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NEUTRON DIFFRACTION STUDY OF LUNAR MATERIALS

Final Report

NASA Order No. T-90270

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ABSTRACT

Three Apollo 12 lunar samples (12070(119), 12071(6), and 12008(7), in the form of fines and chips, have been investigated by means of neutron diffraction at room temperature, 77°K and 4.2°K. The primary purposes of the investigation, namely determination of the magnetic structure of ilmenite and the structure of glasses, could not be fulfilled because of the absence of observable quantities of $FeTiO_3$ and glassy material in the samples provided. Nevertheless, in sample 12071,6 a possible magnetic ordering was discovered; in addition, the observed d-spacings in the samples are tabulated and correlated with possible constituent phases.

NEUTRON DIFFRACTION STUDY OF LUNAR MATERIALS

I. Introduction

The following material is submitted as a final report under NASA Order No. T-90270, dated March 1, 1970. The purpose of this study was to determine the glassy structure, the ilmenite magnetic structure, and the crystalline phases in lunar material by means of neutron diffraction methods. In all, some 35 diffraction patterns were taken at various wavelengths and temperatures of the three samples made available. None showed the presence of glassy material or $FeTiO_3$ in sufficient amount to be visible in the diffraction patterns, so that the primary objectives of the study could not be carried out. Nevertheless, some qualitative information about the composition of the samples was obtained from the observed d-spacings, and the major part of the results presented here are a tabulation of the observed lines and their intensities, with a tentative assignment to various mineral phases. In addition, in one sample evidence of magnetic ordering was observed at low temperatures, most probably due to an iron-rich pyroxene phase.

II. Experimental Procedure

1. The powder neutron diffraction method. The applicability of this method is twofold: the scattering amplitudes are not systematic as with x-rays (for instance, hydrogen is visible compared to heavy atoms, some metals have negative scattering amplitudes); and the neutron-spin, unpaired-electron interaction gives an additional magnetic intensity component in the presence of ordered magnetic arrangements. Monochromatic incident neutrons were obtained by collimating and reflecting the reactor spectrum (peaked near 1.3 A), from the (111) planes of a deformed Ge crystal, and recording the reflected spectrum from the sample by step-scanning a BF_3 detector. The experiments were performed at the National Bureau of Standards 10 MW reactor using an automated, computer controlled spectrometer control system.[1]

2. Description of samples. The three samples made available for this study, described in Table 1, were used as received with no physical alteration. The first was studied at room, liquid N_2 and liquid He temperatures; the second at room and liquid He; and the third at room temperature only. The specimens were placed in either thin walled Al or V cylindrical sample holders (in air) and attached to the cold-finger of a N_2-jacketed He dewar.

3. Summary of experiments. A summary of the experimental data runs with the pertinent parameters is given in Table II. The incident neutron fluxes were 2.2×10^6 n/cm^{2}sec for the 2.38 data and 3.0×10^6 n/cm^{2}sec for the 1.36 A data; these are approximate levels determined from the efficiency and area of the monitor counter through which the incident beam passes. The incident neutron energies for 1.36 and 2.38 A are 44.2 and 14.4 millielectron volts, respectively.

It will be noted that many of the runs are repetitions; this procedure is followed to improve data quality by checking reproducibility, and to minimize the effect of intermittent noise or possible equipment failure. With the computer that operates the spectrometer control system, data reduction can readily be done; the combination of the individual runs are listed in Table III as collated runs.

III. Experimental Results

1. Sample 12070(119). This sample was first studied with 2.38 A neutrons to give high resolution diffraction patterns. No evidence was seen in the room temperature runs for $FeTiO_3$, nor were there any broad humps which might indicate amorphous or glassy phases. The runs at 77 K and 4 K, covering the region where strong magnetic peaks from the antiferromagnetic ilmenite lattice would appear, showed no additional peaks.

Additional data were obtained at 1.36 A to increase the range of observable d-spacings. Diffraction patterns taken at 300 K and 4.2 K are reproduced in Figure 1 and 2, where the expected positions for the strongest ilmenite peaks are indicated. Since some weak additional peaks, of possible magnetic origin, were observed at low angles in Figure 2, the region from 8-20 deg was scanned with higher statistics. Some peaks are indeed present in this range, as can be seen from Figures 3a and b; but a subtraction of these runs (Figure 3c), which should exhibit only magnetic scattering, shows no peak clearly outside statistical error. In particular, the first magnetic peak for $FeTiO_3$ should appear[2] between (111) and (100). We therefore conclude this sample contains little if any $FeTiO_3$, and probably shows no magnetic ordering of any type. Some evidence of a broad hump appears in the region of 15-25° in these patterns, but this was later shown to be a characteristic of the background from the sample holder.

