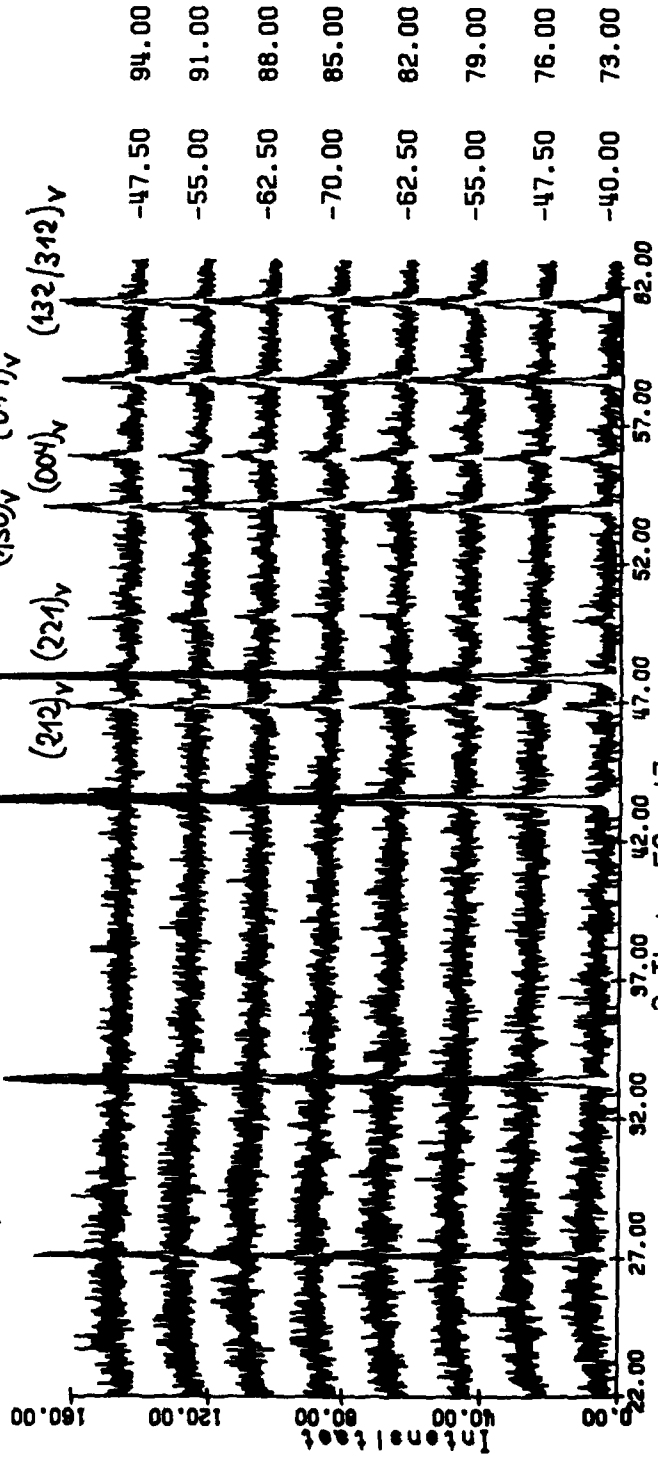
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(002)<sub>v</sub>

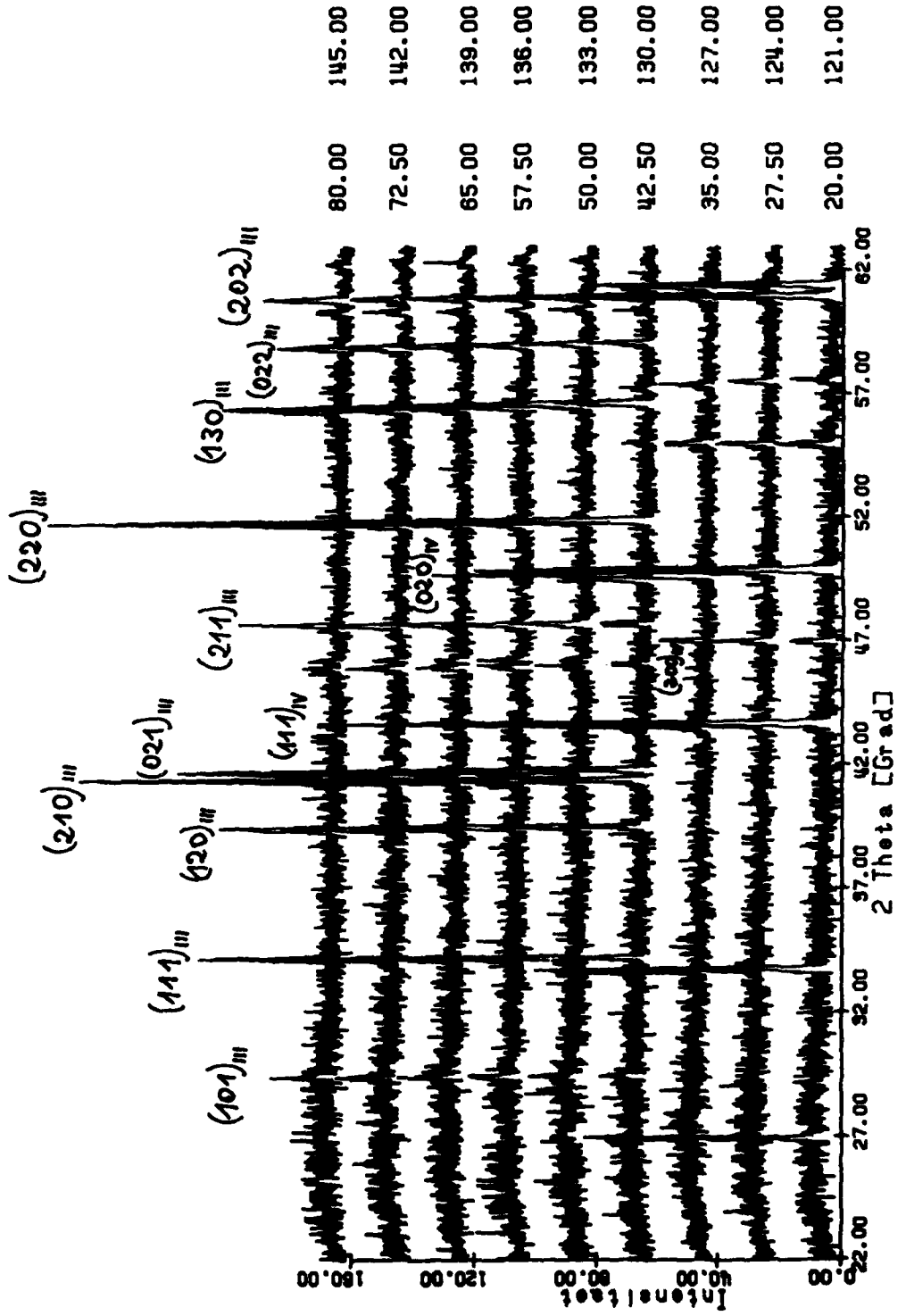
(200)<sub>v</sub>

(212)<sub>v</sub> (221)<sub>v</sub> (130)<sub>v</sub> (014)<sub>v</sub> (132/342)<sub>v</sub>





kf250288



***Series***  
***KF 170388***

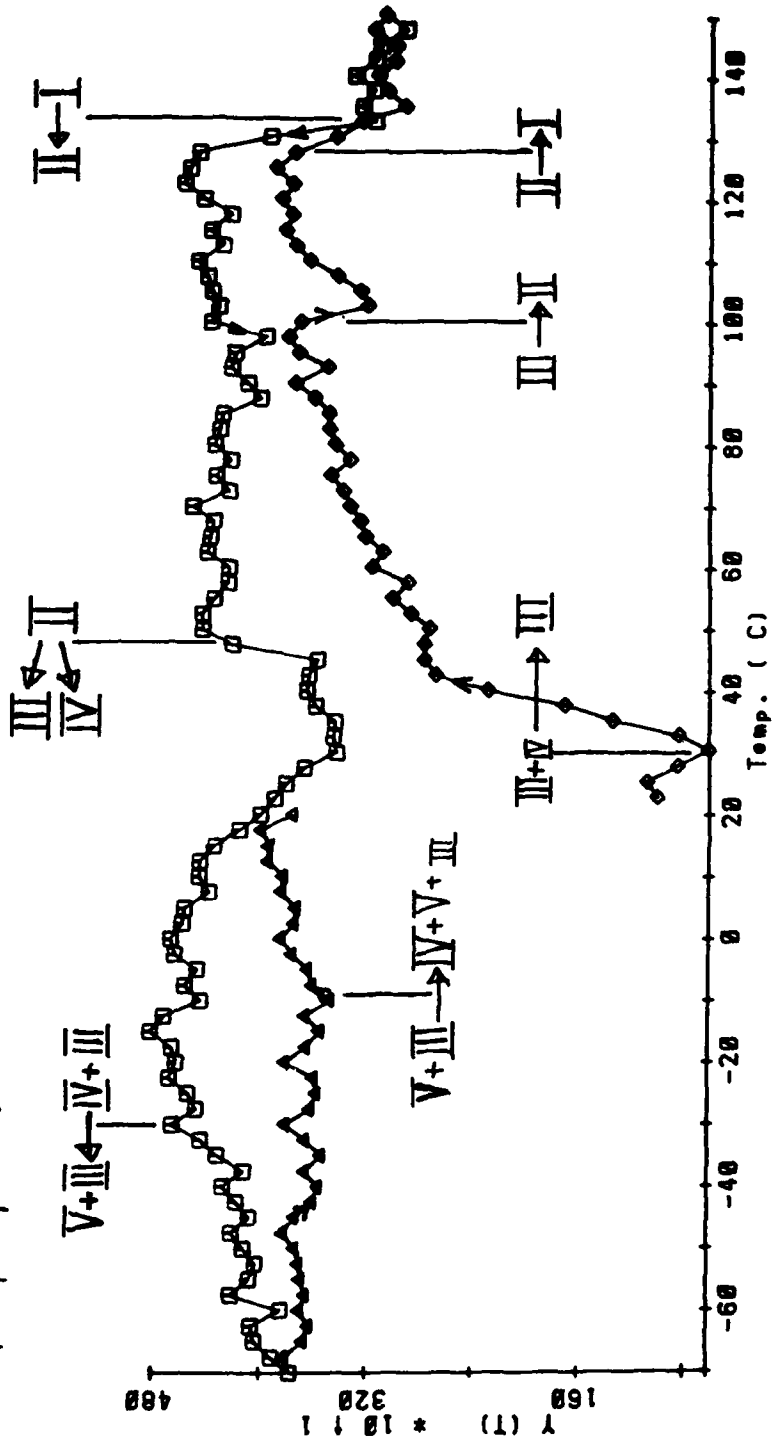
***Temperature***  
***Program***  
***20/150/-70/20***

Difference Curve

KF170388

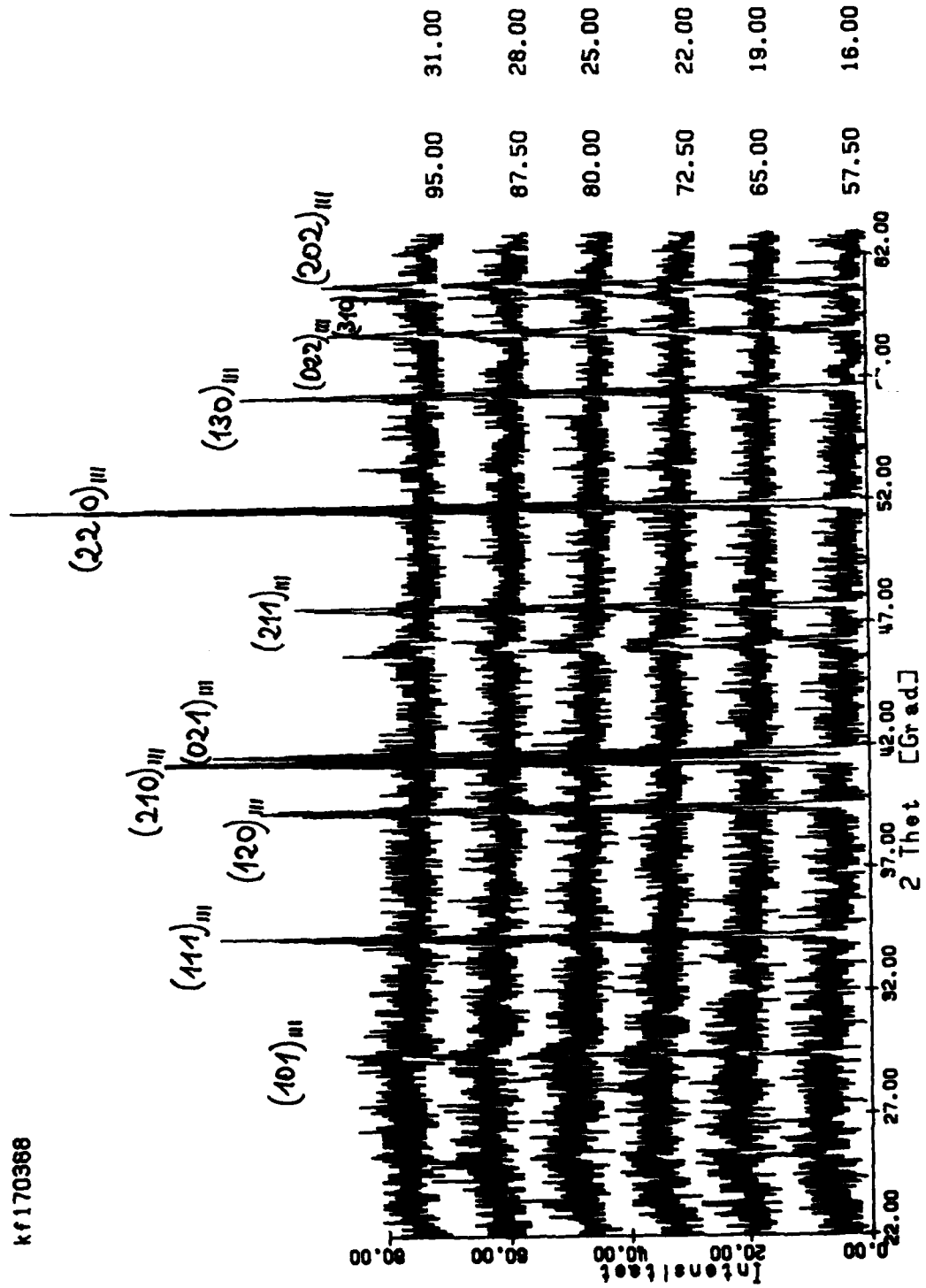
Y (T)