The observed d-spacings and relative intensities are listed in Table IV.

2. Sample 12071,6. Runs were taken on this sample at two temperatures, 300 and 4.2 K (Figs. 4 and 5). Disregarding the strong lines due to the Al sample holder, there are obvious similarities with the fines sample, 12070,119. Again, no clearcut evidence of an $FeTiO_3$ phase is observed, but in the low temperature run an extra peak is clearly visible near 8°. This is attributed to a possible magnetic ordering, which will be discussed later. Table V lists the observed d-spacings.

3. Sample 12008,7. This sample was studied at room temperature only. Reference to the diffraction pattern (Fig. 6) shows some possibility that a $FeTiO_3$ phase is present, but the agreement with expected lines is not unambiguous. This reason, and because of the future possibility of obtaining ilmenite rich samples, no low temperature data were taken. The data in Fig. 6, as distinct from the previous two samples, shows an obviously different composition. Observed d-spacings are listed in Table VI.

Since this sample was in the form of a chip, the possible presence of single crystal ilmenite grains was checked. In the final run (35) the counter was set at the Bragg angle expected for the (111) reflection and the chip rotated through a range of 40°. A constant level was observed within statistical error, making it unlikely that any sizeable grains were present.

IV. Discussion of Results

1. Analysis of Mineral Phases. No specific knowledge of any individual sample constitution was available; we therefore considered all minerals identified in the preliminary investigation of Apollo 12 samples[3]: plagioclase (anorthite, albite, sanidine); olivine (forsterite, fayalite); pyroxene (augite, pigeonite); spinel, quartz, cristobalite, ilmenite and troilite.

An unambiguous identification of mineral phases is hampered by two factors. First, the available neutron flux results in a low inherent resolution. Although most of the data were taken with 20' collimation throughout (in-pile, before the sample and before the counter, which is relatively high for neutron patterns), the resolution is not good enough to distinguish small distortions, such as found between orthrhombic and triclinic plagioclases. It can be seen from the diffraction patterns that some narrow peaks appear comparable to the resolution width, while others are much wider, clearly superpositions of unresolved lines. For this reason the relative accuracy of the d-spacings is not better than roughly ±1%. The low resolution is especially troublesome because many of the plagioclases and pyroxenes have strong reflections at similar Bragg angles. Not many of the complex

silicate minerals have been studied by neutron diffraction; in cases where they have, such as fayalite, comparison of the neutron[4] and x-ray diffraction patterns show wide differences at high angles. This is basically because the difference in relative amplitudes (e.g., O is roughly 1.5 > Si), magnified by the increasing phase differences at large Bragg angles, is not reduced by the form-factor fall-off as in with x-rays. In other cases, such as Mn or Ti, negative scattering amplitudes cause a reversal in relative intensities, as in the case of ilmenite.[2]

To illustrate these differences, a calculation was made of the neutron intensities for the tetragonal low cristobalite phase. These are compared with observed x-ray intensities[5] in Table VII.

Of course, these differences are in reality an advantage because they provide additional, complementary information to x-ray data that has been used to advantage in many structure determinations. To exploit this information in the present case would require synthesis and neutron diffraction measurements of the phases in question; such a comprehensive program is outside the scope of this work.

We have listed after the d-spacings in each of the tables some probable assignments to crystal phases, which must be considered tentative in view of the above comments. As a result of these assignments, we make the following qualitative estimates as to composition:

(1) samples 12070,119 and 12071,6 are almost identical in composition, containing predominantly plagioclase (anorthite, sanidine), also pyroxenes (augite pigeonite); olivines (forsterite) in lesser amounts; quartz, cristobalite and spinel possibly present; trolite and ilmenite probably not present.

(2) sample 12008,7 is probably predominantly pyroxenes (augite, pigeonite, eulite) and olivines (forsterite); quartz, cristobalite, ilmenite and spinel possibly present; plagioclases probably only in small amounts; troilite not present.