20|450|-70|20 °C

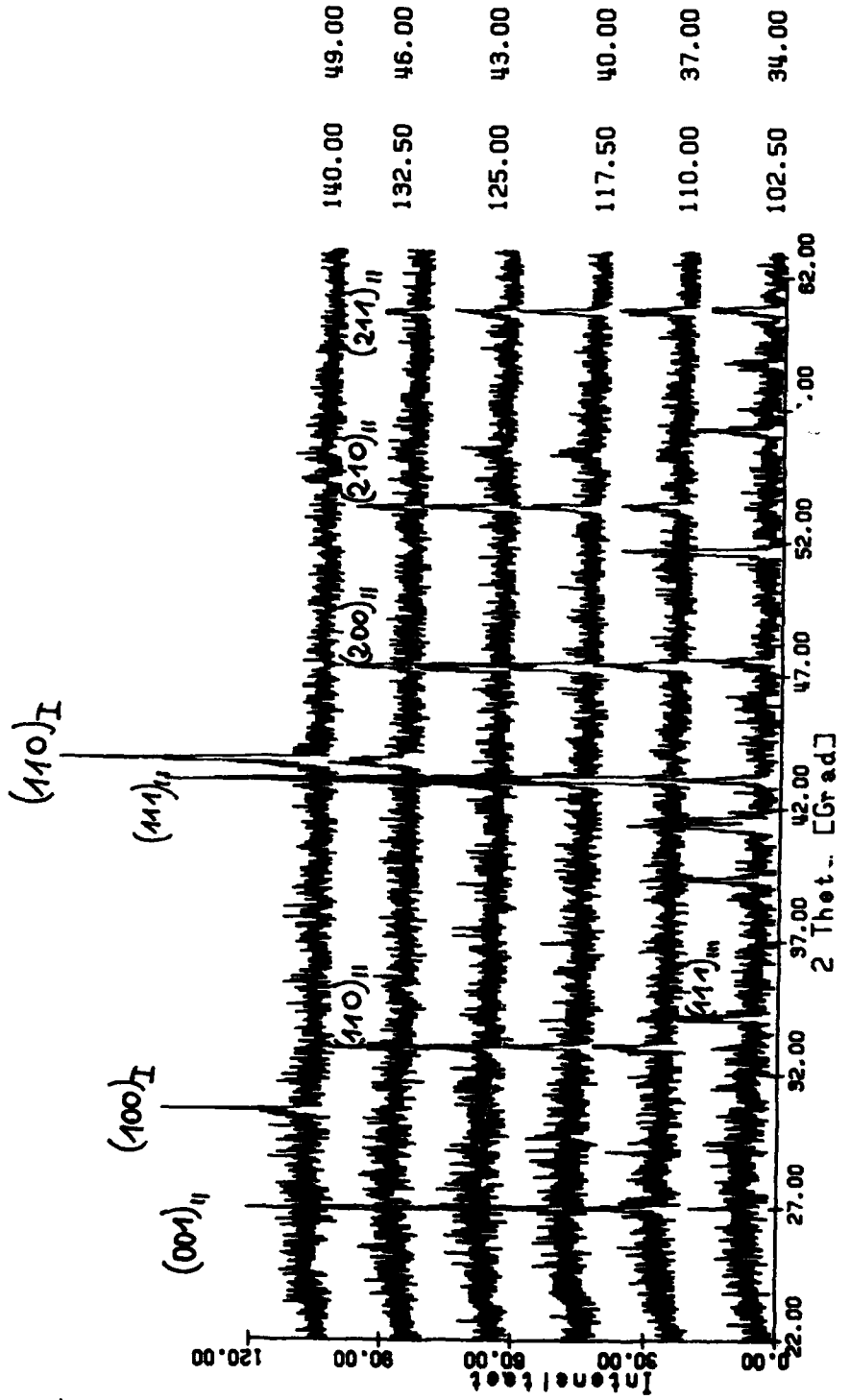




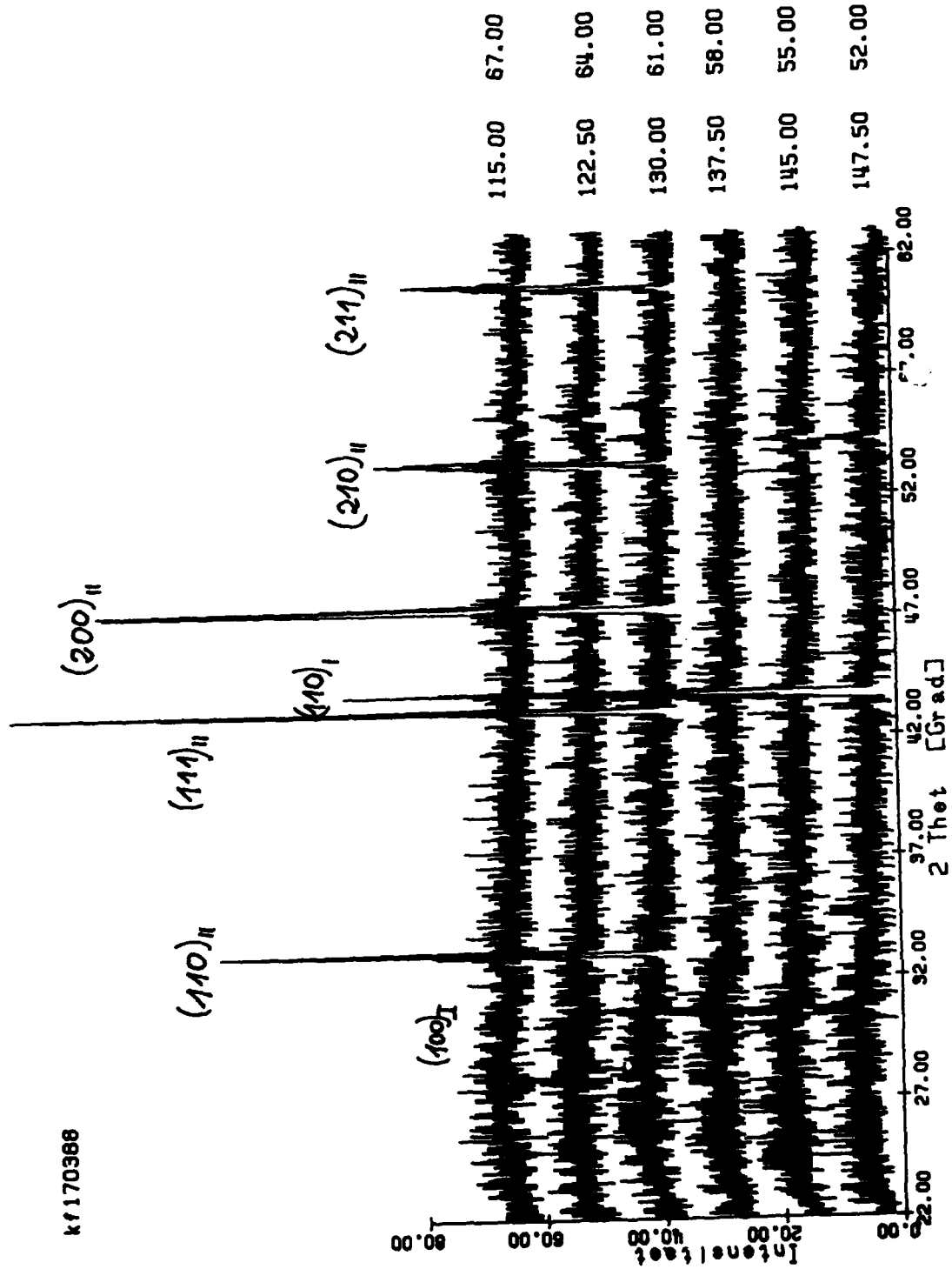
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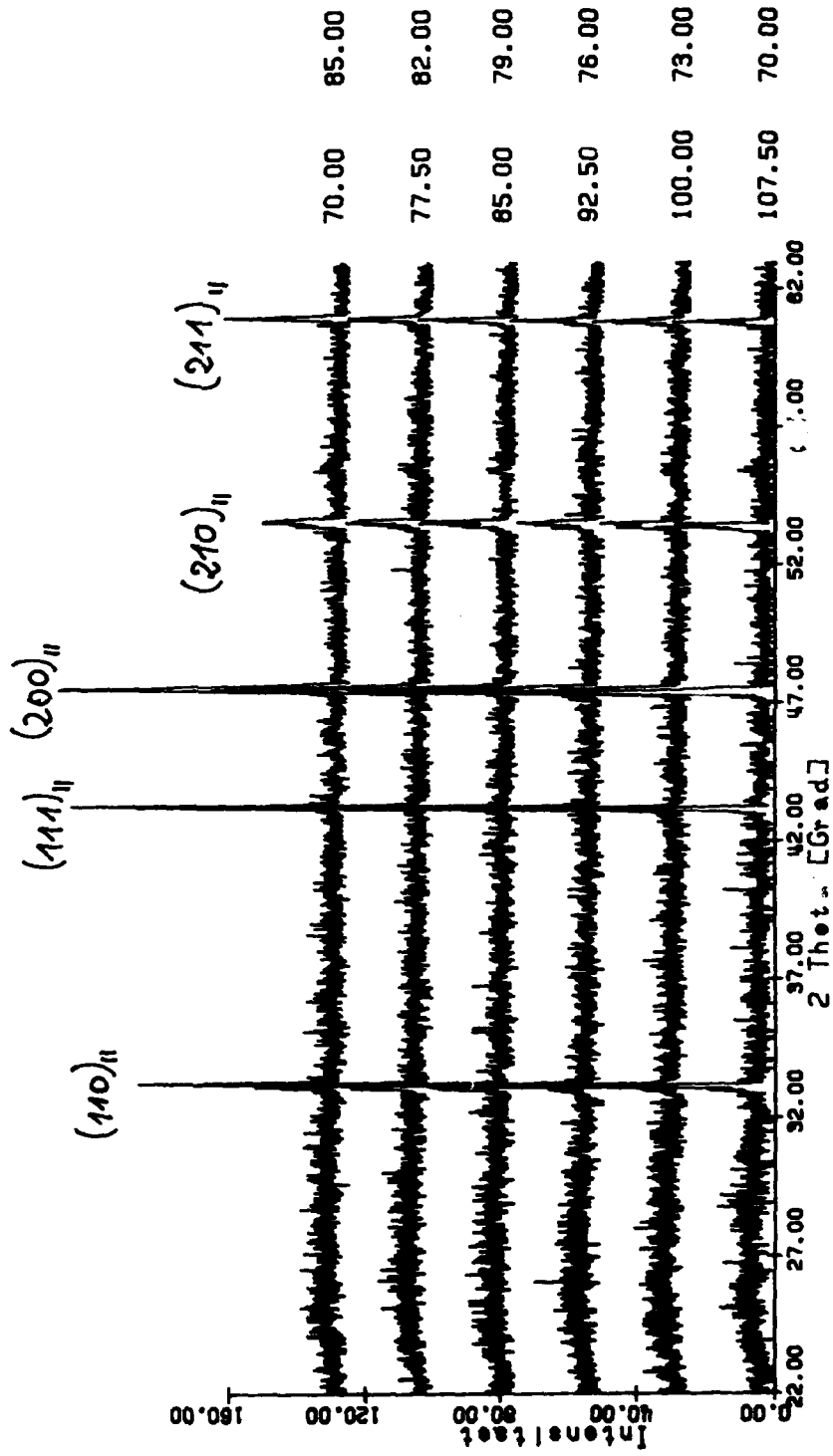
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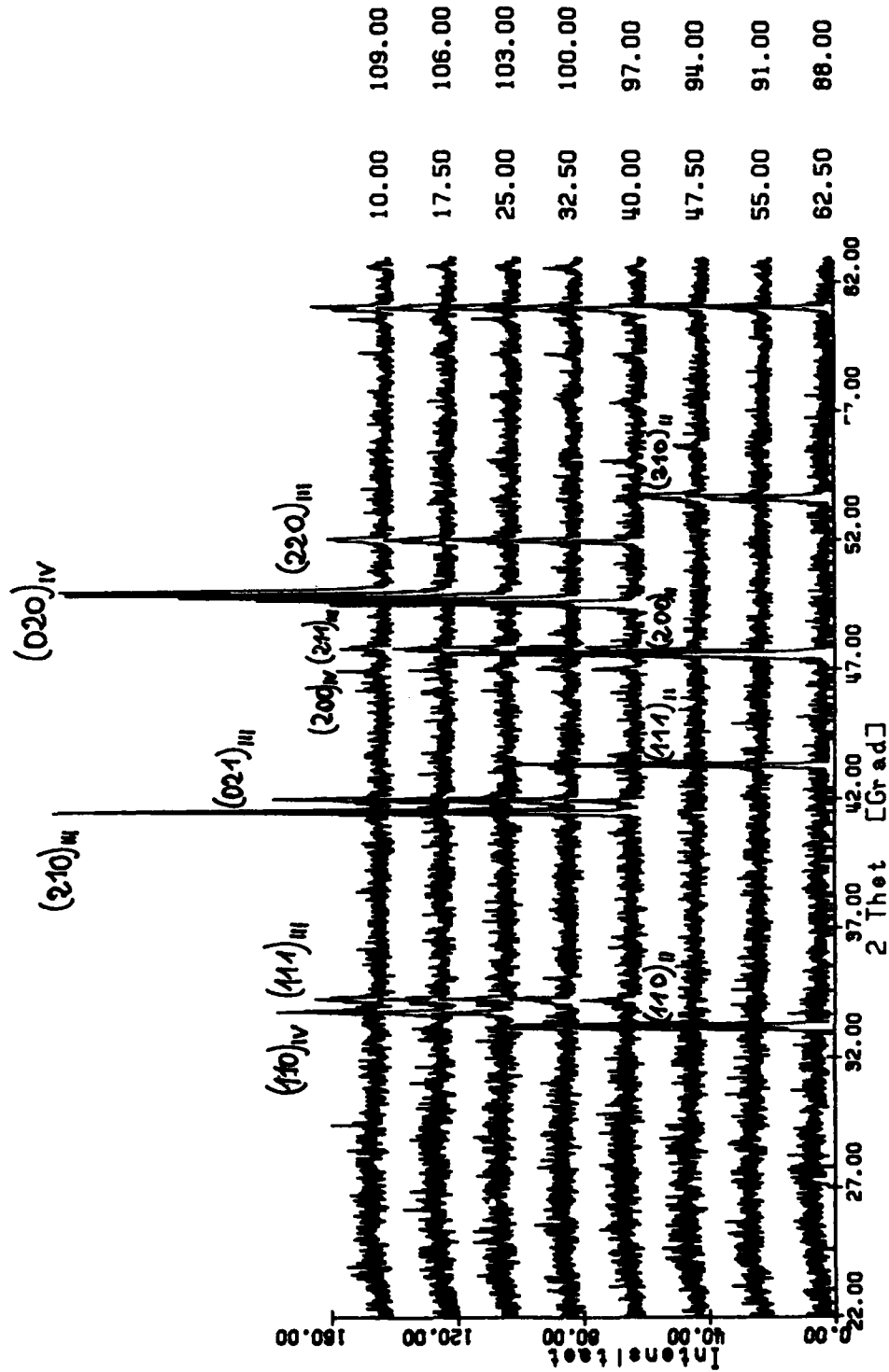
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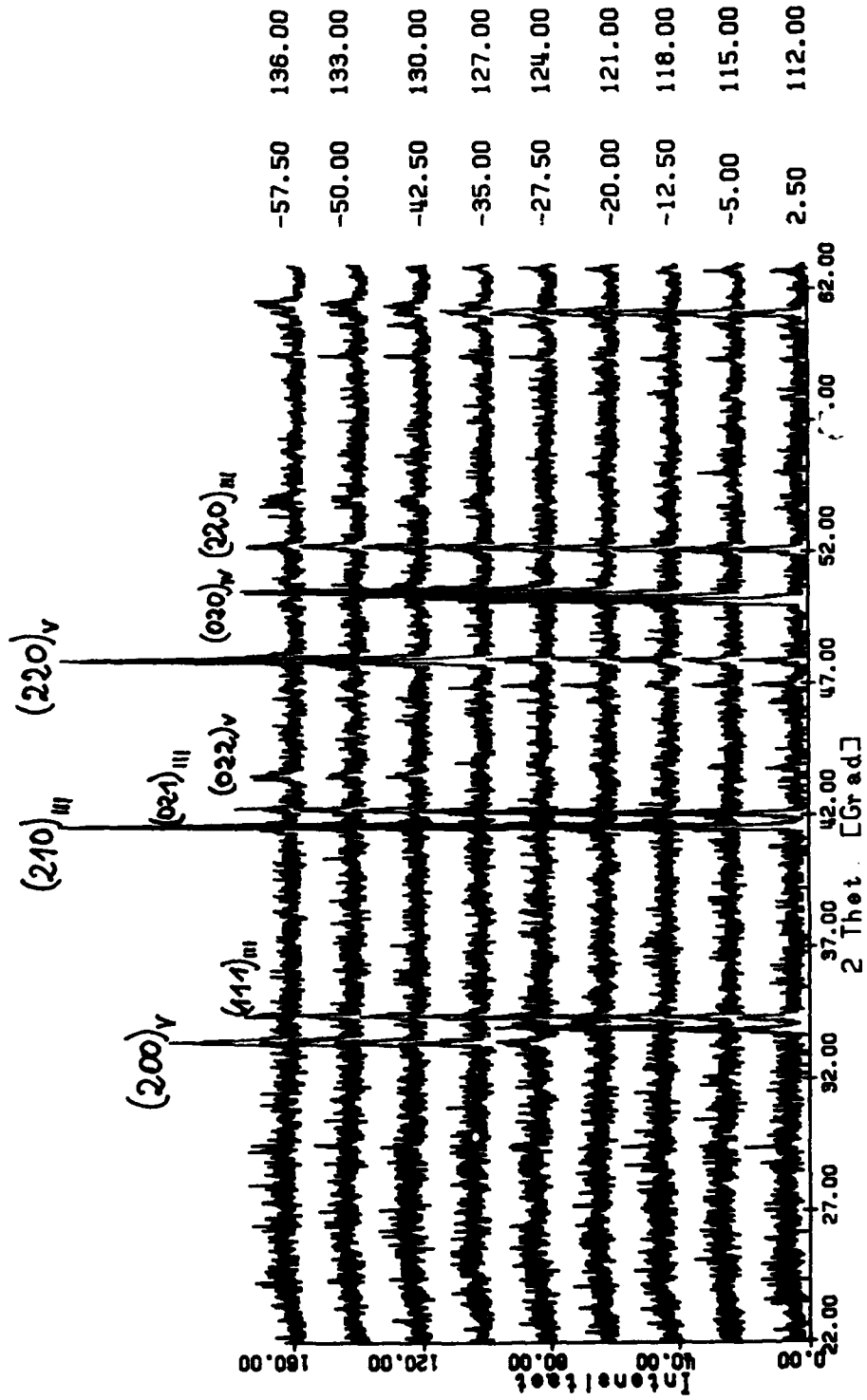
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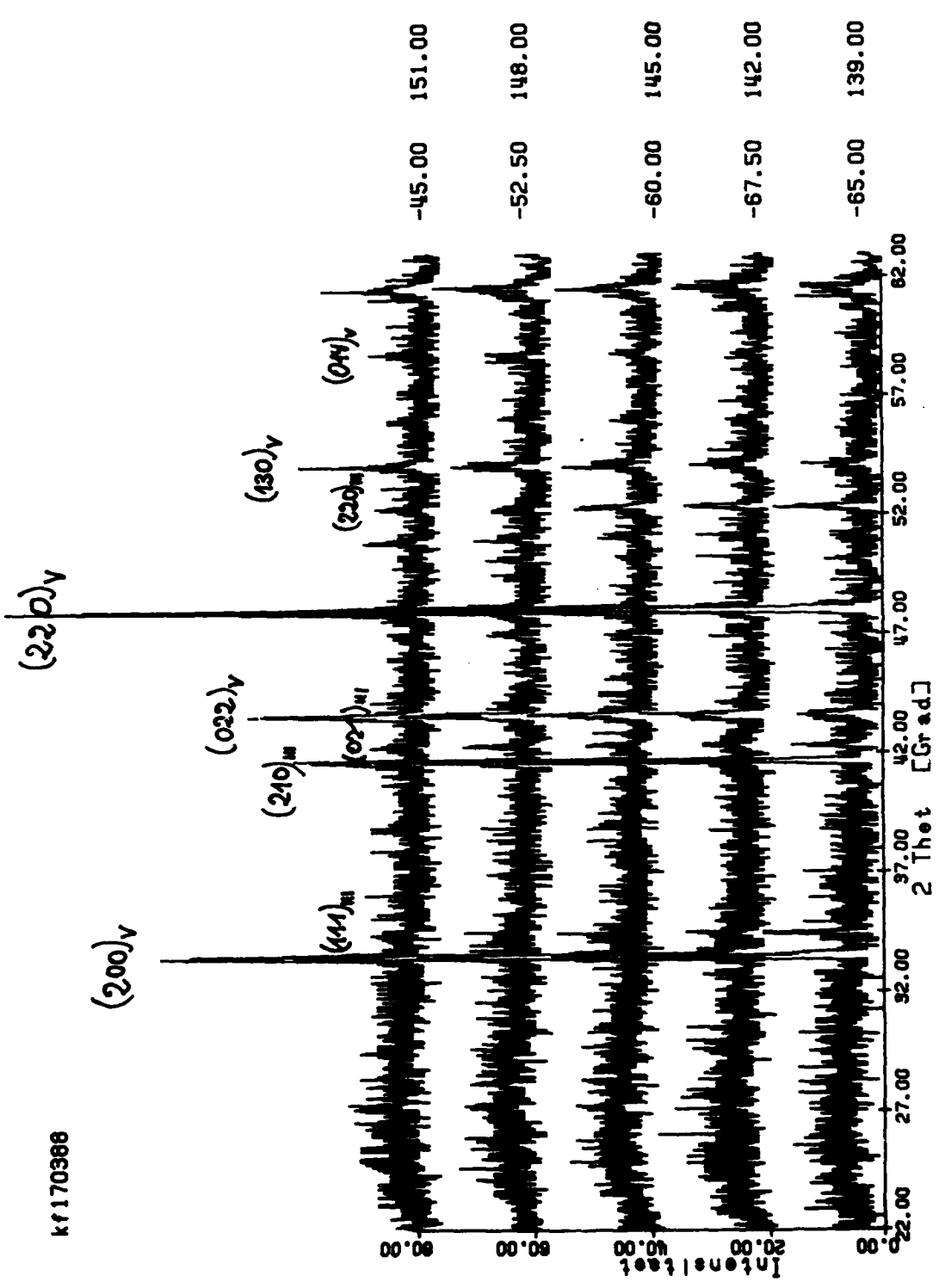
KF170366



kf170388



kf170366



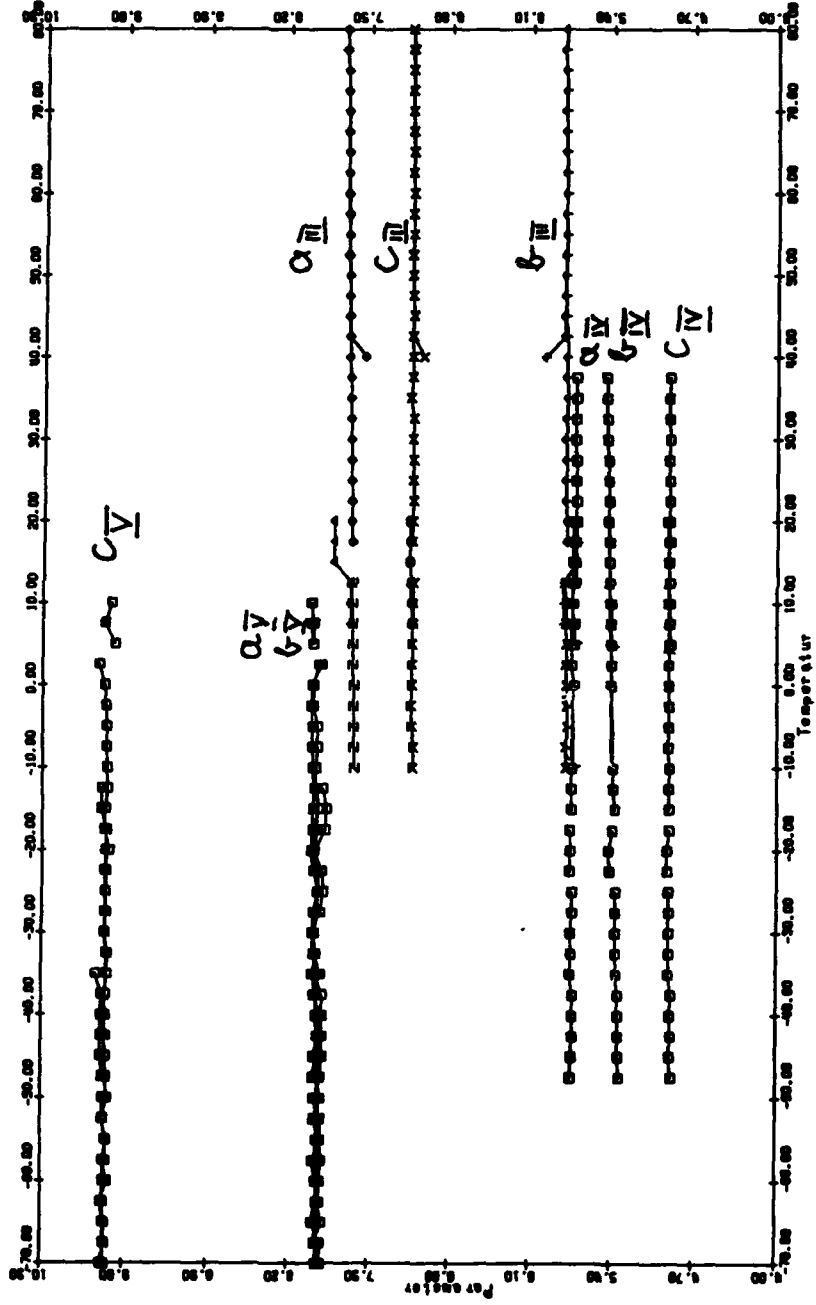


***Series***  
***KF 230388***

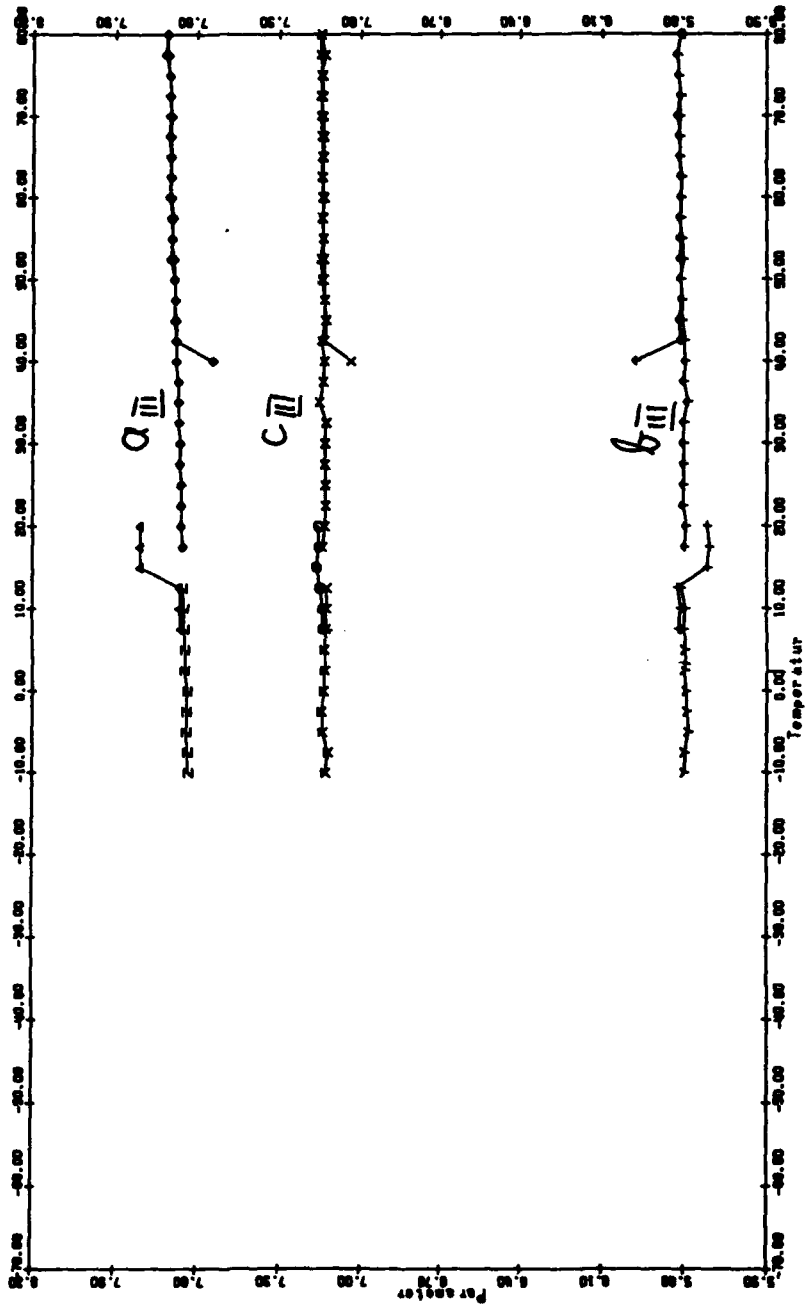
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***Program***  
***20/-70/80/-70***

kF 230388  
20|-70|80|-70

Lattice Parameters

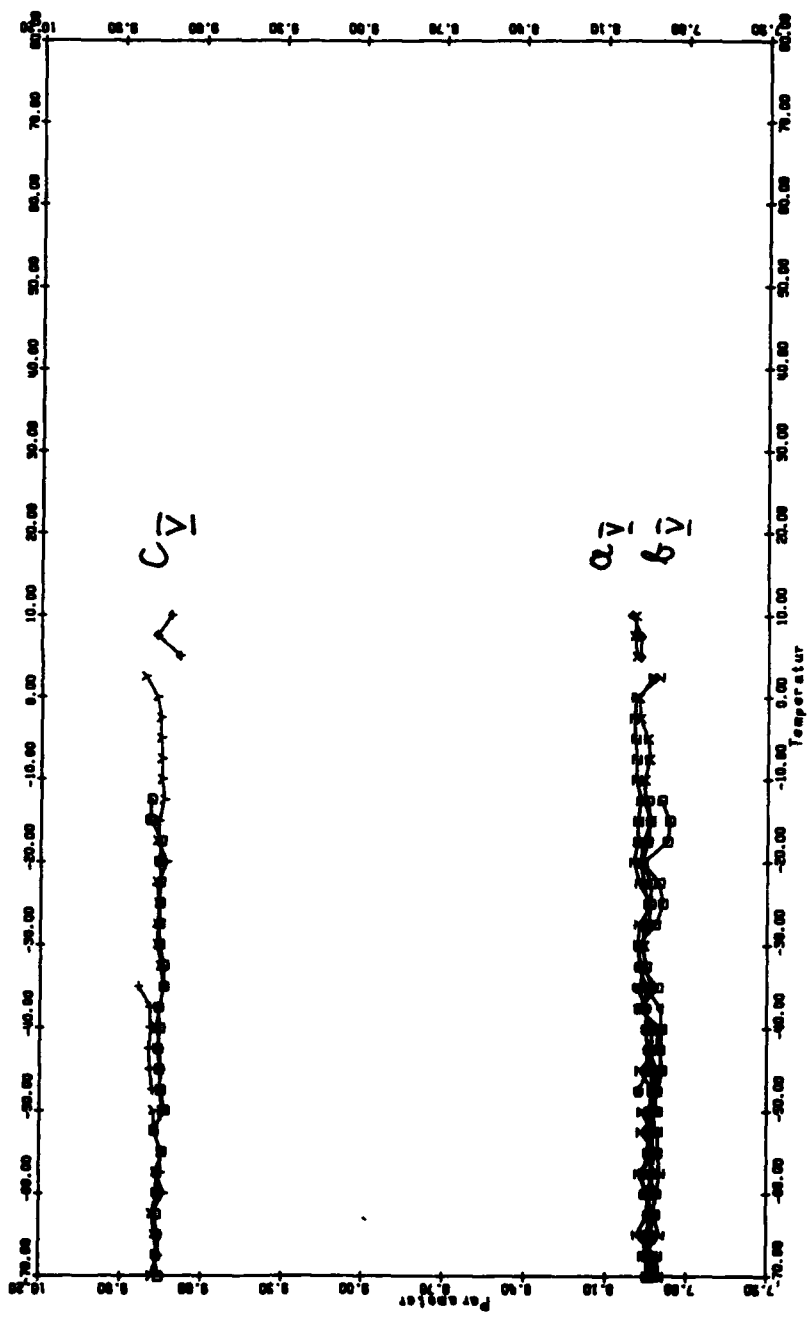


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20/-70/80/-70

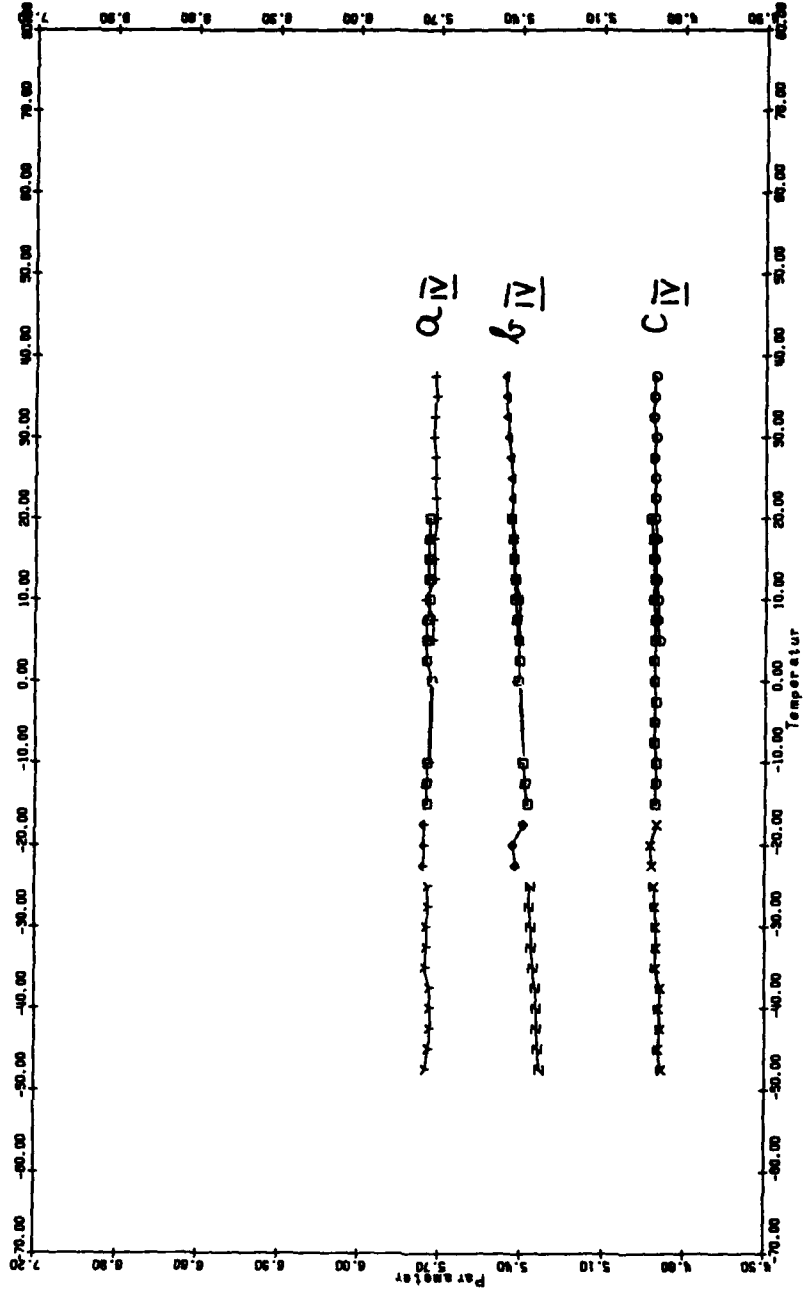


KF 230388  
20|-70|80|-70

Lattice Parameters

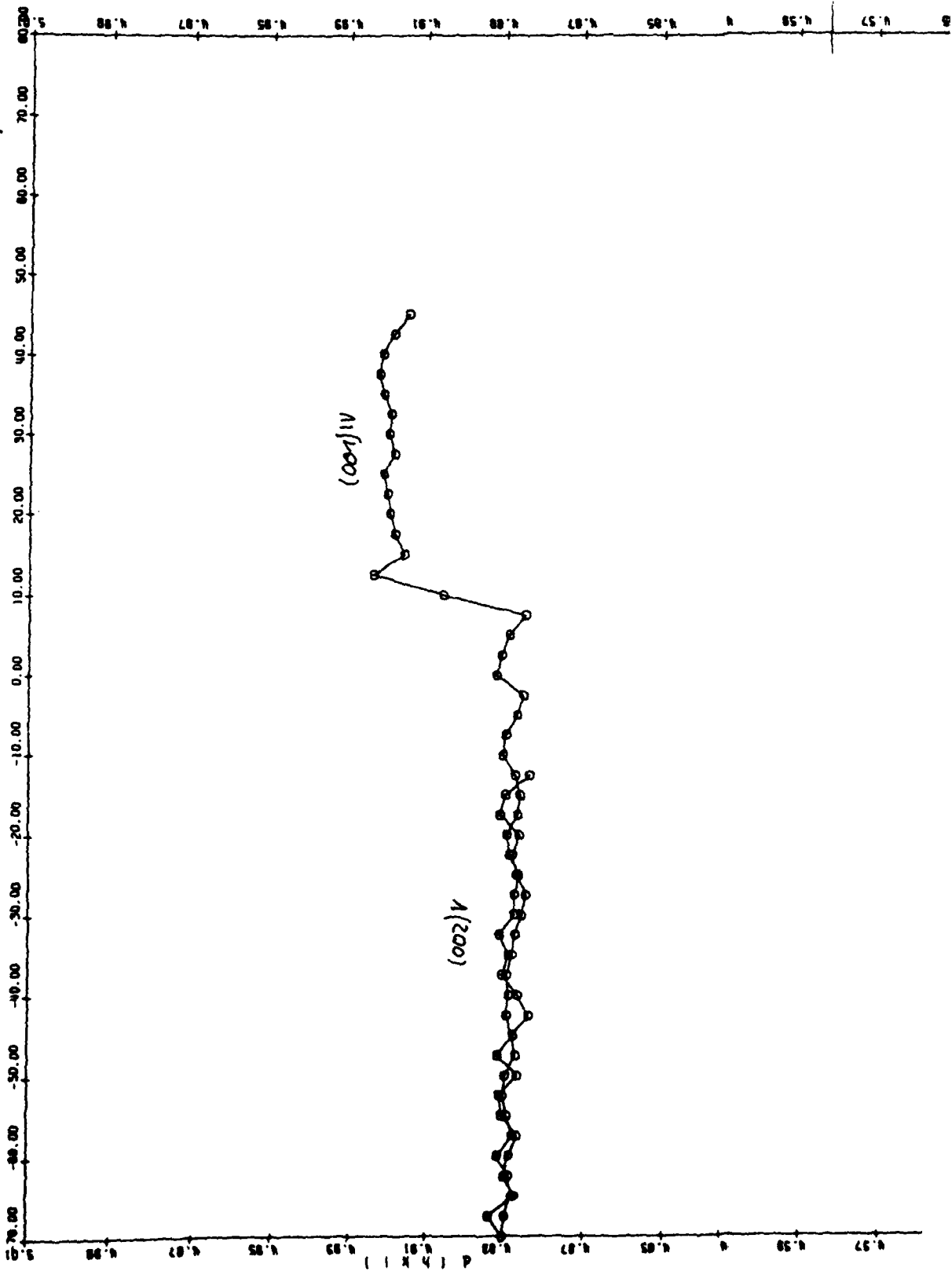


KF 230388  
20|-70|80|-70



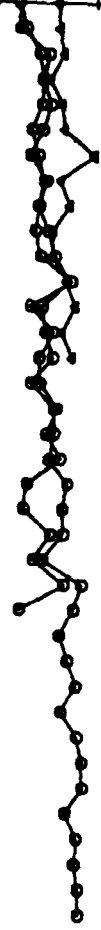
K7250288

Lattice Distances (

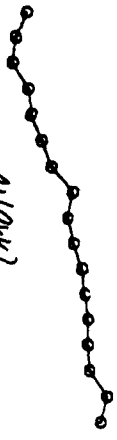


0.91 0.90 0.89 0.88 0.87 0.86 0.85 0.84 0.83 0.82 0.81 0.80 0.79 0.78 0.77 0.76 0.75 0.74 0.73 0.72 0.71 0.70 0.69 0.68 0.67 0.66 0.65 0.64 0.63 0.62 0.61 0.60 0.59 0.58 0.57 0.56 0.55 0.54 0.53

(100) III



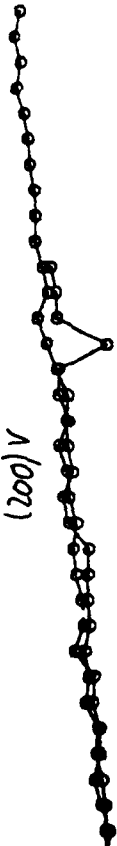
(110) IV



(111) III

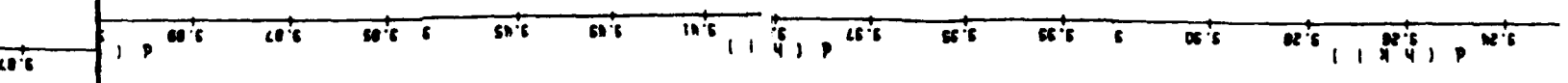
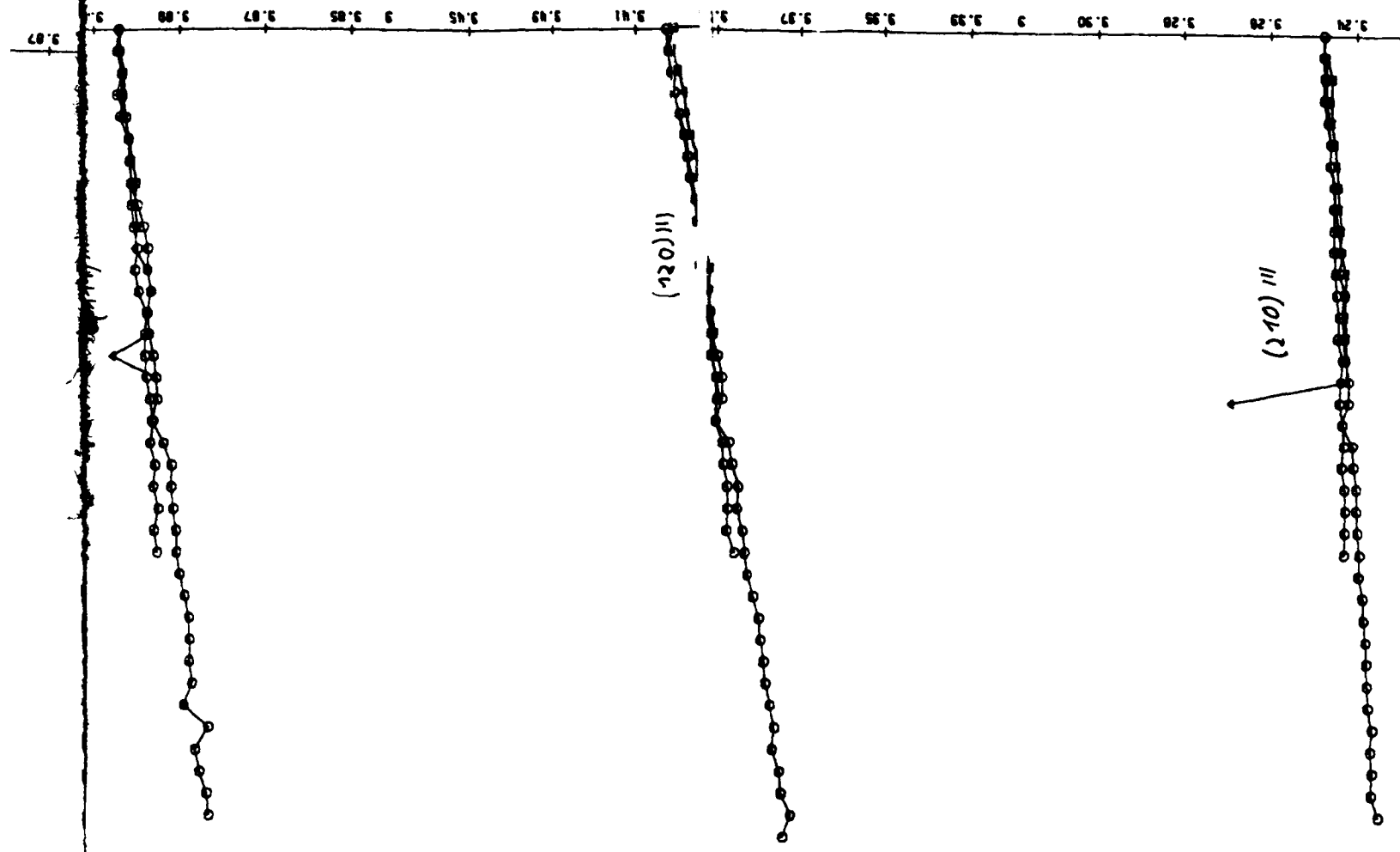


(200) V

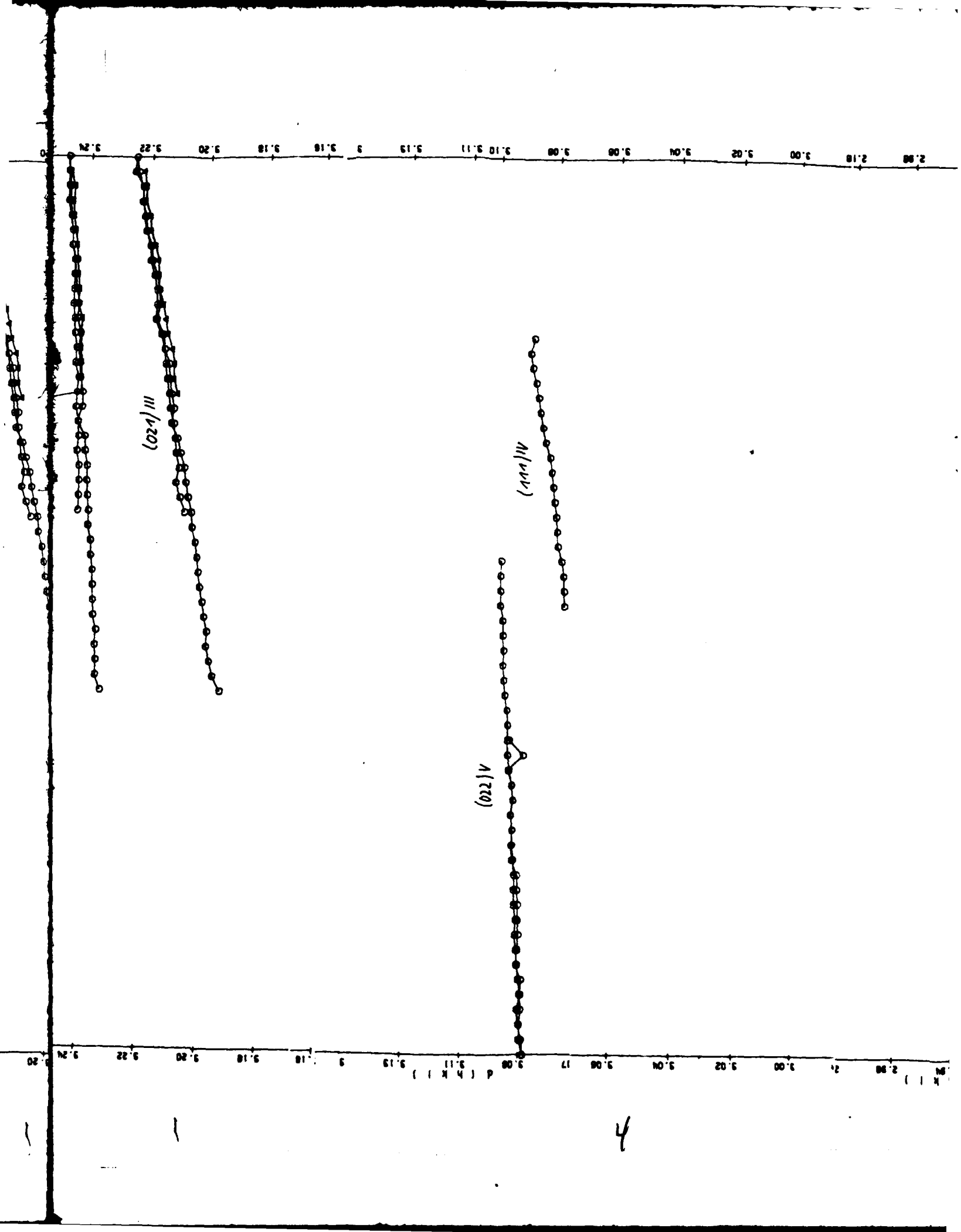


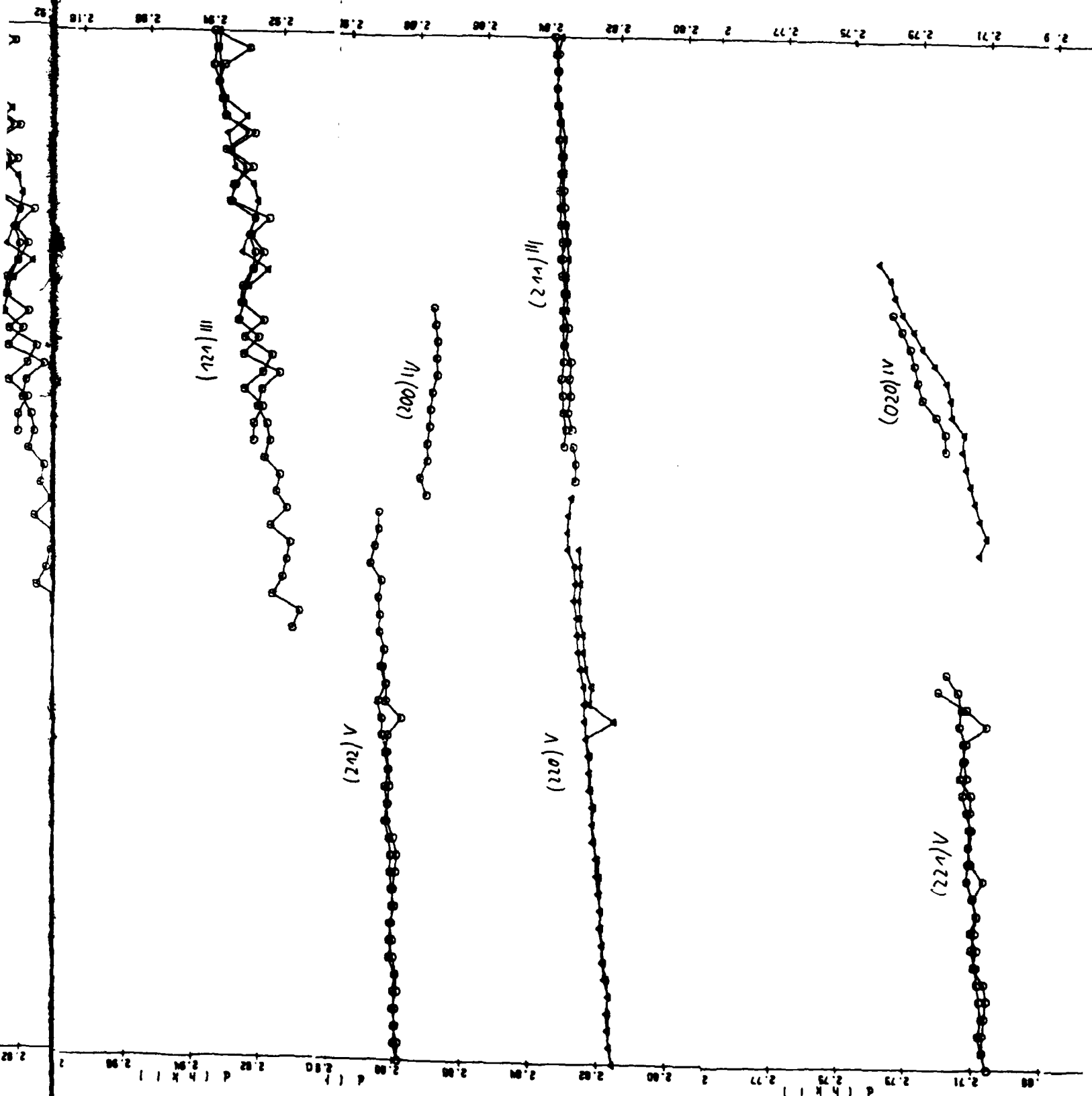
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2



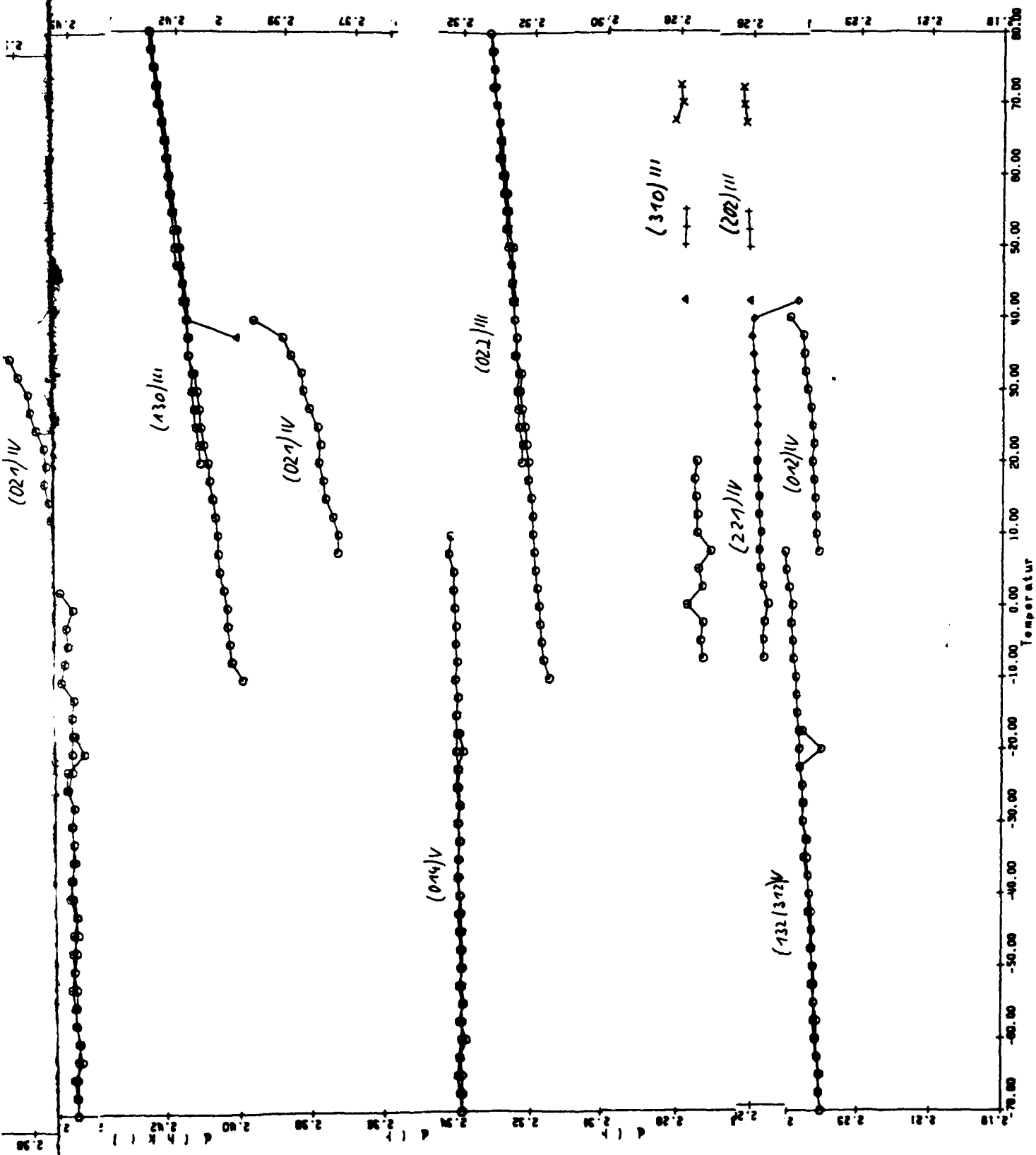
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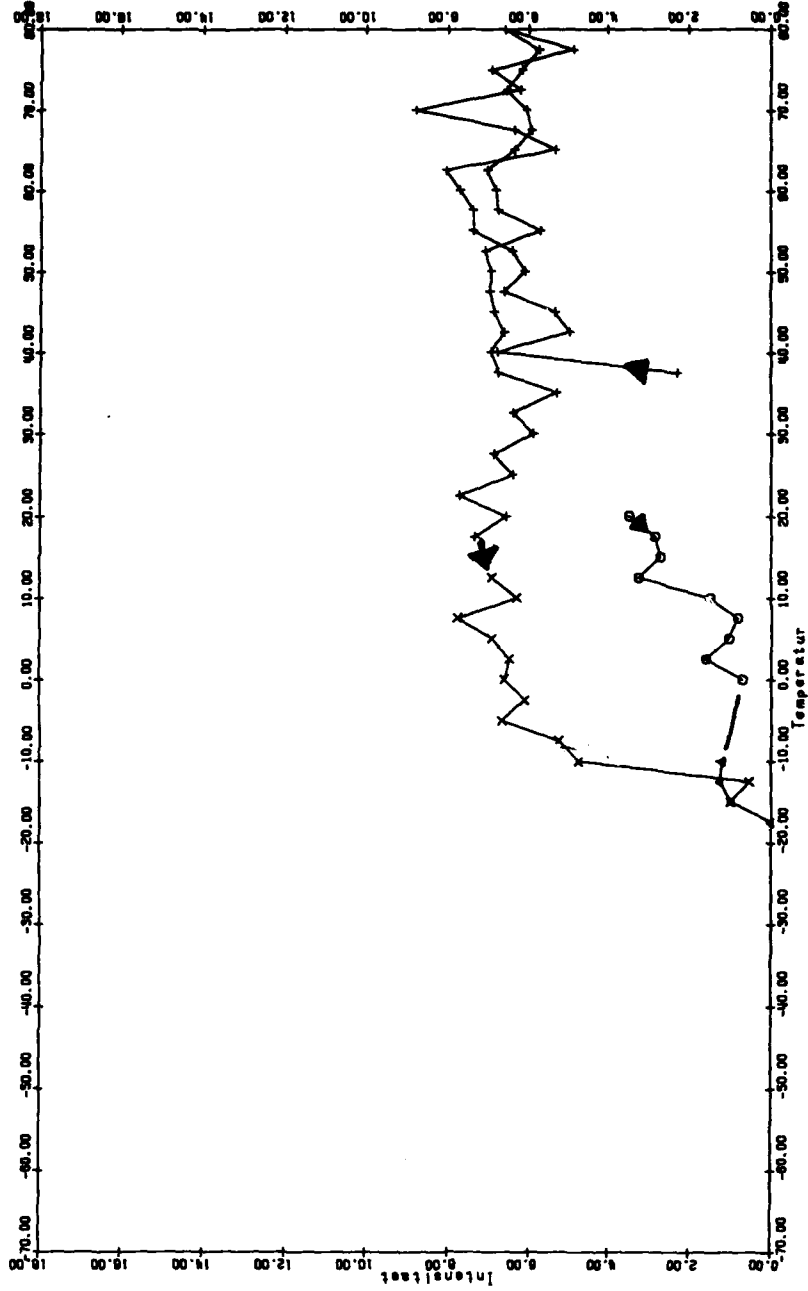
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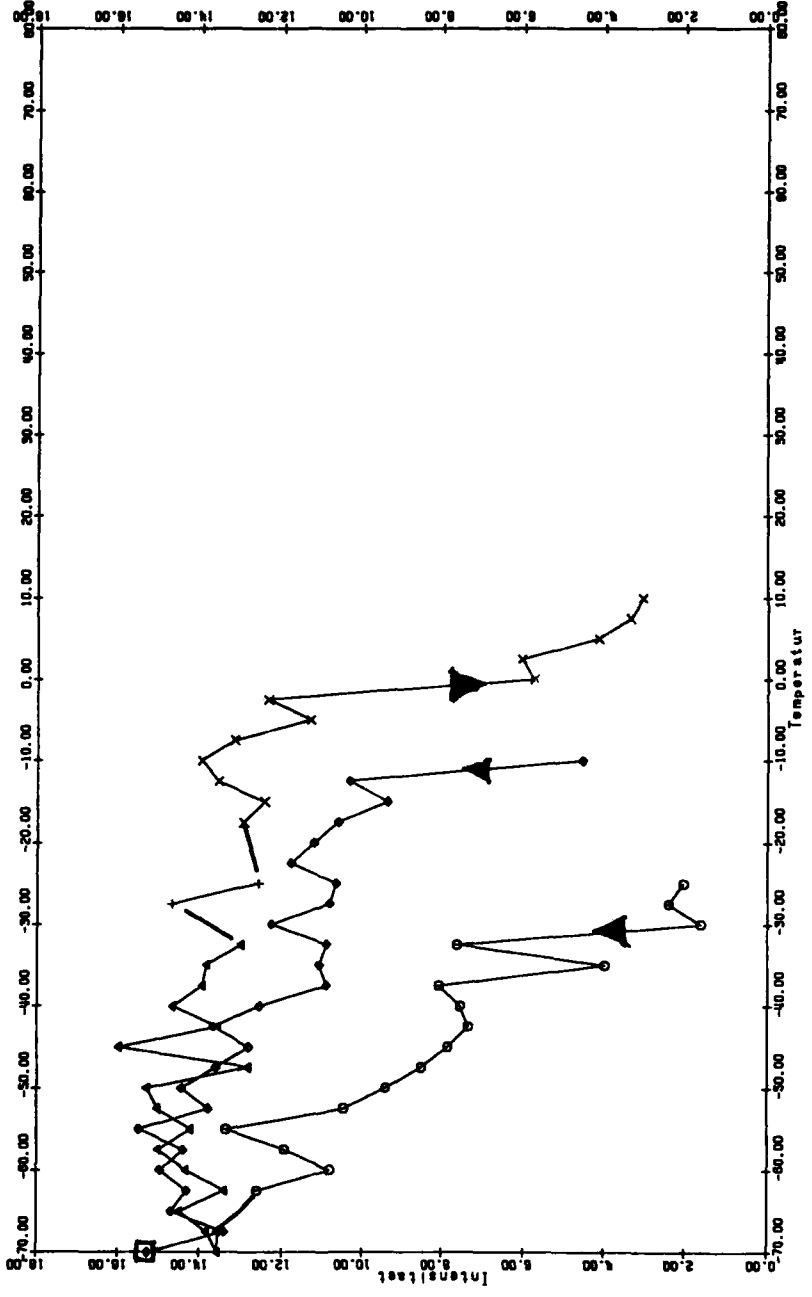
kF 230388