2. Possible Magnetic Ordering. The observation of a possible magnetic reflection in the low temperature data on sample 12071,6 is intriguing, primarily because we can rule out any known magnetic structure so far determined by neutron diffraction.

The known possible antiferromagnetic materials in the phases present are troilite (FeS), fayalite (Fe_2SiO_4) and ferrosilite ($FeSiO_3$), the iron analog of pyroxmangite. The magnetic structures of the first two are known[4,6] and no magnetic reflection coincides with the one observed, namely 9.18 A.

However, there is a very good fit with the (010) reflection of a synthetic orthoferrosilite,[7] raising the likely possibility that it may be due to a high-Fe silicate, approaching eulite. This phase has not yet been studied with neutron diffraction, and of course, not much can be said on the basis of such limited data about the structure, other than that the (010) would arise from spin moments alternating along the b-axis. If subsequent study on terrestrial material should prove this ordering to exist, it will probably be the only antiferromagnetic structure first determined from lunar material.

V. Conclusions

Although this is only a preliminary study (involving about two man-months effort) and its main intention was frustrated, we may conclude:

(1) neutron diffraction methods can aid in the identification of crystalline mineral phases in lunar material, particularly if expanded efforts are made to obtain characteristic diffraction patterns of the isolated phases.

(2) magnetic ordering effects can be studied and should be pursued on synthetic pyroxene structures to confirm the suspected origin of the magnetic diffraction effects reported above.

(3) As a result of (2), we believe it is quite feasible to detect antiferromagnetic ordering in lunar ilmenite if proper samples are available, and that it should be investigated because of the relevance of this material to studies of remanent magnetizations of various types.

References

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TABLE I

DESCRIPTION OF SAMPLES

NASA No.	Weight (gm)	Form
12070,119	0.97	fines
12071,6	2.07	3 chips + residual fines
12008,7	1.409	single chip

TABLE II

SUMMARY OF EXPERIMENTAL RUNS

Run No.	Sample	Wavelength (Å)	Temp (K)	Angular Range (deg)	Holder	Monitor Setting
0	12070,119	2.38	300	3-100	1/8"V	1.08×10^6
1	"	"	77	5-37.1	"	7.92×10^5
2	"	"	4.2	5-34.9	"	"
3	"	1.36	300	5-55	"	6×10^5
4-5	"	"	"	"	"	"
6	12070,119	1.36	4.2	5-55	"	"
7-9	"	"	"	"	"	"
10 (terminated)						
11	12070,119	1.36	4.2	8-20	"	"
12-17	"	"	"	"	"	"
18	12070,119	1.36	300	8-20	"	"
19-24	12070,119	1.36	4.2	8-20	"	"
25 Empty V sample holder						
26	12071,6	1.36	300	5-55	1/2"Al	7.2×10^5
27,28	"	"	"	"	"	"
29	12071,6	1.36	4.2	"	"	"
30-32	"	"	"	"	"	"
33	12008,7	"	300	"	1" Al	7.2×10^5
34	"	"	"	"	"	"
35	12008,7	1.36	300	(sample rotated)		1×10^5

Monitor count rate: 4500/sec at 2.38 Å
6500/sec at 1.36 Å

TABLE III

COLLATED DATA RUNS

Run No.	Sample	Wavelength	Temp	Raw Data	Monitor Setting
100	12070,119	1.36	300	adds 3-5	1.8×10^6
101	12070,119	1.36	4.2	adds 6-9	2.4×10^6
102	12070,119	1.36	4.2	adds 11-17	4.2×10^6
103	12070,119	1.36	300	adds 18-24	4.2×10^6
104	12070,119	1.36	-	subtracts 102-103	4.2×10^6
110	12071,6	1.36	300	adds 26-29	1.44×10^6
111	12071,6	1.36	4.2	adds 30-32	1.44×10^6
112	12071,6	1.36	-	subtracts 111-110	1.44×10^6
120	12008,7	136	300	adds 33,34	1.44×10^6