Intensities (220) III



KF 230388

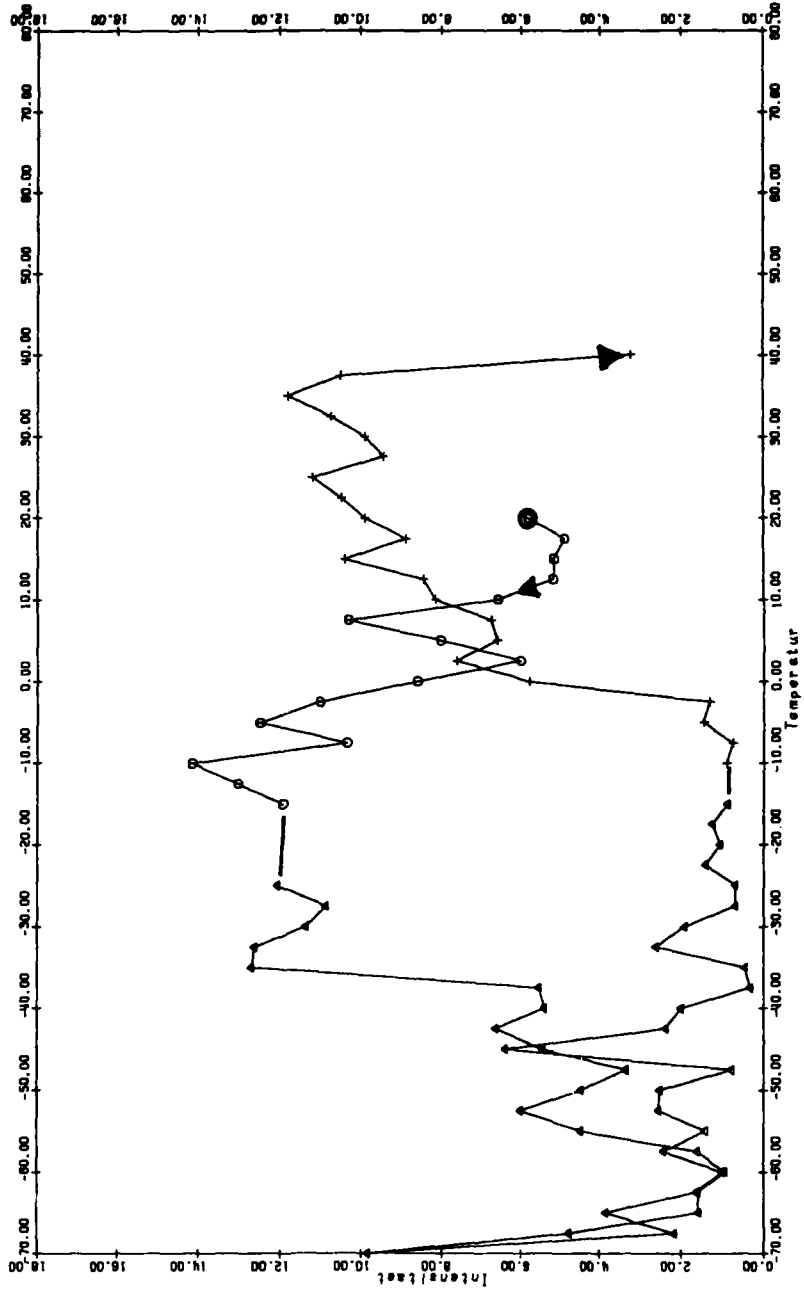
Intensities  
(022)<sub>V</sub>  
(111)<sub>II</sub>



KF 2303 88

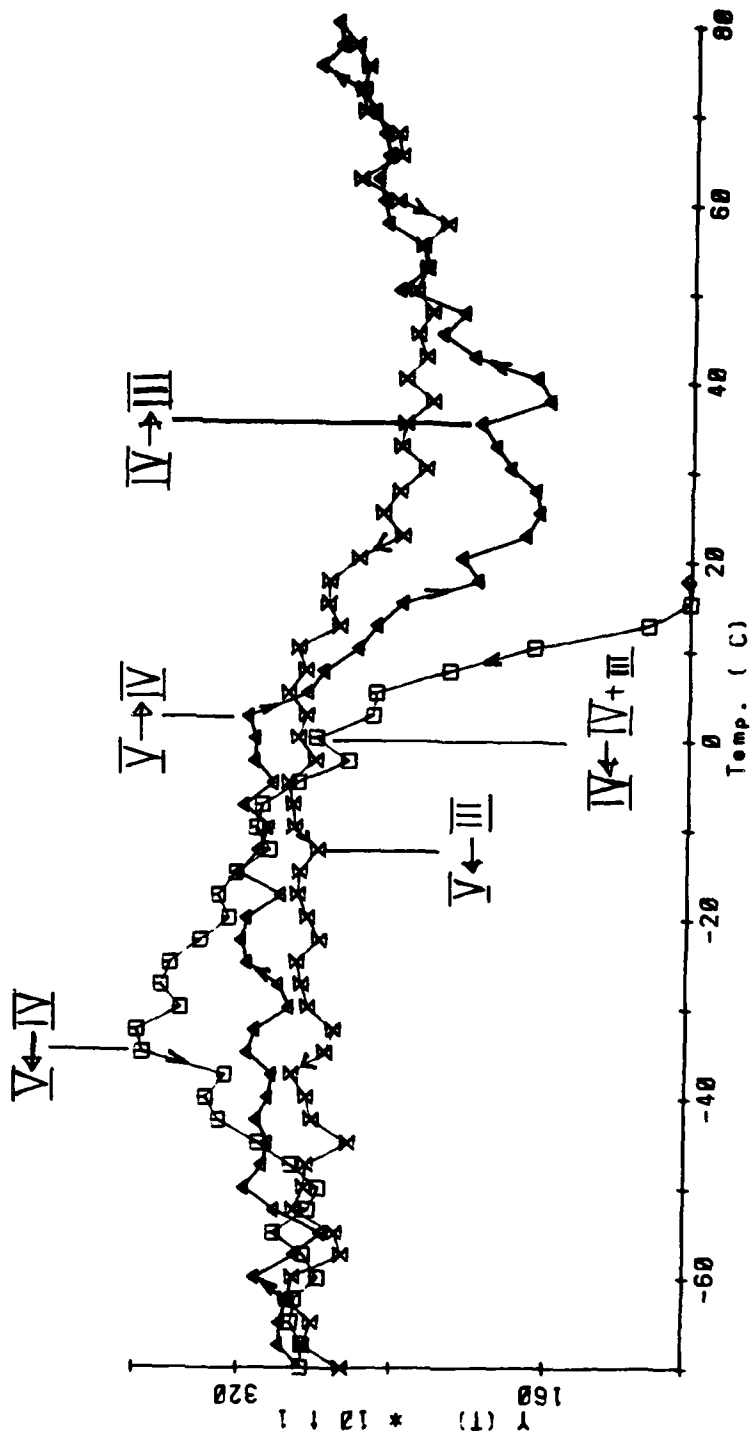
(020) IV

Intensities



Difference Curve

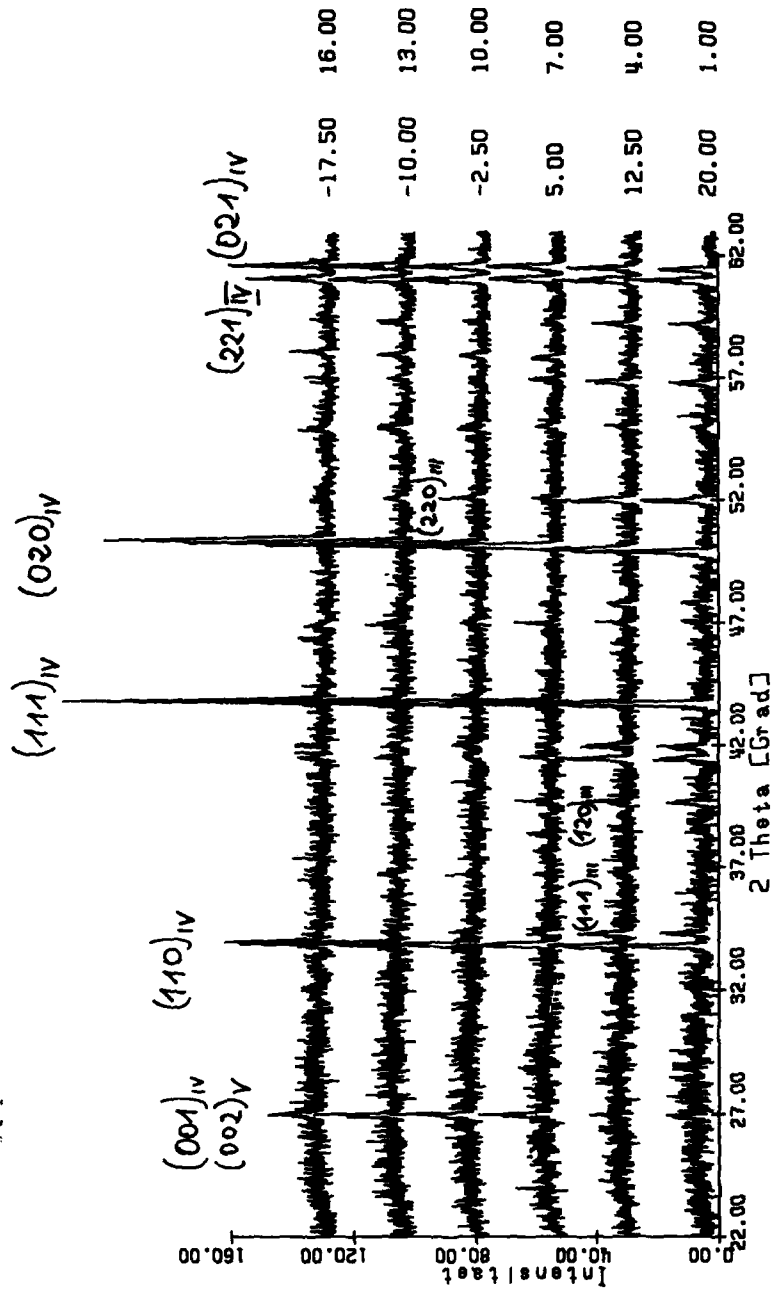
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Y (T)



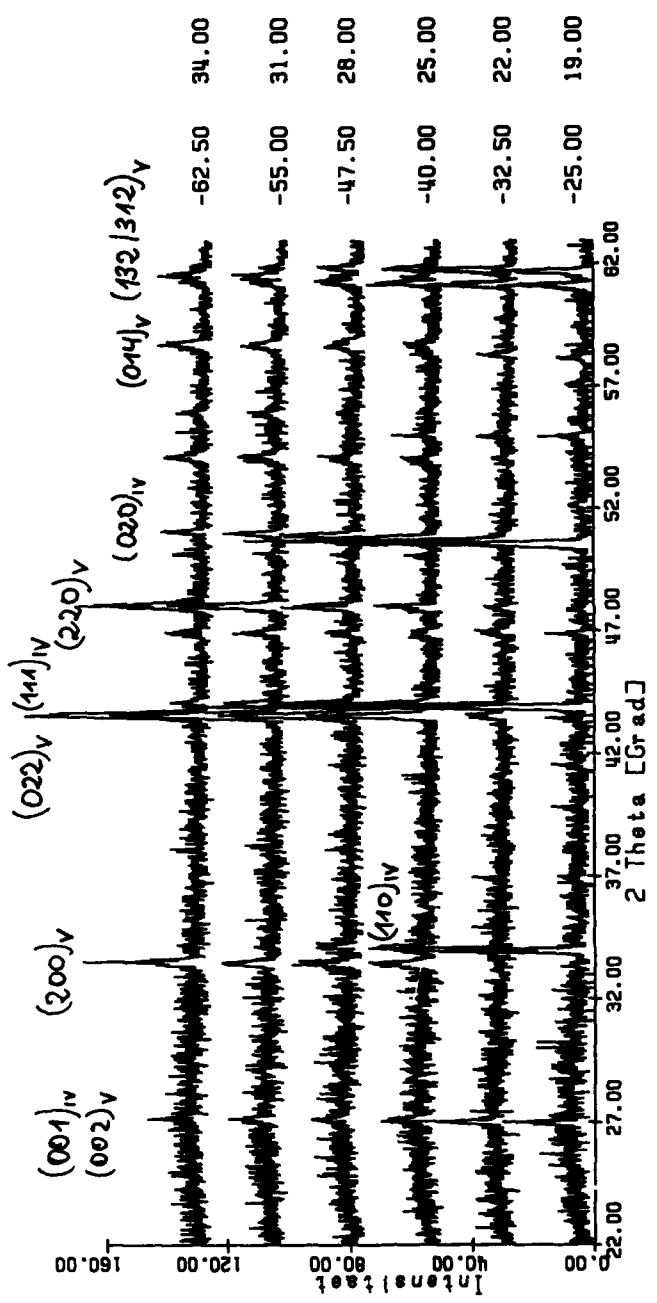
kf230388

20/-70/80/-70 °C

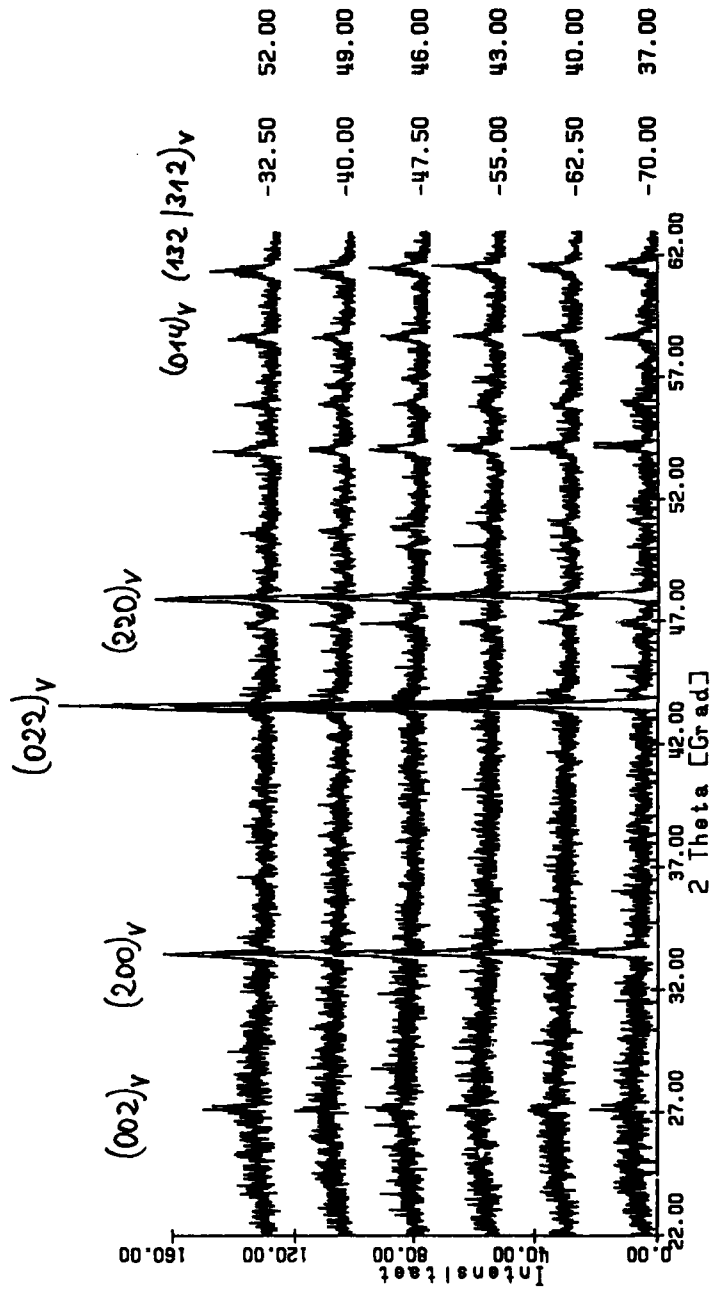
Diffraction Patterns



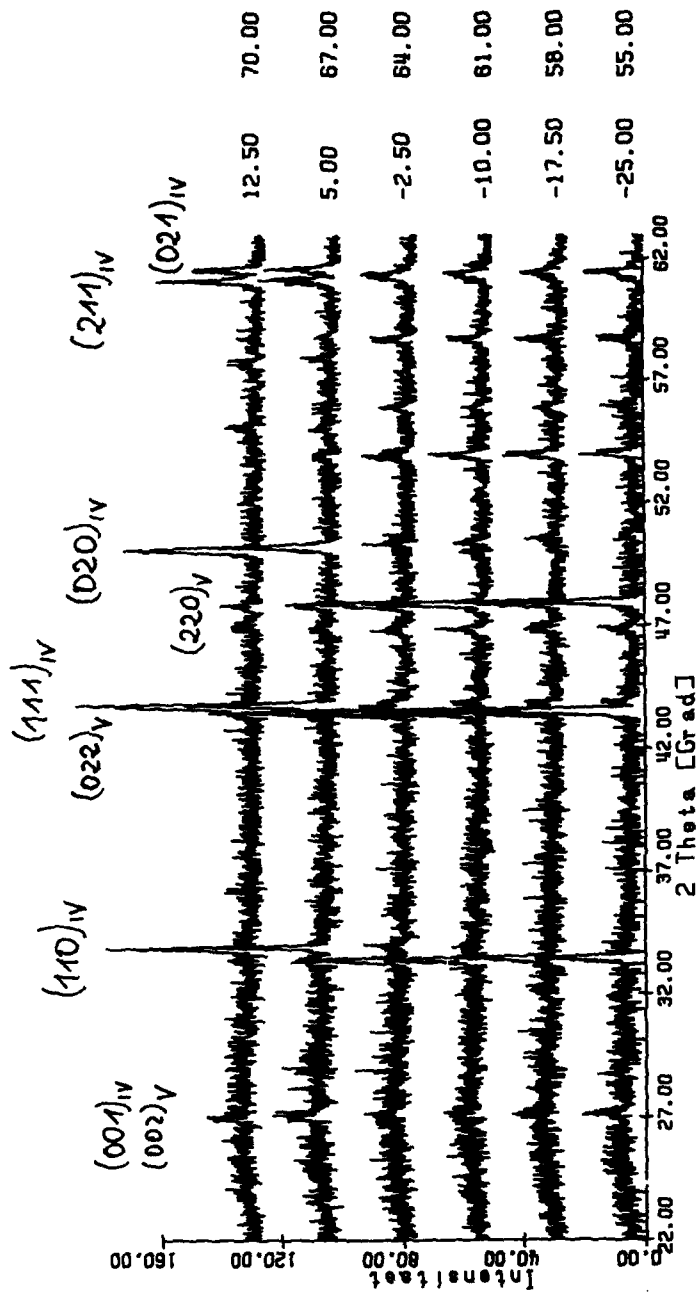
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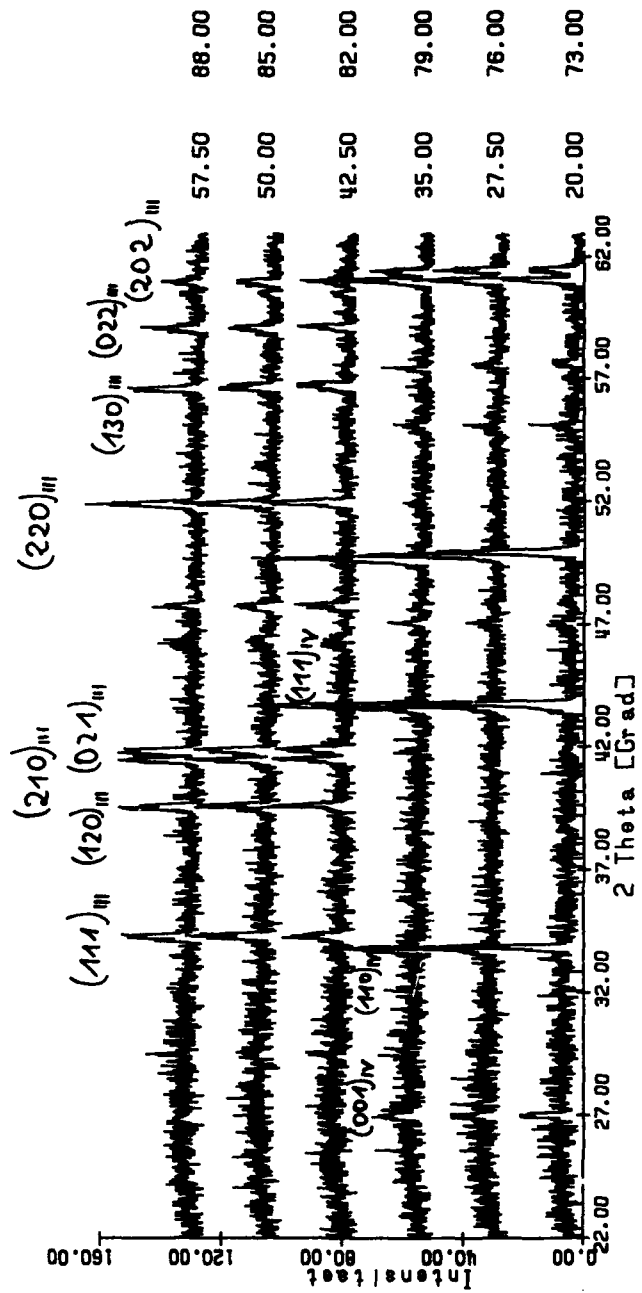
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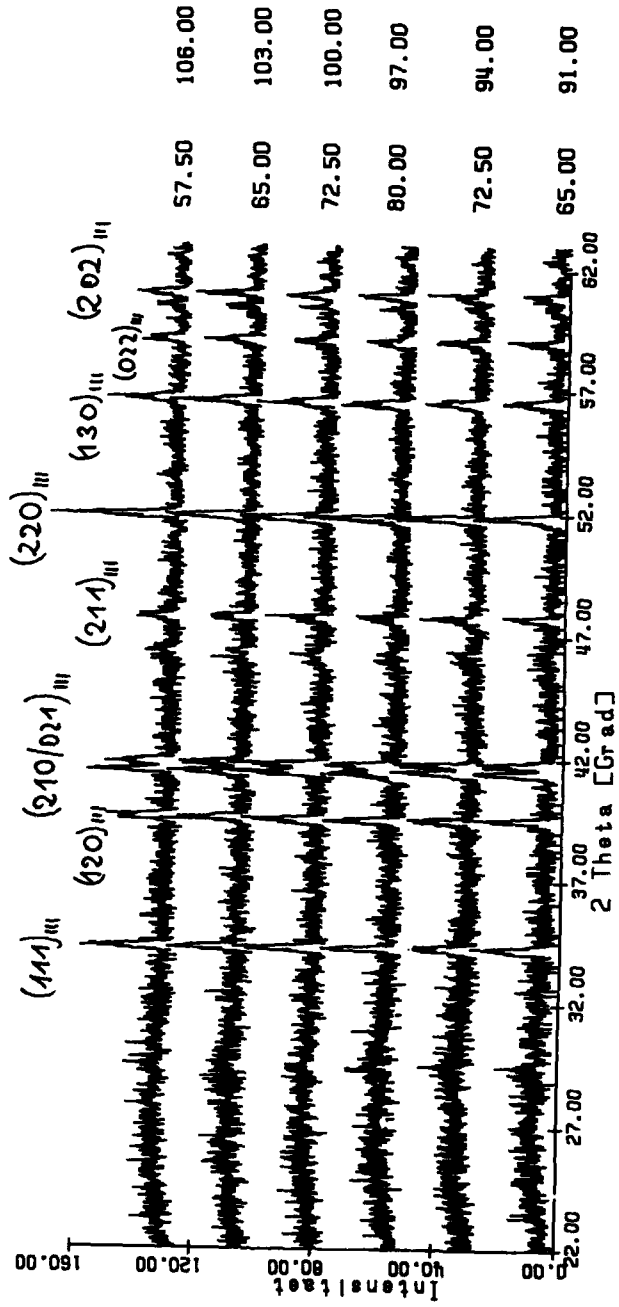
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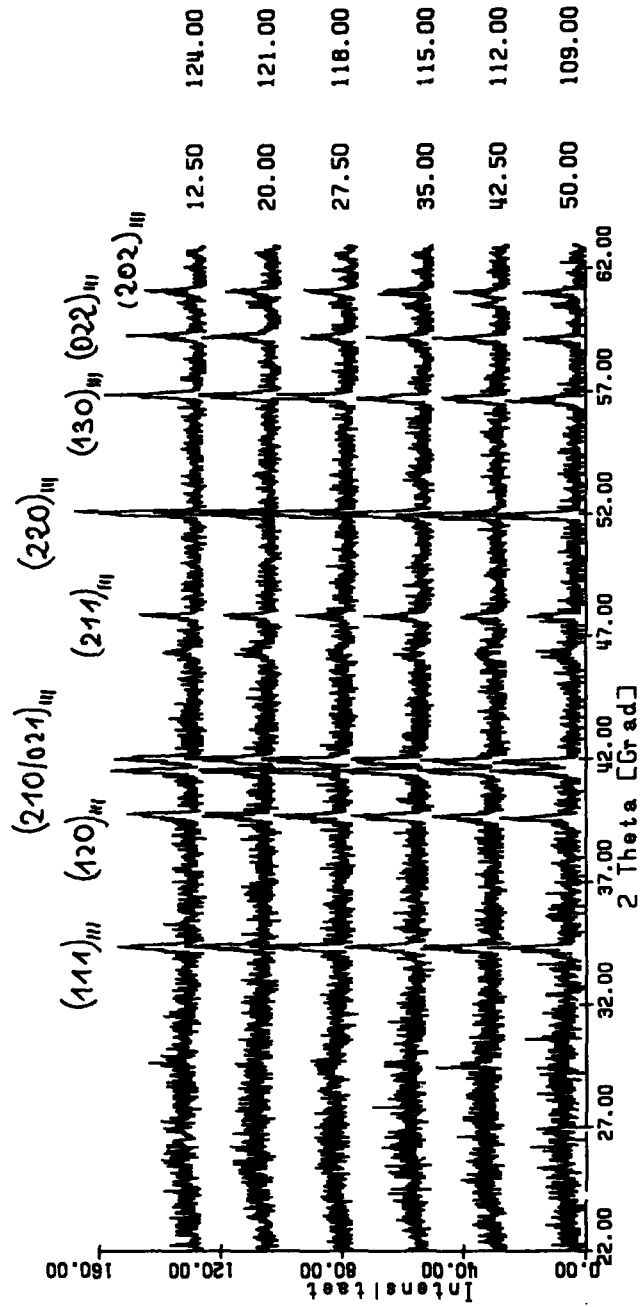
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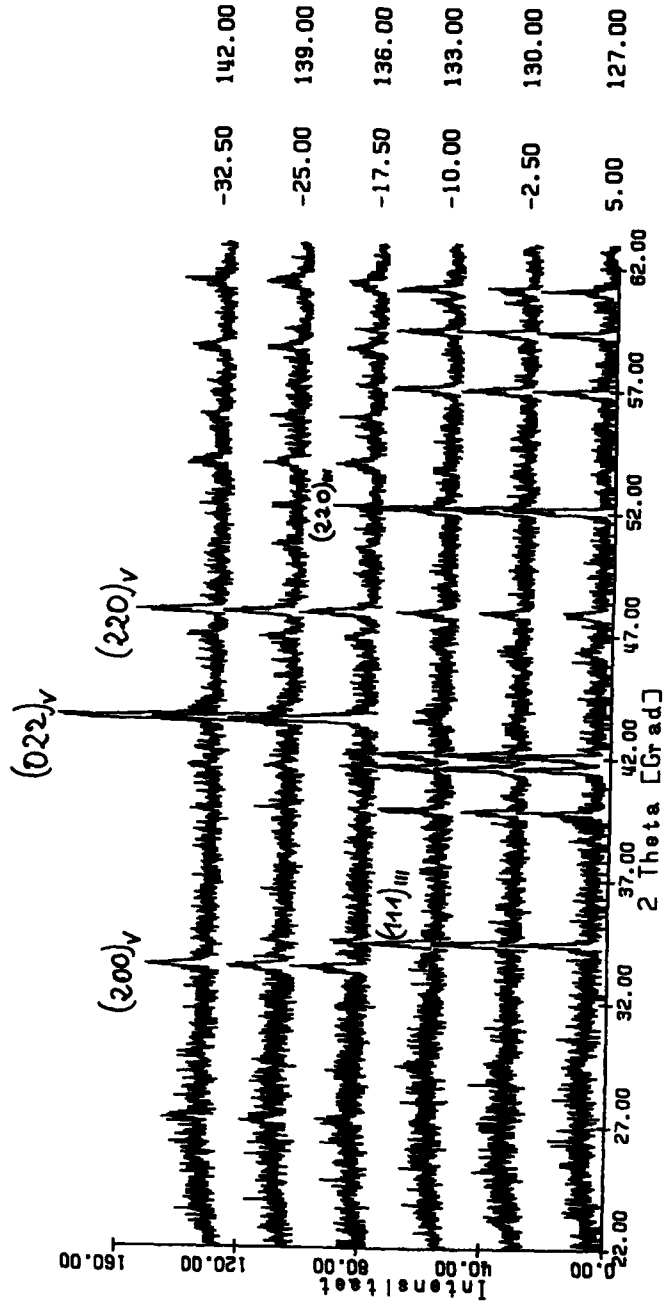
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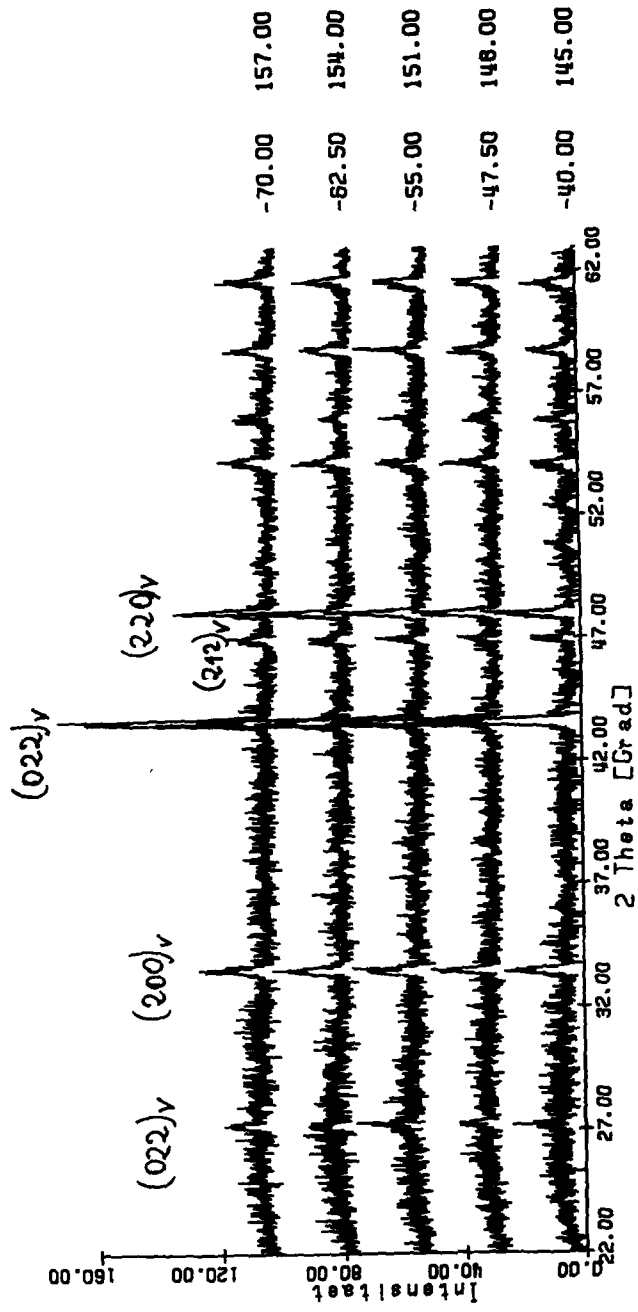
KF230388



kf 230388



Kf230388

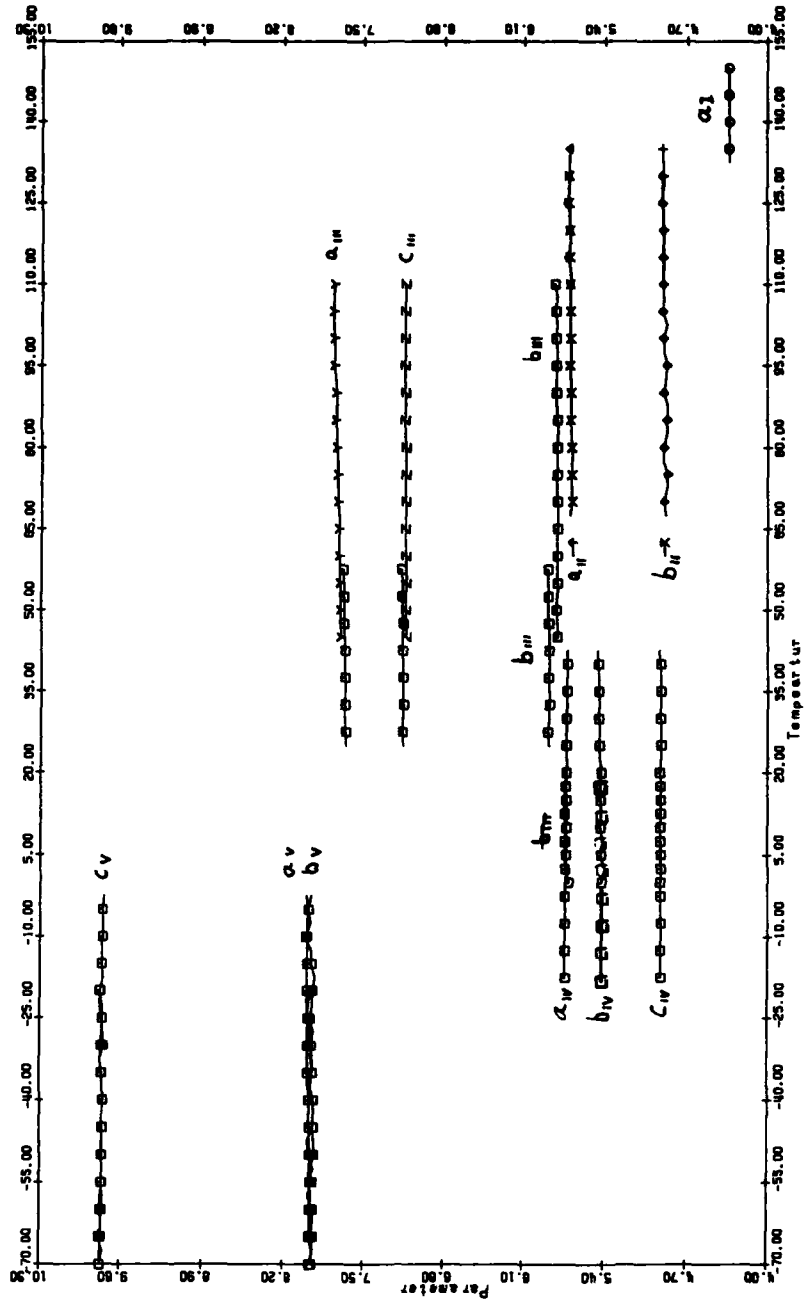


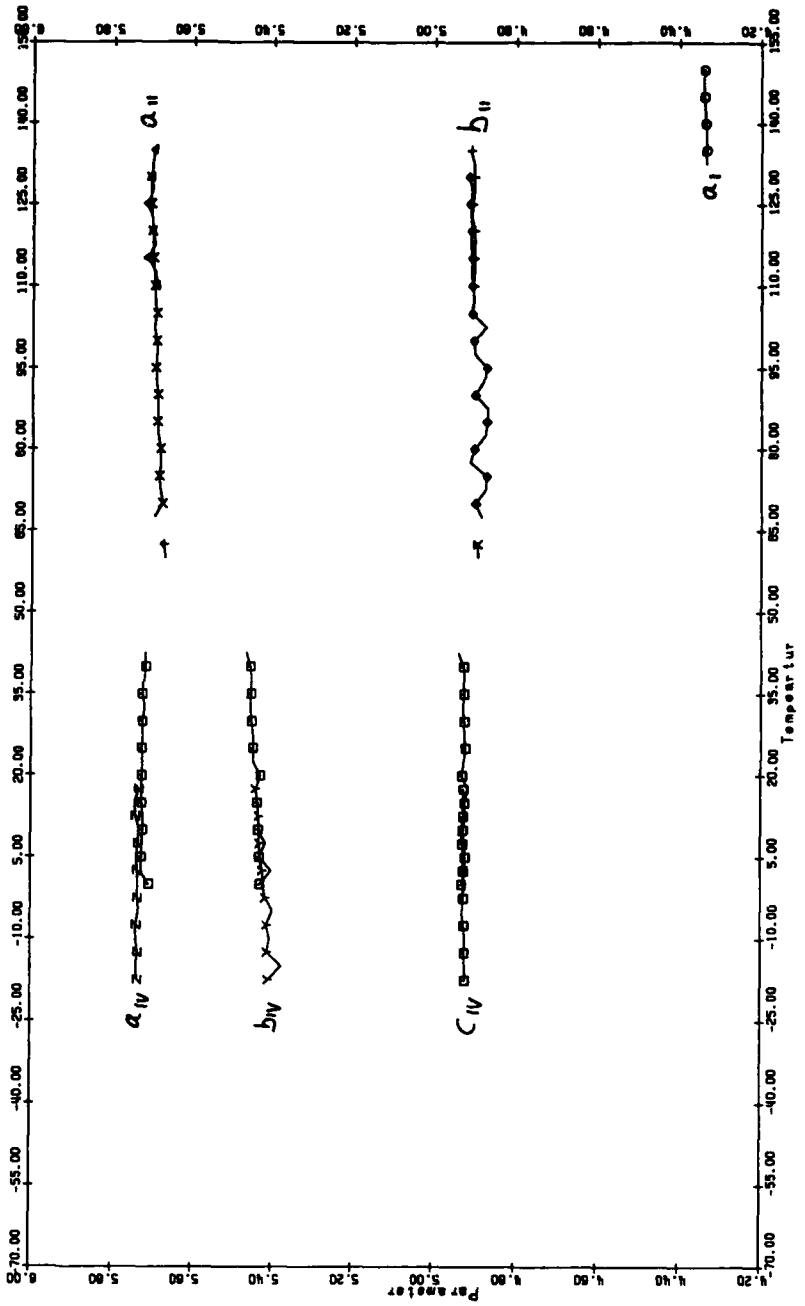
***Series***  
***KF 290388***

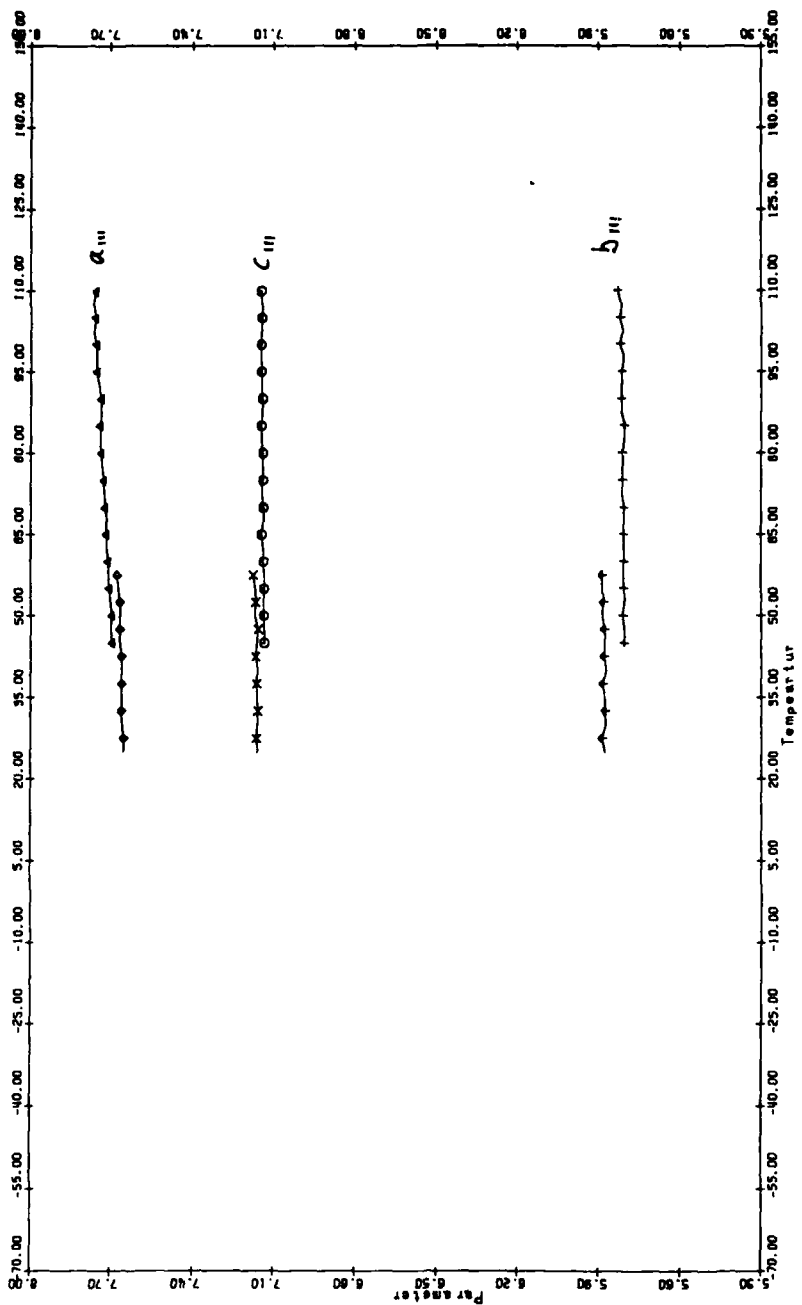
***Temperature***  
***Program***  
***20/-70/150/20***