TABLE IV

OBSERVED d-SPACINGS - SAMPLE 12070,119

d(A)	I^*_{rel}	Possible Origin**
6.96	w	
6.40	w	
4.66	w	Pi,Sp
4.01	mw	An,C
3.88	w	O
3.75	w	Sa,O
3.34	mw	Sa,An,Au,Q
3.19	s	An,Pi,Au
2.99	ms	An,Pi,Au,O
2.91	ms	Pi,Au
2.79	w	O,Au
2.50	ms(u)	An,Pi,Au,O
2.36	mw	Au
2.27	ms(u)	O,Au
2.22	mw	Pi,Au
2.13	s	Pi,Au
2.03	m	Pi,Au,Sp
1.95	mw(u)	Pi,Au
1.82_7	mw	Pi,Au
1.75_7	ms	O,Pi,Au
1.63_0	m	Pi,Au,O
1.49_4	ms	Pi,Au,O

* w = weak, mw = medium weak, m = medium, ms = medium strong, s = strong, u = unresolved.

**An = anorthite, Sa = sanidine, Au = augite, Pi = pigeonite, O = olivine (forsterite), Sp = spinel, C = low cristobalite, Q = α-quartz.

TABLE V

OBSERVED d-SPACINGS - SAMPLE 12071,6

d(A)	I^*_{rel}	Possible Origin*
7.15	w	
6.46	w	
4.62	w	Pi,Sp
4.02	m	An,C
3.73	mw	Sa,O
3.62	w	
3.49	w	O
3.33	mw	Sa,An,Au,Q
3.18	s	An,Pi,Au
3.00	m	An,Pi,Au,O
2.91	m	Pi,Au
2.79	w	O,Au
2.49	m(u)	An,Pi,Au,O
2.23	m(u)	Pi,Au
2.13	s	Pi,Au
1.93_4	w(u)	Pi,Au
1.80_8	m(u)	Pi,Au
1.75_2	m(s)	Pi,Au,O
1.62_0	m	Pi,Au,O
1.48_5	ms(u)	Pi,Au,O

*See Table IV for meaning of symbols.

TABLE VI

OBSERVED d-SPACINGS - SAMPLE 12008,7

d(Å)	I^*_{rel}	Possible Origin*
6.40	w	
5.13	w	O
4.66	w	Pi,Sp
4.39	w	
4.07	mw	An,C
3.89	w	O
3.73	w	O,Sa
3.50	w	O
3.31	w	Sa,An,Au,Q
3.21	w	An,Pi,Au
2.98	m	An,Pi,Au,O
2.91	mw(u)	Pi,Au
2.77	m	O,Au
2.52	ms	An,Pi,Au,O
2.46	mw(u)	O,Sp,Pi,C
2.32	ms	O,Au,Al(111) (sample holder)
2.26	s	O,Pi,Au
2.12_5	m	Pi,Au
2.02_0	m	Sp,Pi,Au,Al(200)
1.81_4	mw	Pi,Au
1.74_5	ms	O,Pi,Au
1.64	m(u)	O,Pi,Au
1.48_5	ms	O,Pi,Au

*See Table IV for meaning of symbols.

TABLE VII

COMPARISON OF X-RAY AND NEUTRONS FOR CRISTOBALITE (LOW)

hkl	d	I_{rel} (x-ray)	I_{rel} (neutron)
(101)	4.04	100	100
(111)	3.14	12	11
(102)	2.85	14	17
(200)	2.49	18	20
(112)	2.47	6	< 1
(201)	2.34	< 1	8
(211)	2.12	4	10
(202)	2.02	3	19
(113)	1.935	4	21
(212)	1.875	4	29
(220)	1.760	1	< 1
(004)	1.735	1	< 1
(203)	1.697	3	10
(104)	1.640	1	6
(301)	1.613	5	27
(213)	1.605	2	< 1
(310,222)	1.572	1	1
(311)	1.535	2	7
(302)	1.496	3	6
(312)	1.432	2	7
(204)	1.425	1	1
(223)	1.401	1	11
(214)	1.370	1	18
(321)	1.353	1	2
(303)	1.348	1	2
(105)	1.340	1	9
(313)	1.302	2	15
(322)	1.282	2	16
(224)	1.236	< 1	3
(401)	1.223	< 1	8
(410)	1.207	1	9
(411)	1.112	3	10
(323)	1.185	2	20
(215)	1.180	1	13
(331)	1.156	< 1	2
(420)	1.112	3	10

Figure Captions

1. Neutron diffraction pattern of sample 12070,119 at room temperature. Positions for first two strong ilmenite peaks are indicated. In this and subsequent patterns the observed angle should be increased by a +0.2° zero correction.