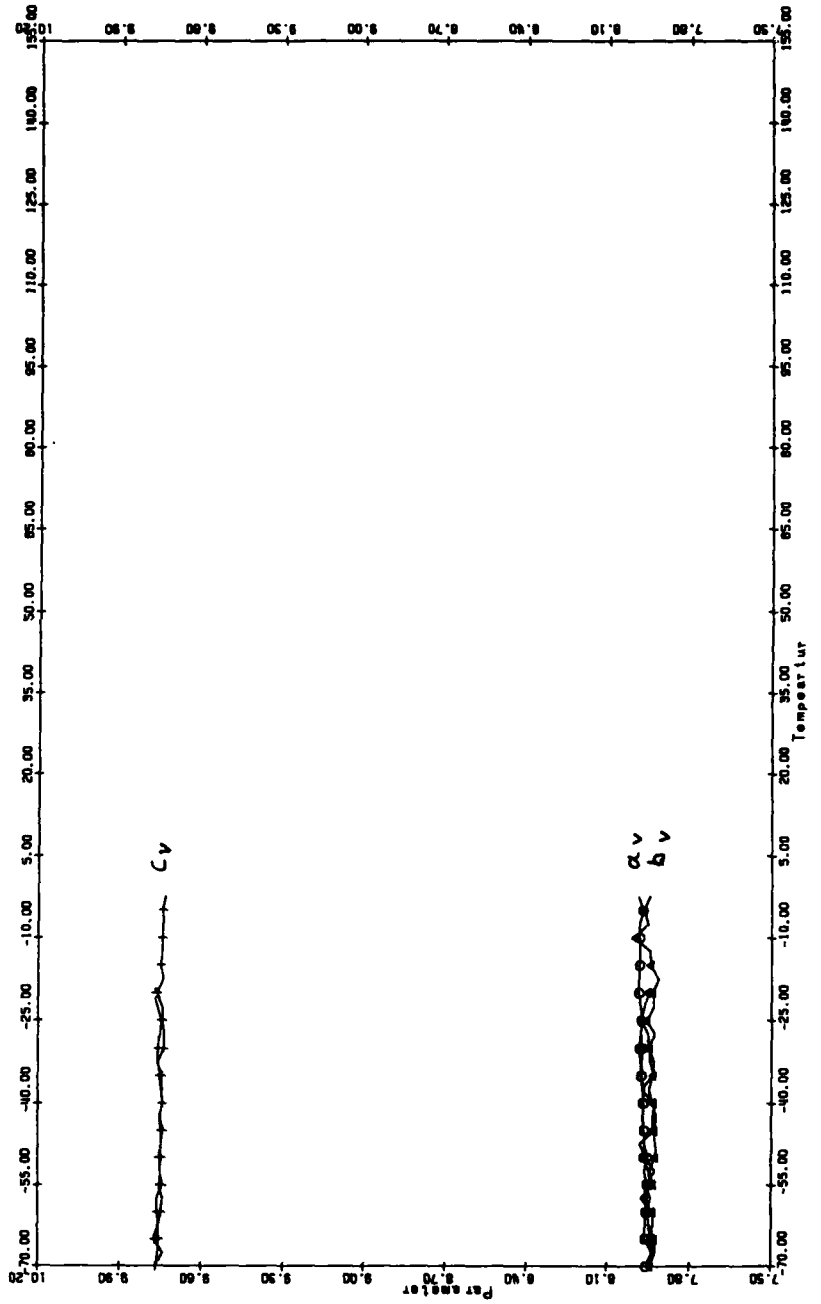
KF 250388  
201-70/450/20

### Lattice Parameters



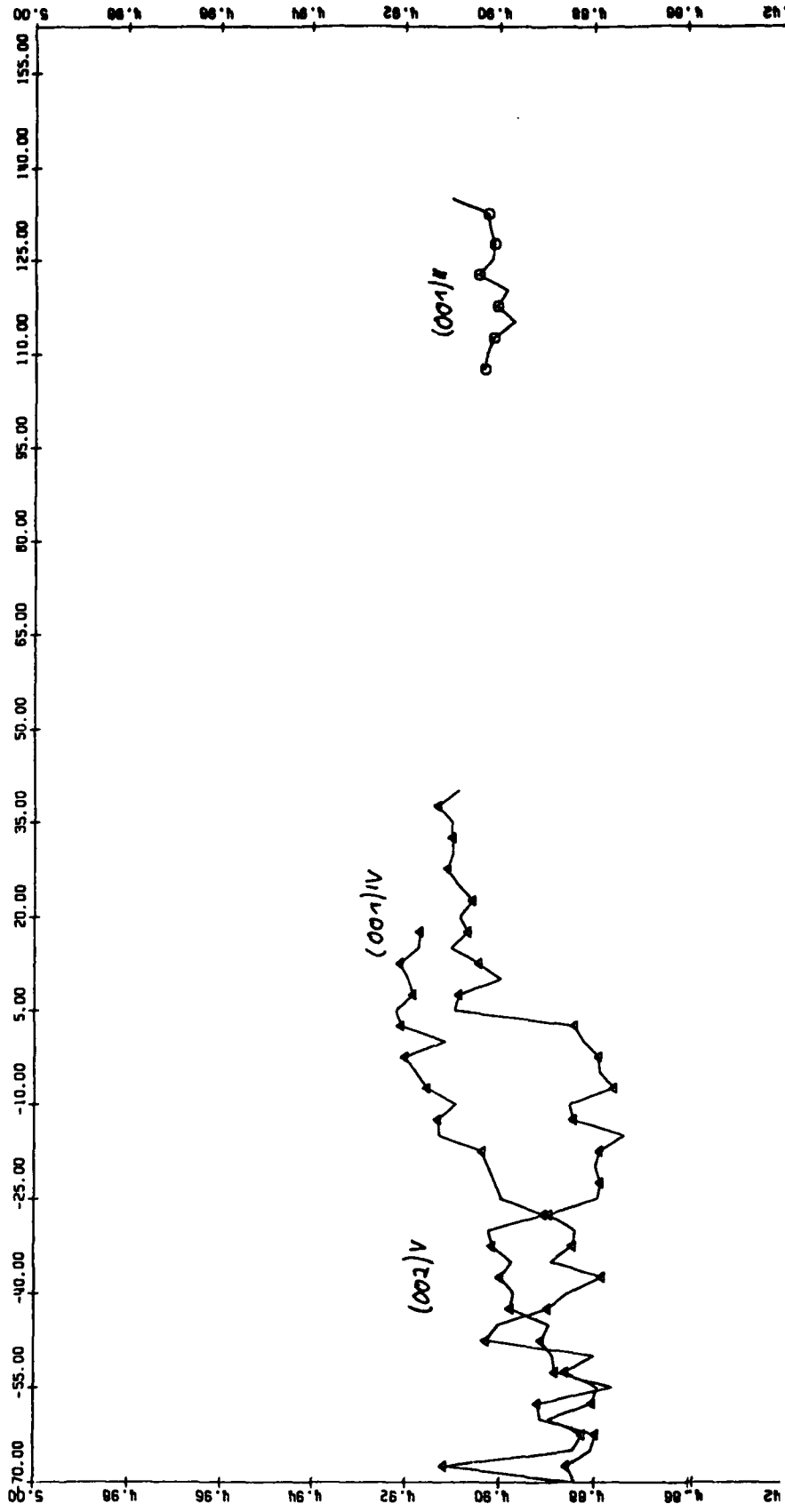






K7290388

Lattice Distances (d)



0h' 98 2h' 0h' 96 4h' 96 6h' 96 8h' 96 10h' 96 12h' 96 14h' 96 16h' 96 18h' 96 20h' 96 22h' 96 24h' 96

(100)I

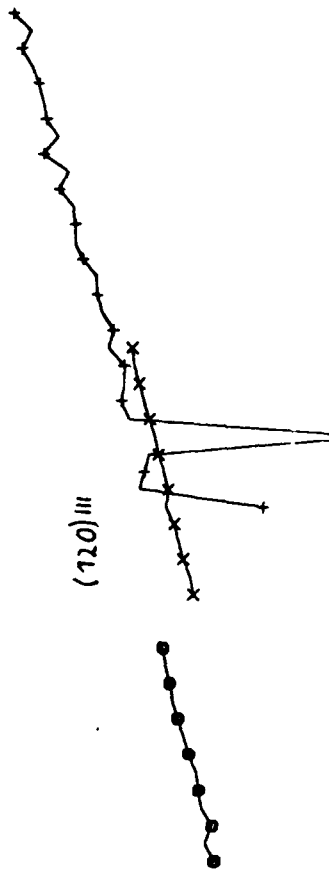
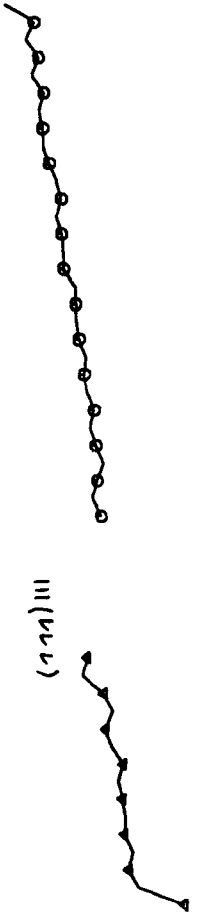
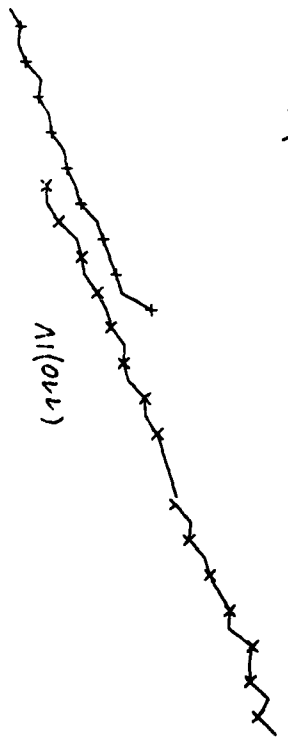
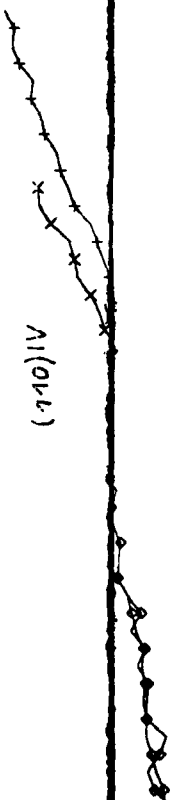
(110)II

(200)V

2

0h' 98 2h' 0h' 96 4h' 96 6h' 96 8h' 96 10h' 96 12h' 96 14h' 96 16h' 96 18h' 96 20h' 96 22h' 96 24h' 96

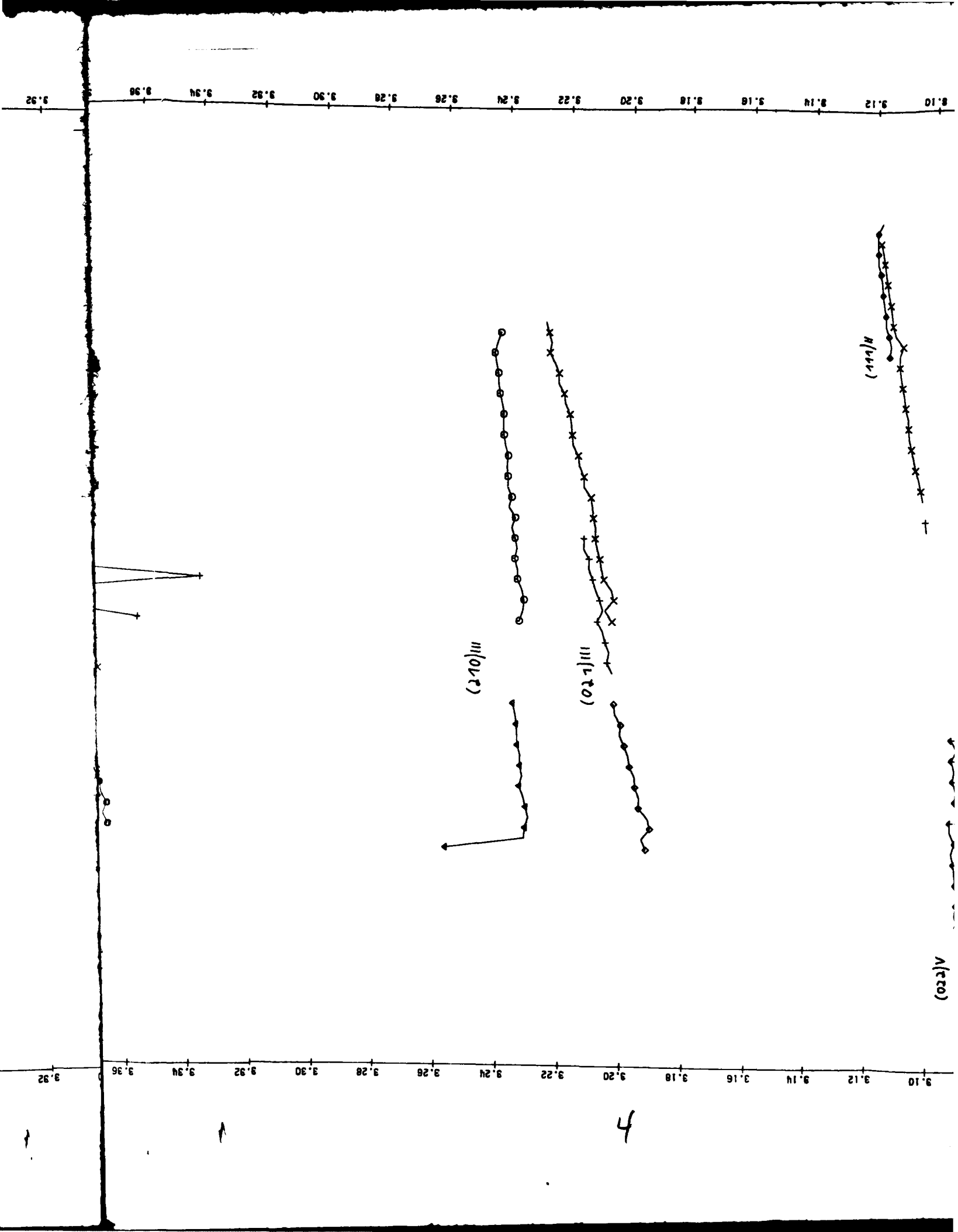
3.98 3.96 3.94 3.92 3.90 3.88 3.86 3.84 3.82 3.80 3.78 3.76 3.74 3.72 3.70 3.68 3.66 3.64 3.62 3.60 3.58 3.56 3.54 3.52 3.50 3.48 3.46 3.44 3.42 3.40 3.38 3.36 3.34 3.32 3.30 3.28 3.26 3.24 3.22 3.20 3.18 3.16 3.14 3.12 3.10 3.08 3.06 3.04 3.02 3.00 2.98 2.96 2.94 2.92 2.90 2.88 2.86 2.84 2.82 2.80 2.78 2.76 2.74 2.72 2.70 2.68 2.66 2.64 2.62 2.60 2.58 2.56 2.54 2.52 2.50 2.48 2.46 2.44 2.42 2.40 2.38 2.36 2.34 2.32 2.30 2.28 2.26 2.24 2.22 2.20 2.18 2.16 2.14 2.12 2.10 2.08 2.06 2.04 2.02 2.00 1.98 1.96 1.94 1.92 1.90 1.88 1.86 1.84 1.82 1.80 1.78 1.76 1.74 1.72 1.70 1.68 1.66 1.64 1.62 1.60 1.58 1.56 1.54 1.52 1.50 1.48 1.46 1.44 1.42 1.40 1.38 1.36 1.34 1.32 1.30 1.28 1.26 1.24 1.22 1.20 1.18 1.16 1.14 1.12 1.10 1.08 1.06 1.04 1.02 1.00 0.98 0.96 0.94 0.92 0.90 0.88 0.86 0.84 0.82 0.80 0.78 0.76 0.74 0.72 0.70 0.68 0.66 0.64 0.62 0.60 0.58 0.56 0.54 0.52 0.50 0.48 0.46 0.44 0.42 0.40 0.38 0.36 0.34 0.32 0.30 0.28 0.26 0.24 0.22 0.20 0.18 0.16 0.14 0.12 0.10 0.08 0.06 0.04 0.02 0.00



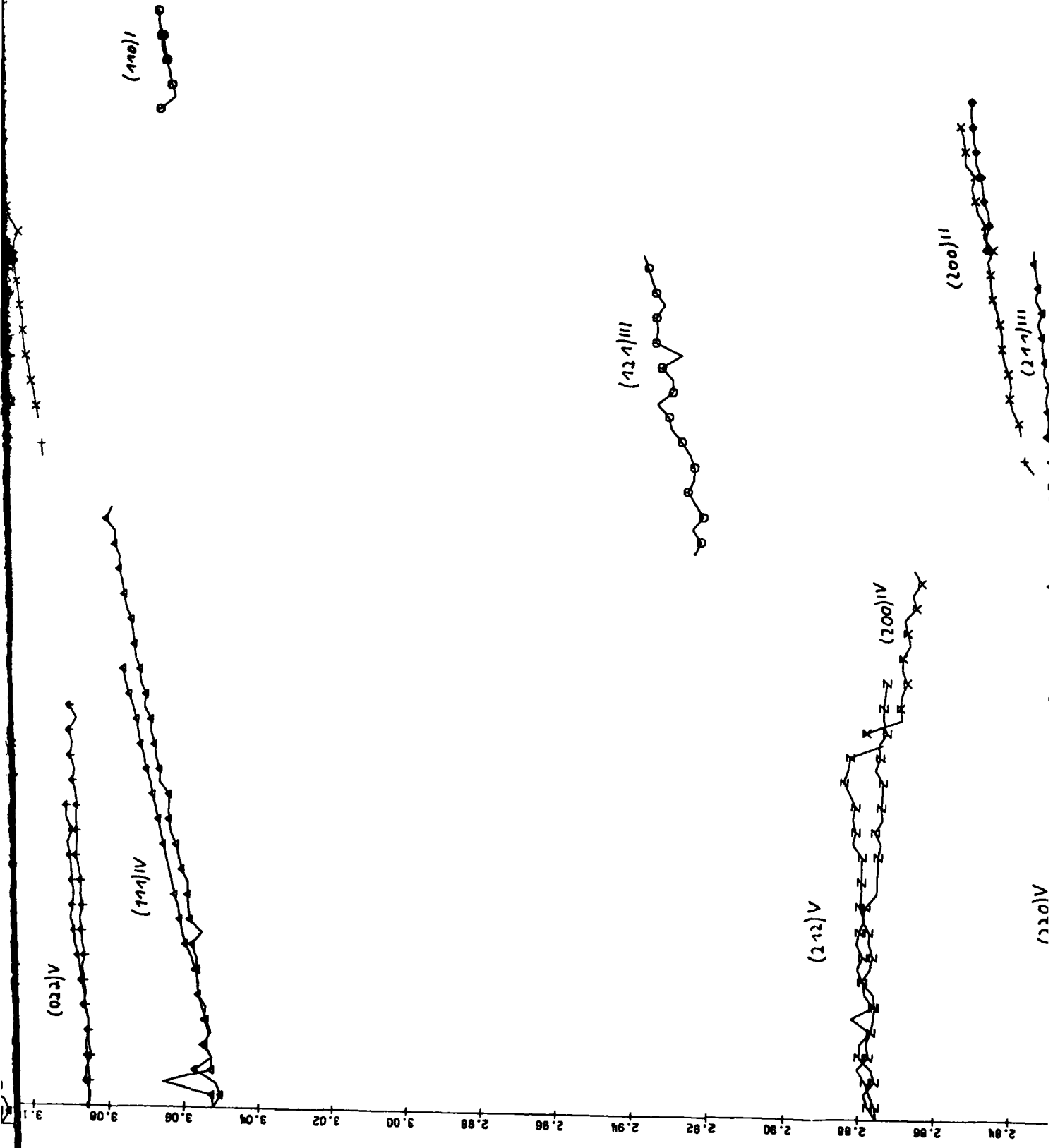
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1

3



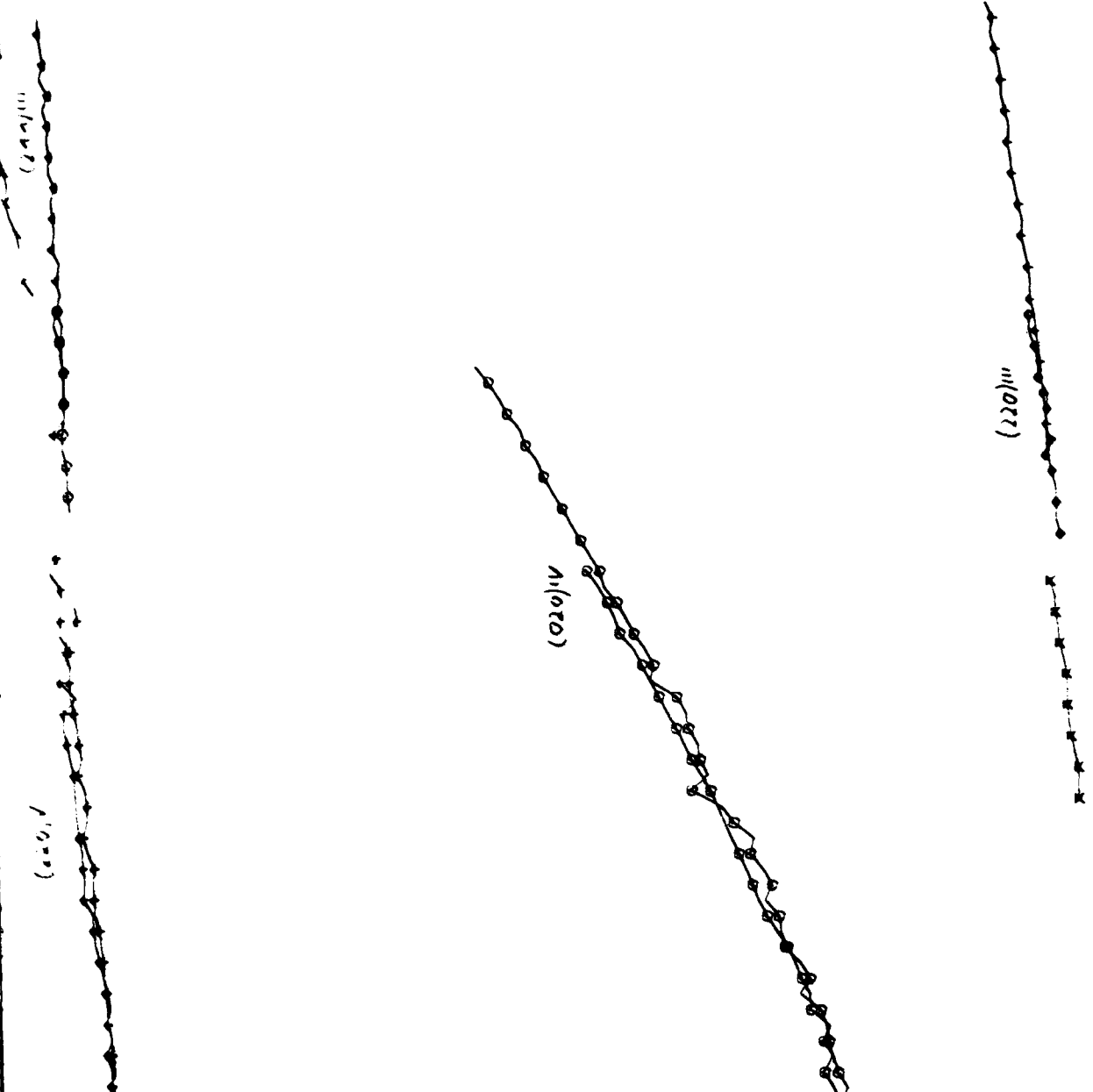
2.84 2.86 2.88 2.90 2.92 2.94 2.96 2.98 3.00 3.02 3.04 3.06 3.08 3.10

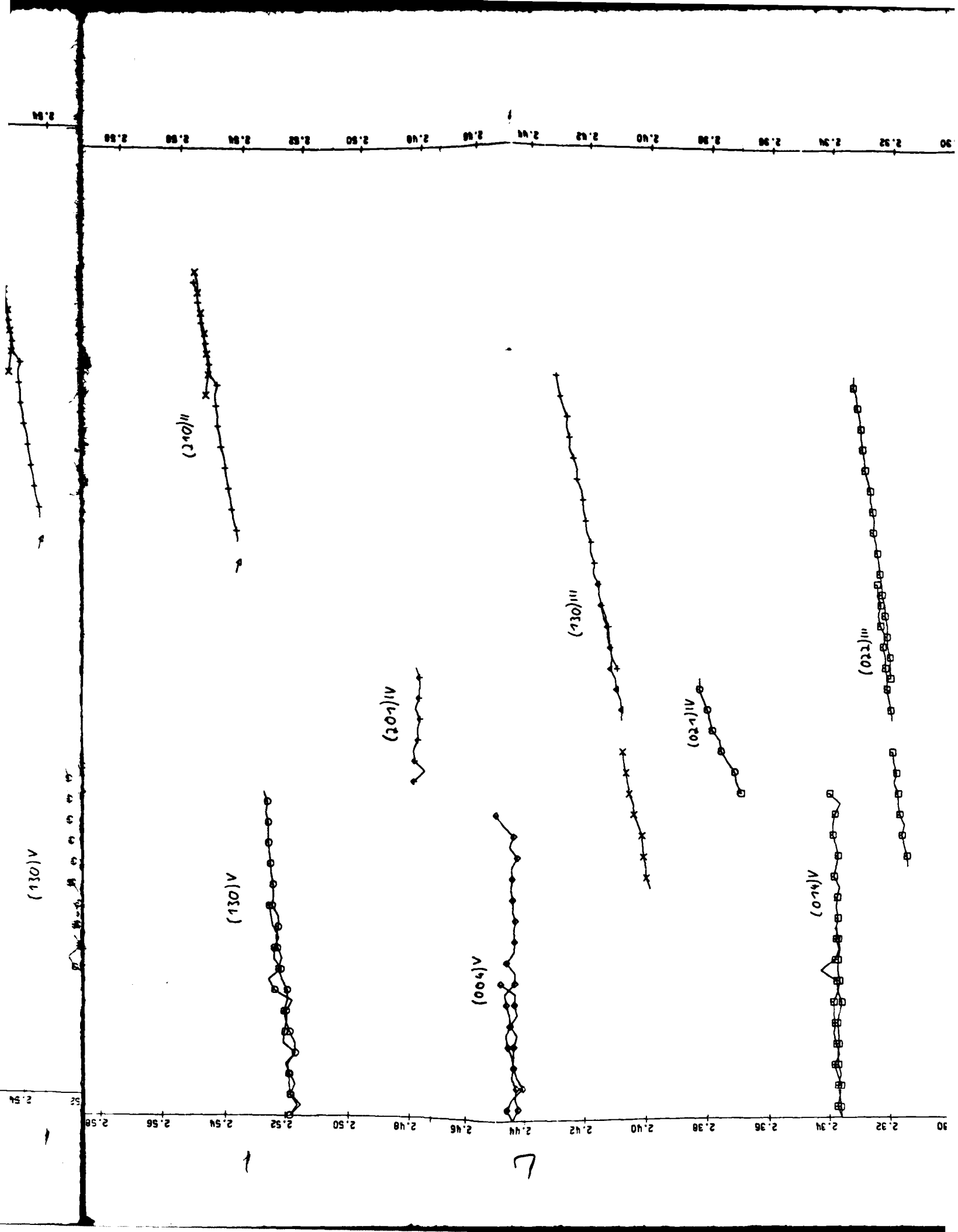


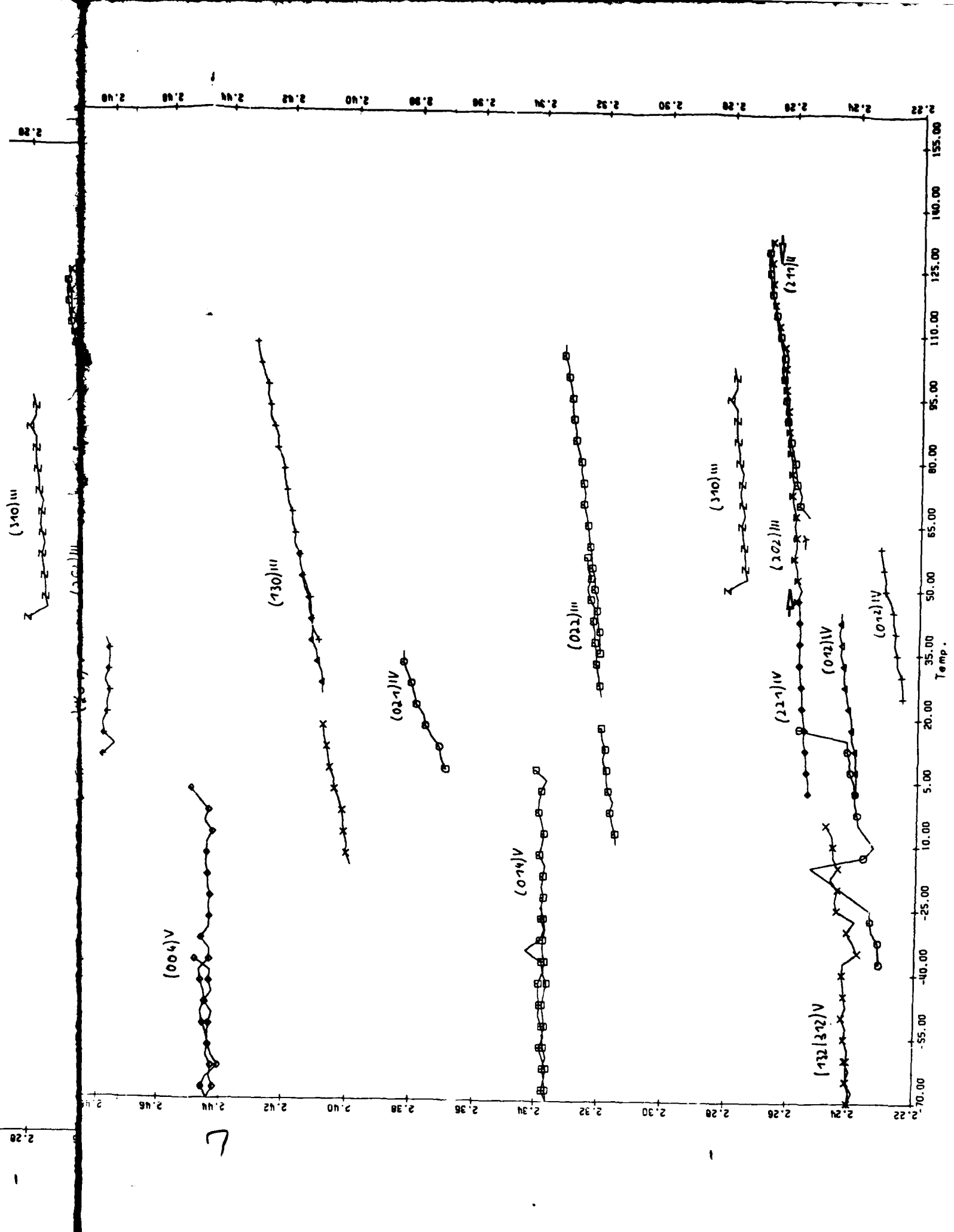
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2.00 2.02 2.04 2.06 2.08 2.10 2.12 2.14 2.16 2.18 2.20 2.22 2.24 2.26 2.28 2.30 2.32 2.34 2.36 2.38 2.40 2.42 2.44 2.46 2.48 2.50

2.00 2.02 2.04 2.06 2.08 2.10 2.12 2.14 2.16 2.18 2.20 2.22 2.24 2.26 2.28 2.30 2.32 2.34 2.36 2.38 2.40 2.42 2.44 2.46 2.48 2.50

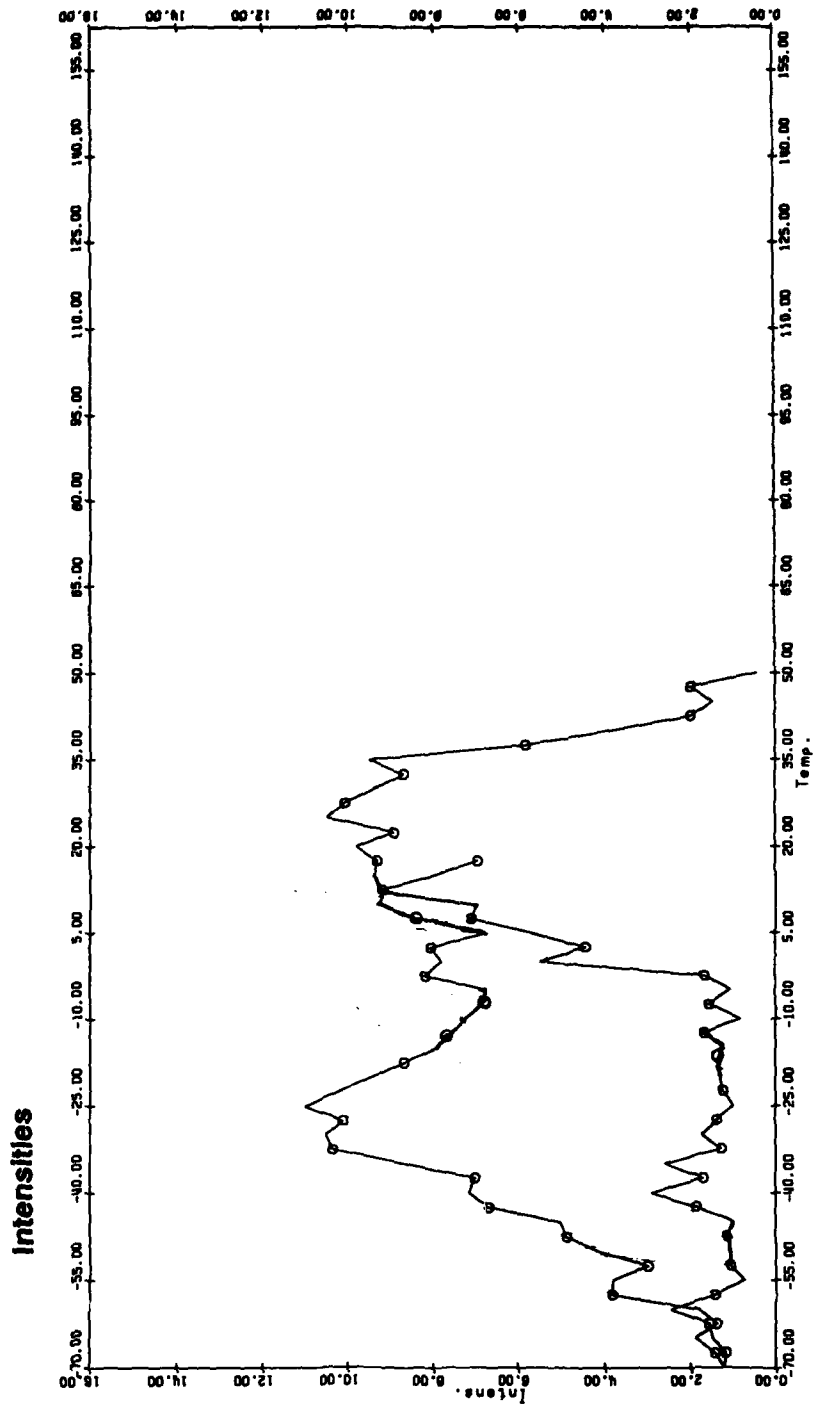






K7 250388  
20|-70|150|30

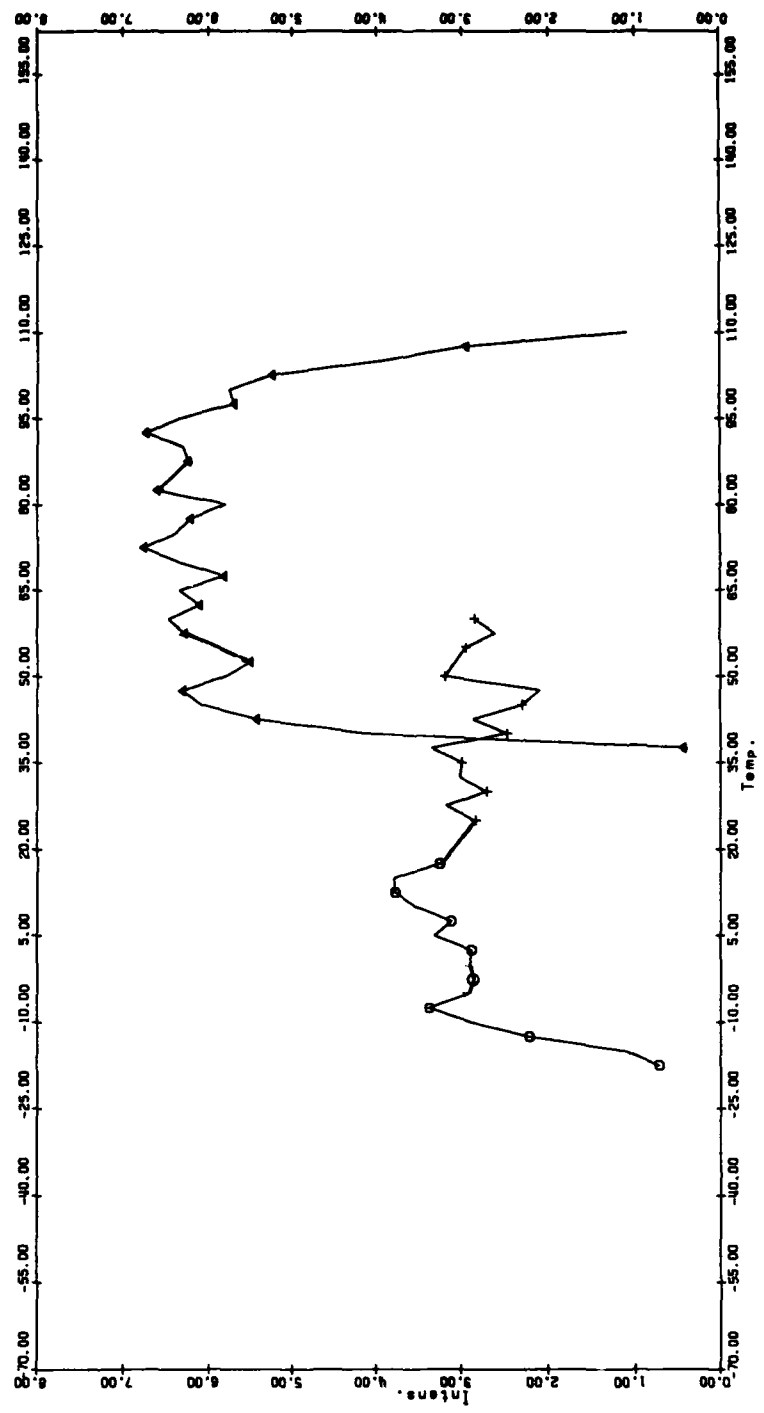
(020)IV



K7 25038  
20|70/450|20

(220) III

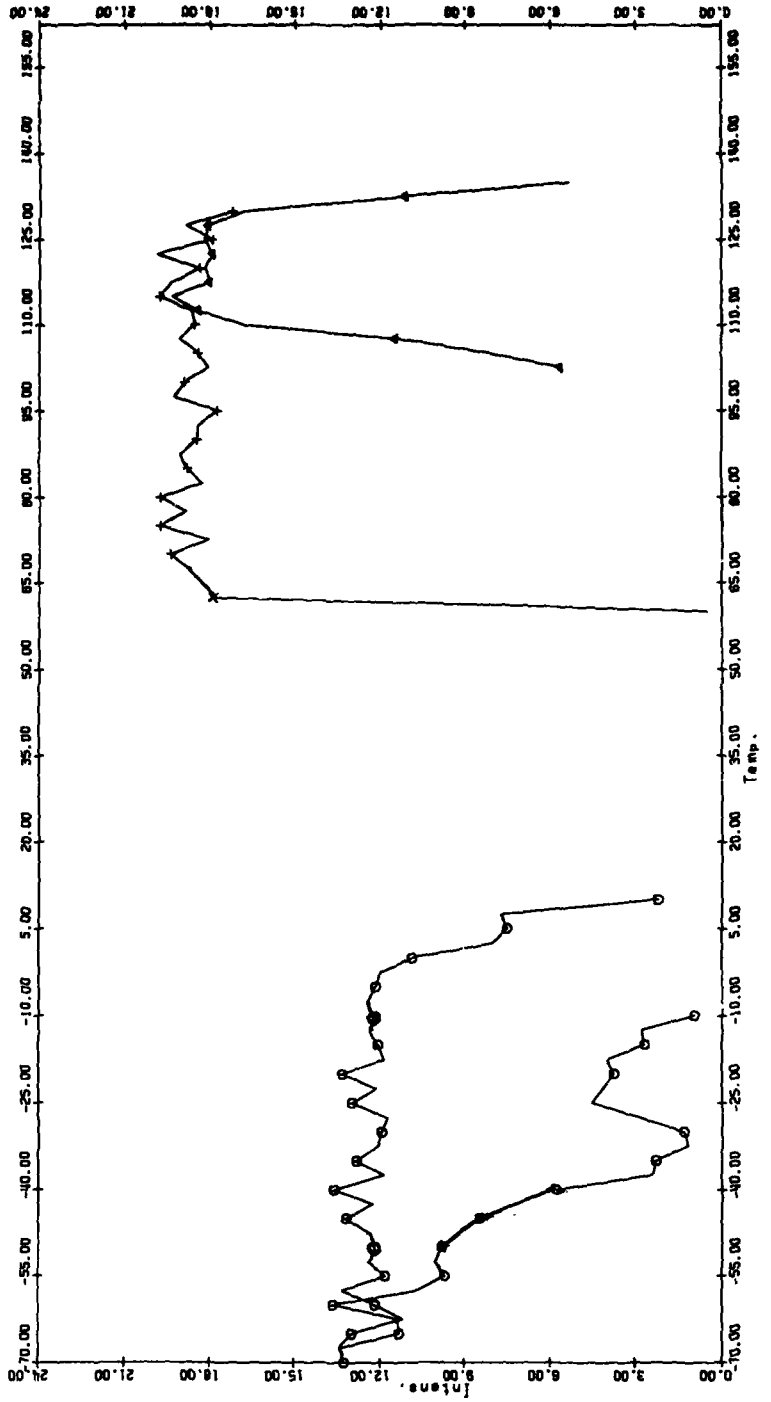
Intensities



KF 250388  
20-10150130

(022)V  
(111)II

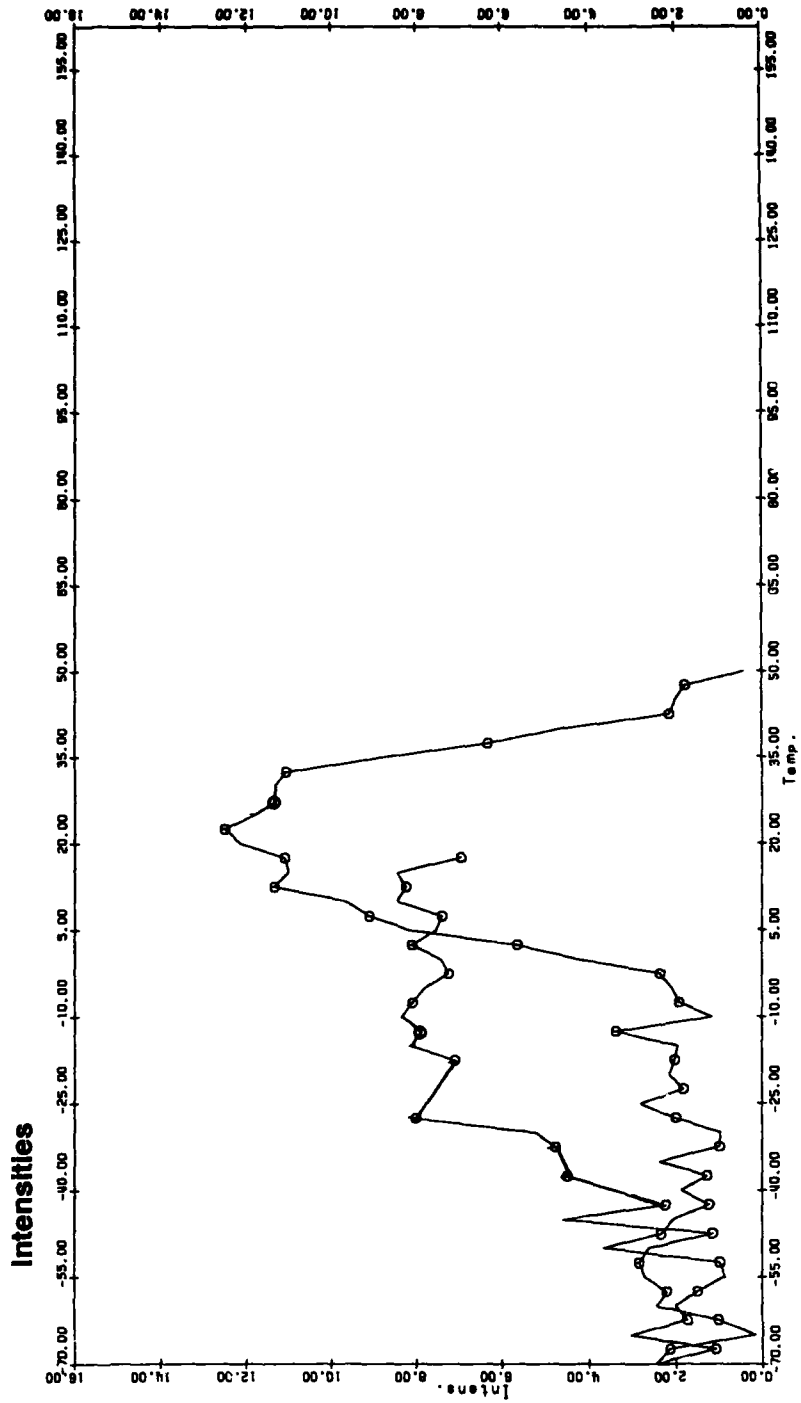
Intensities



KF 290388

201-701450/20

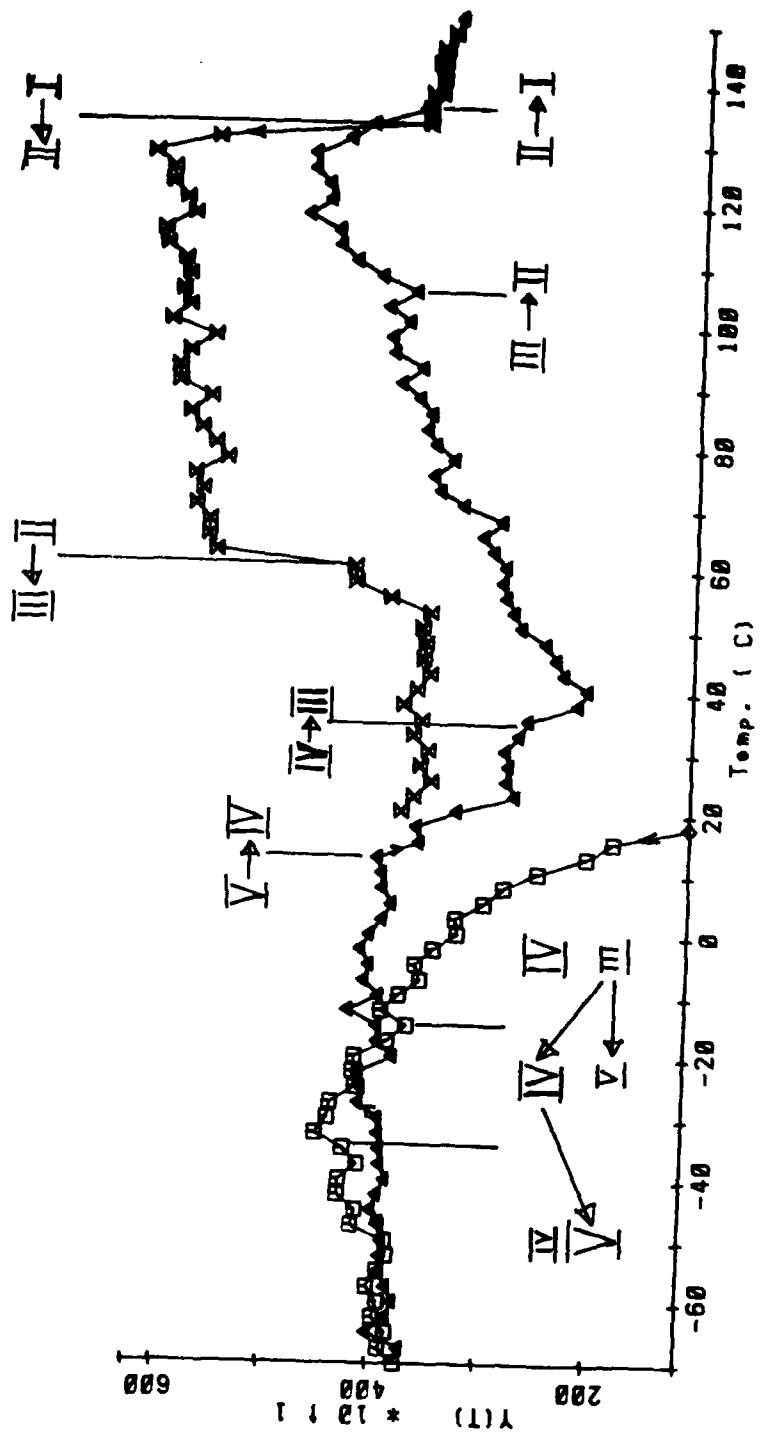
(111)IV



Difference Curve

20 | -70 | 150 | 20

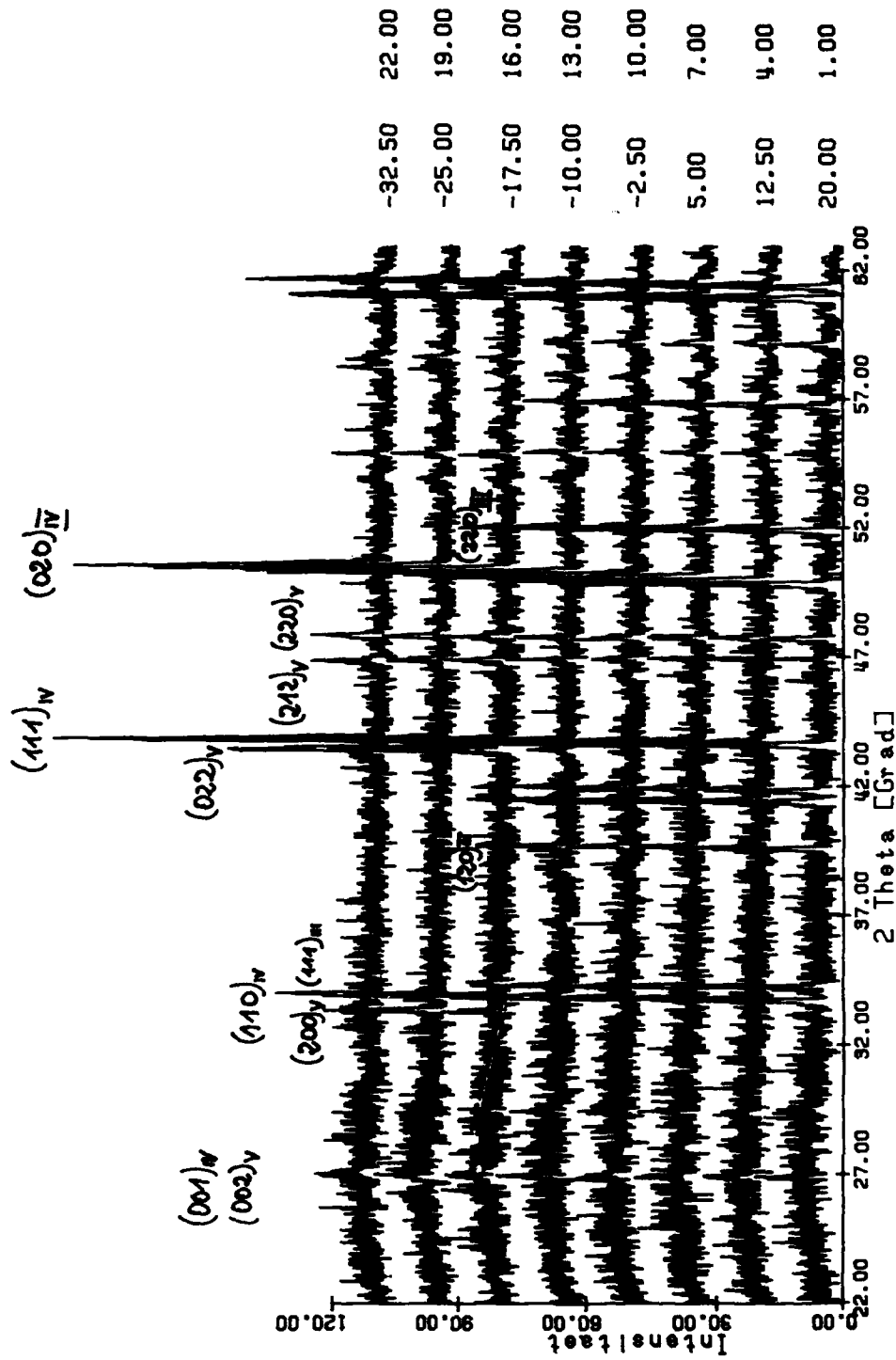
KF290388  
Y(T)



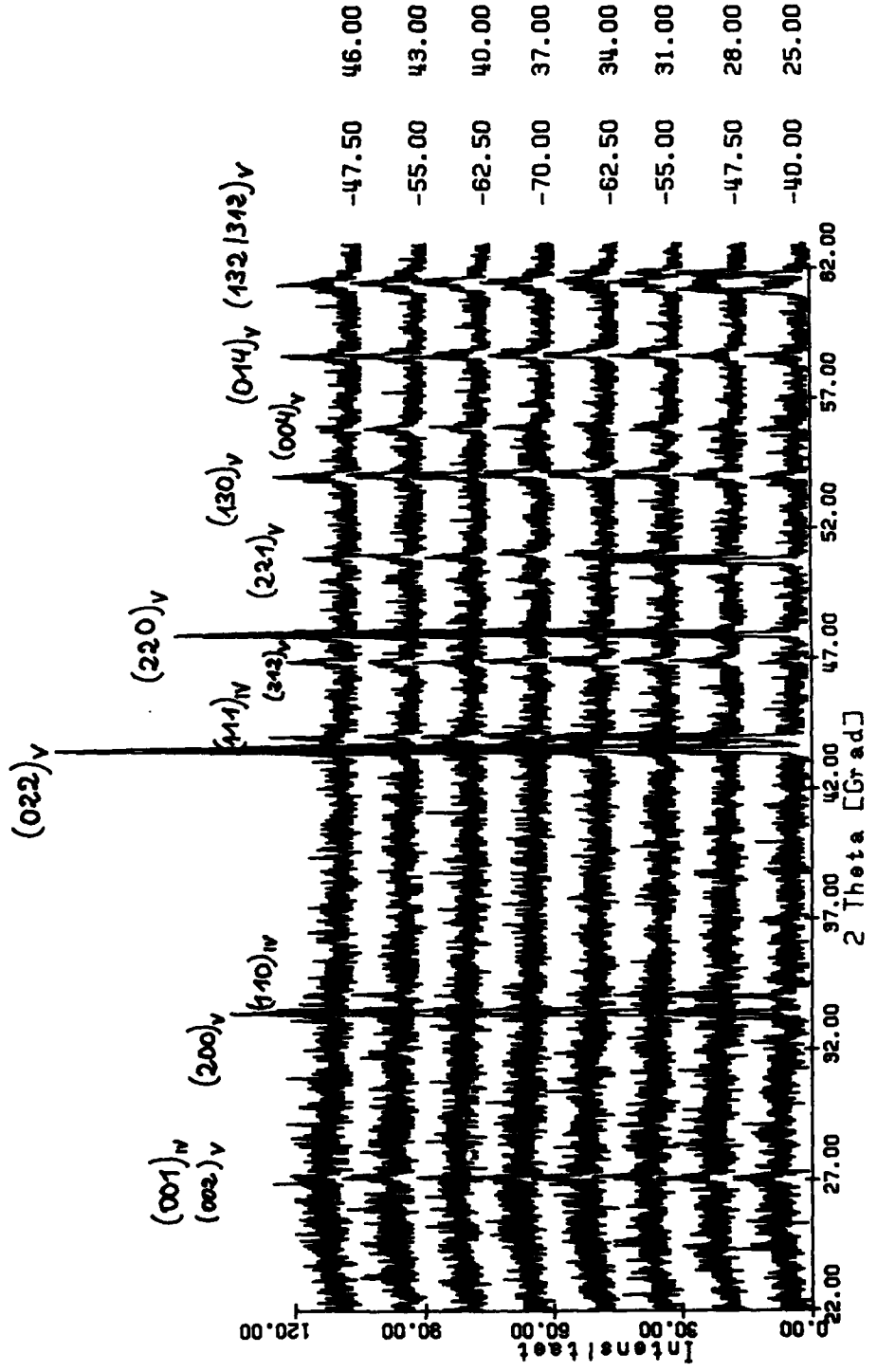
Diffraction Patterns

kf290388

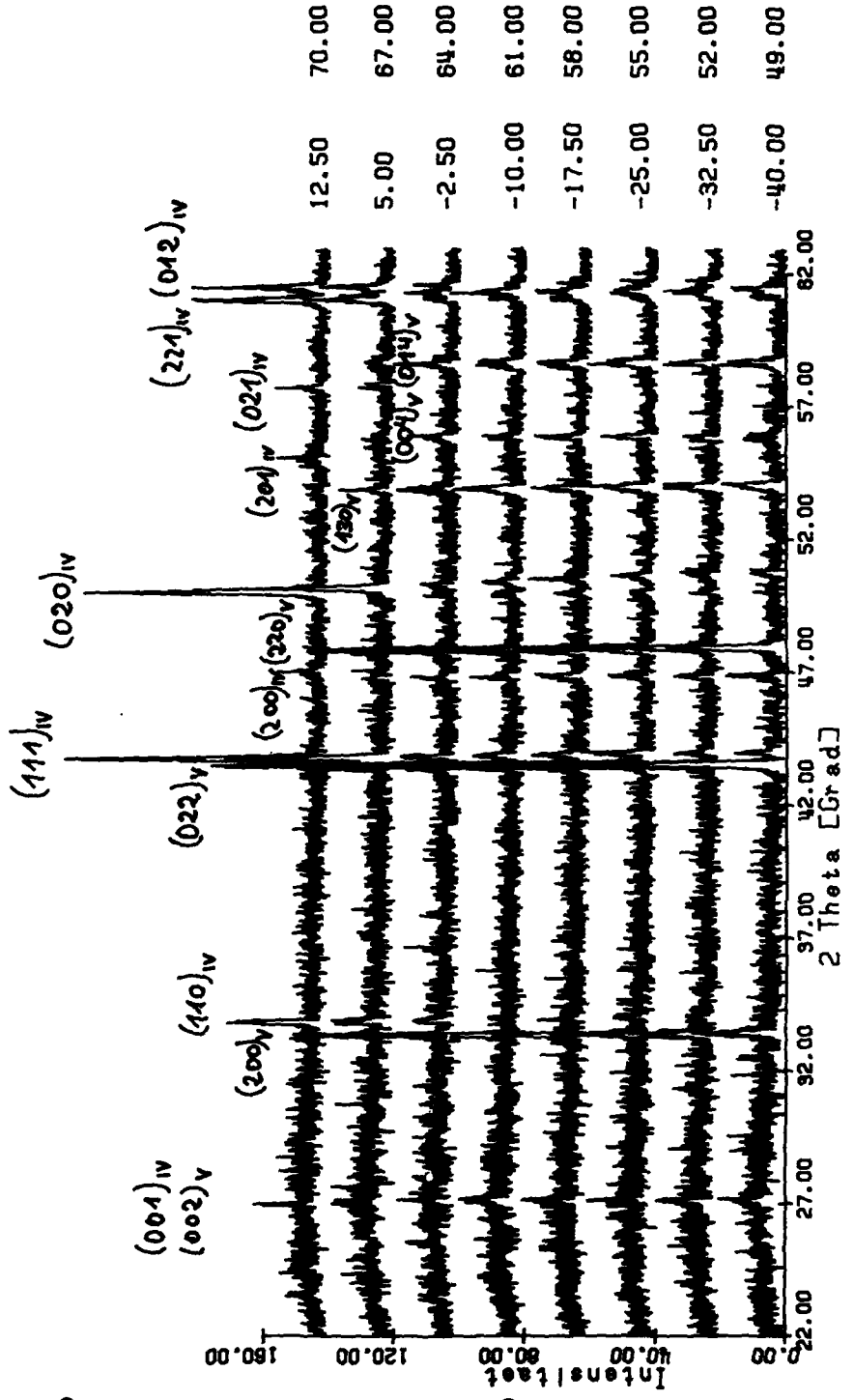
20 | -70 | 150 | 20 °C



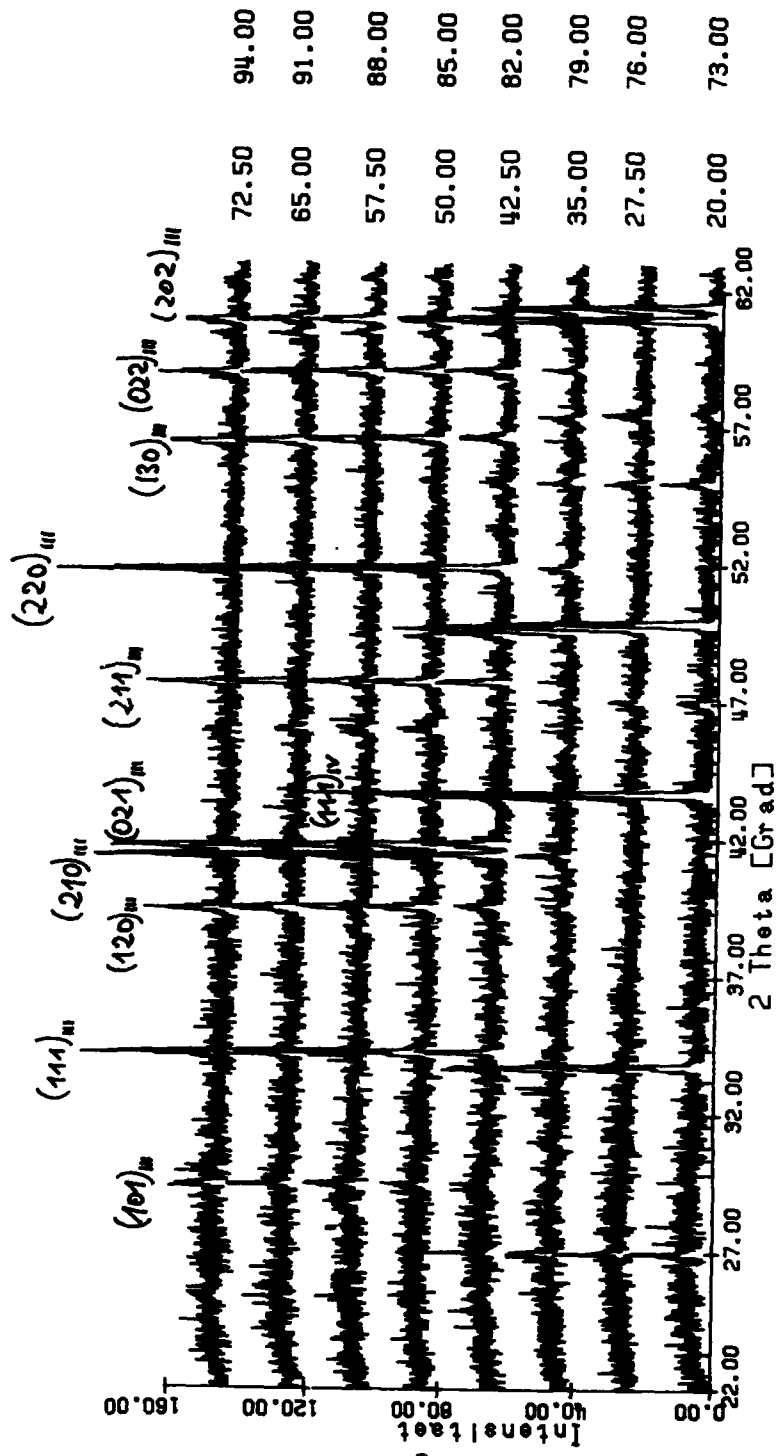
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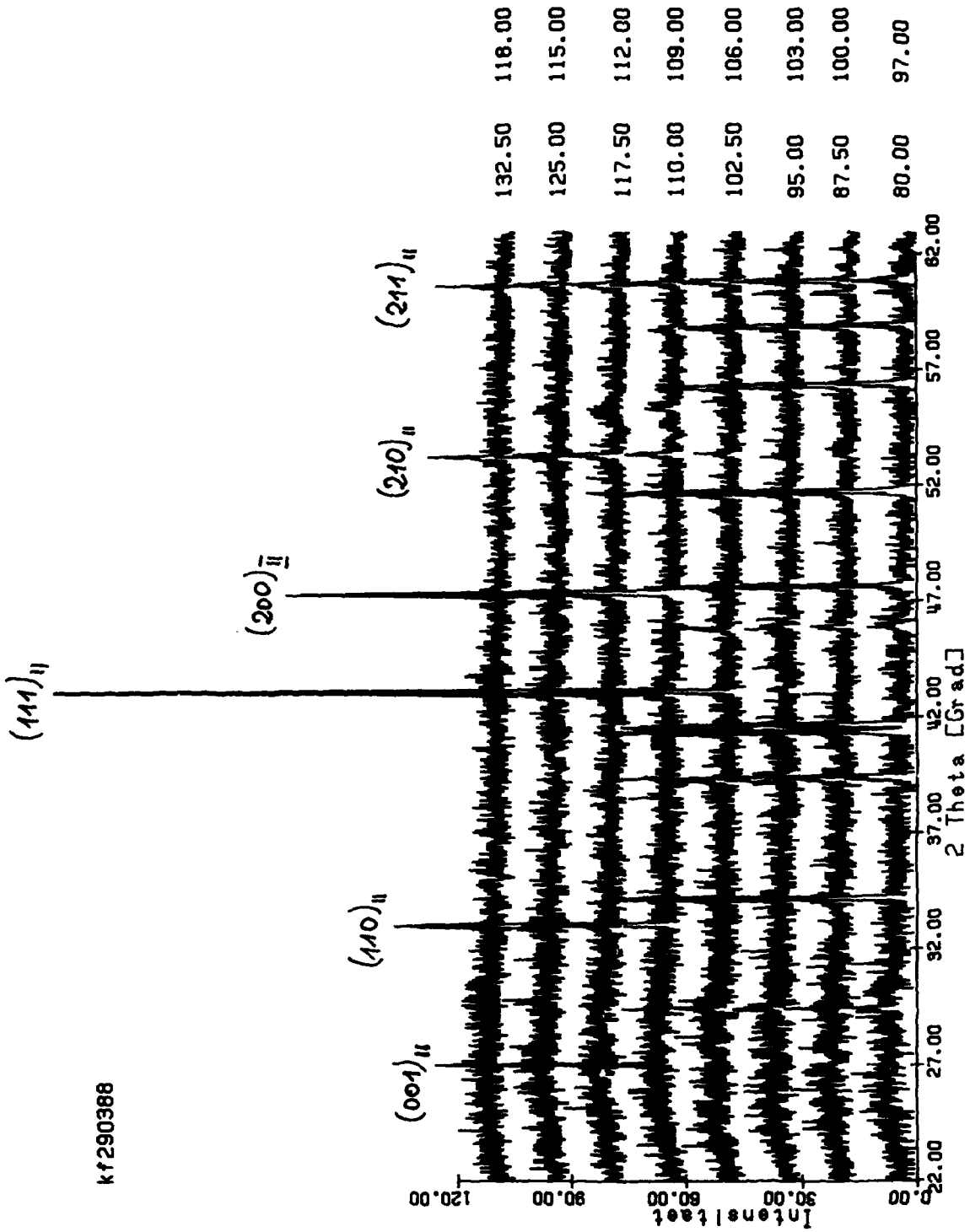
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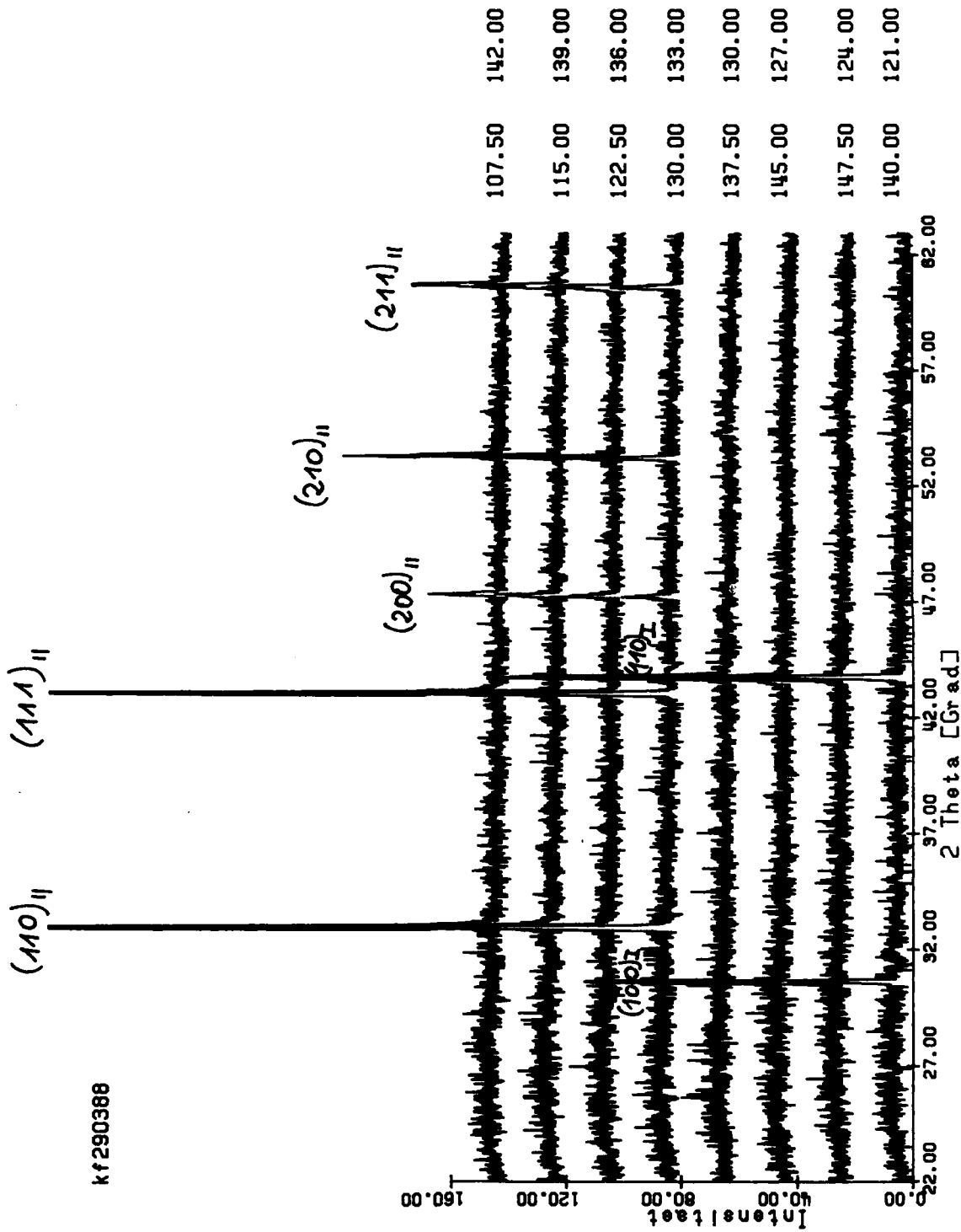


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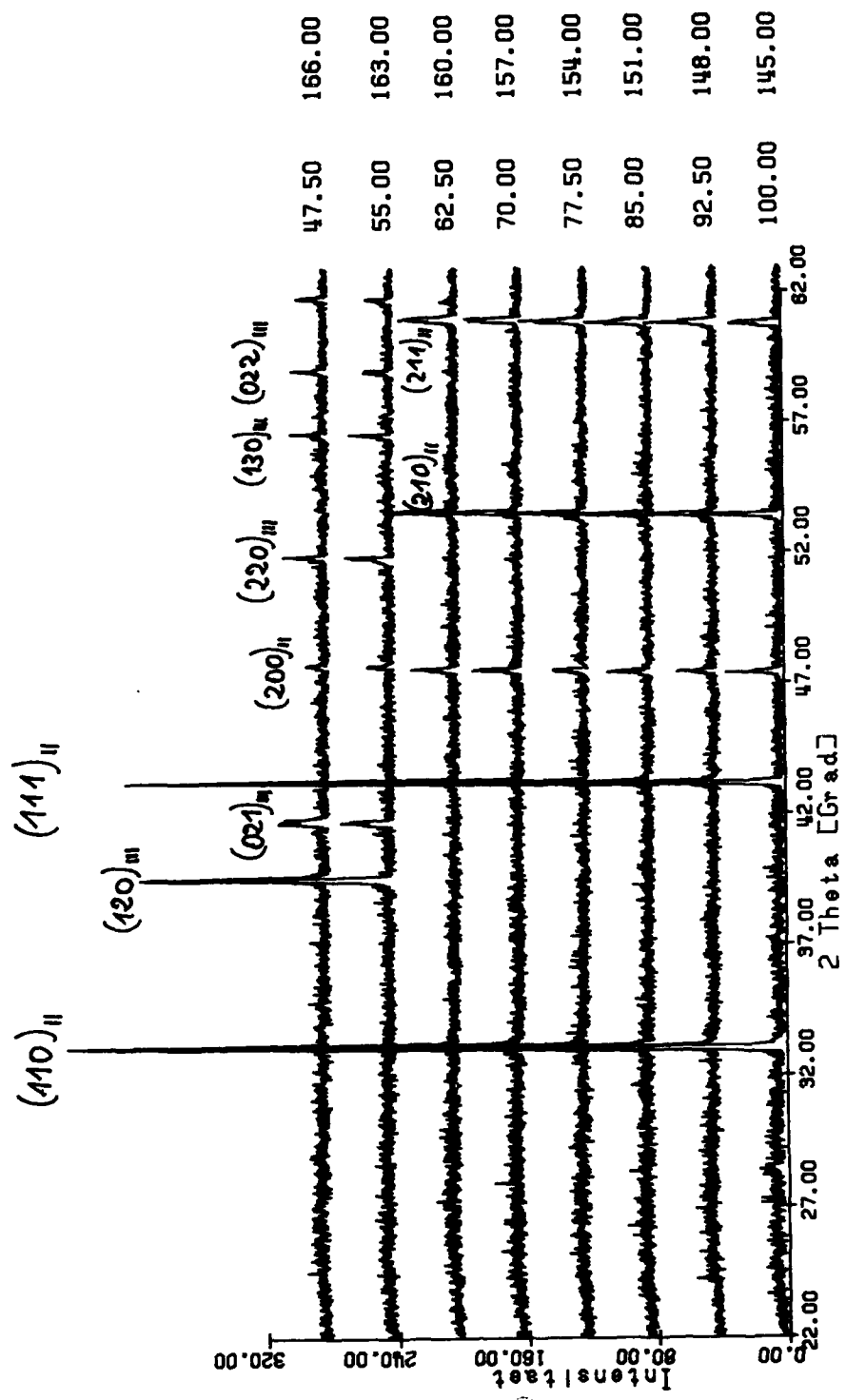


kf290388





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