2. Neutron diffraction pattern of sample 12070,119 at 4.2 K.

3. Low angle neutron diffraction patterns of 12070,119: (a) room temperature; (b) 4.2 K; and (c) subtraction of low from high temperature data.

4. Diffraction pattern of sample 12071,6 at room temperature.

5. Diffraction pattern of sample 12071,6 at 4.2 K.

6. Diffraction pattern of sample 12008,7 at room temperature.

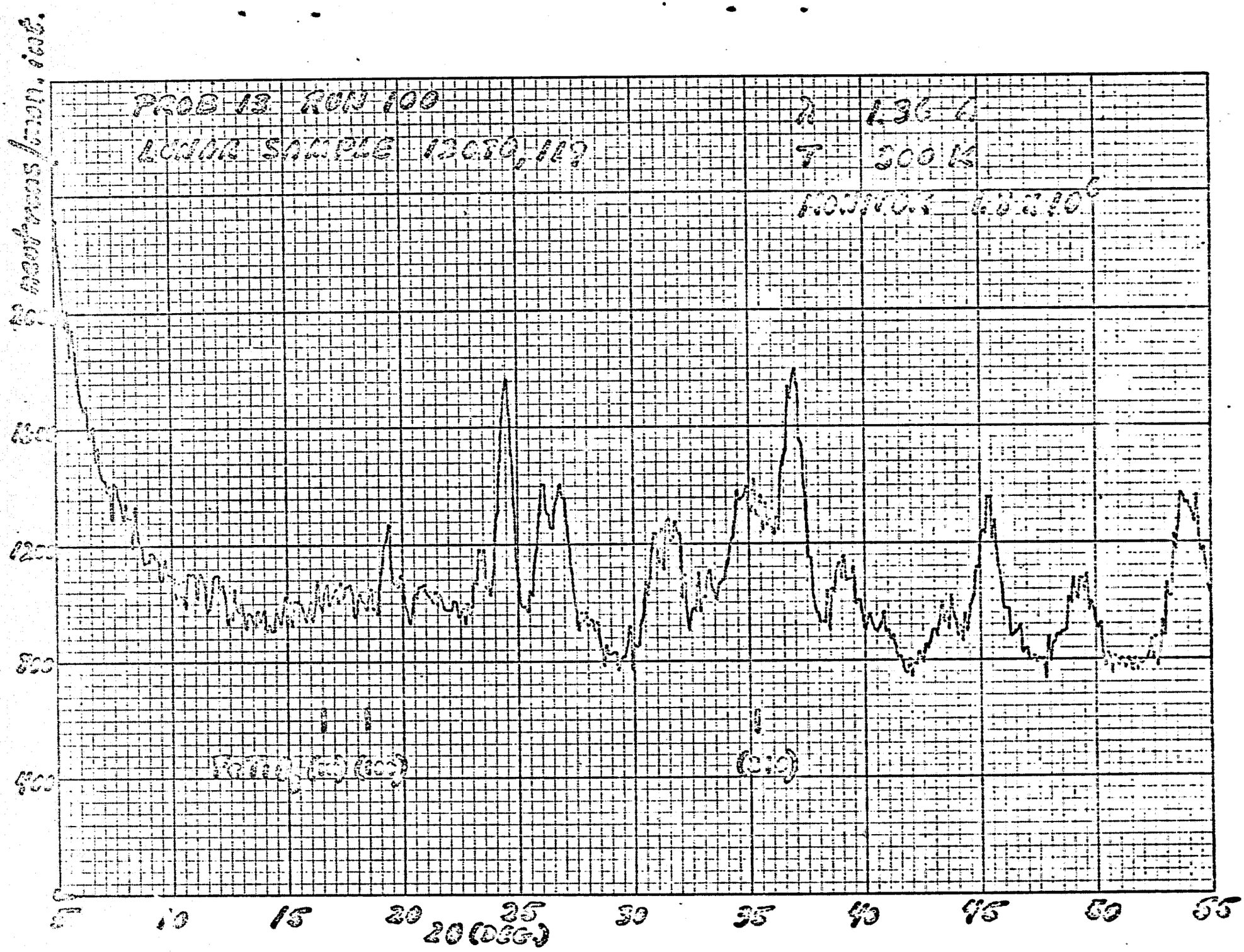

FIG. 1

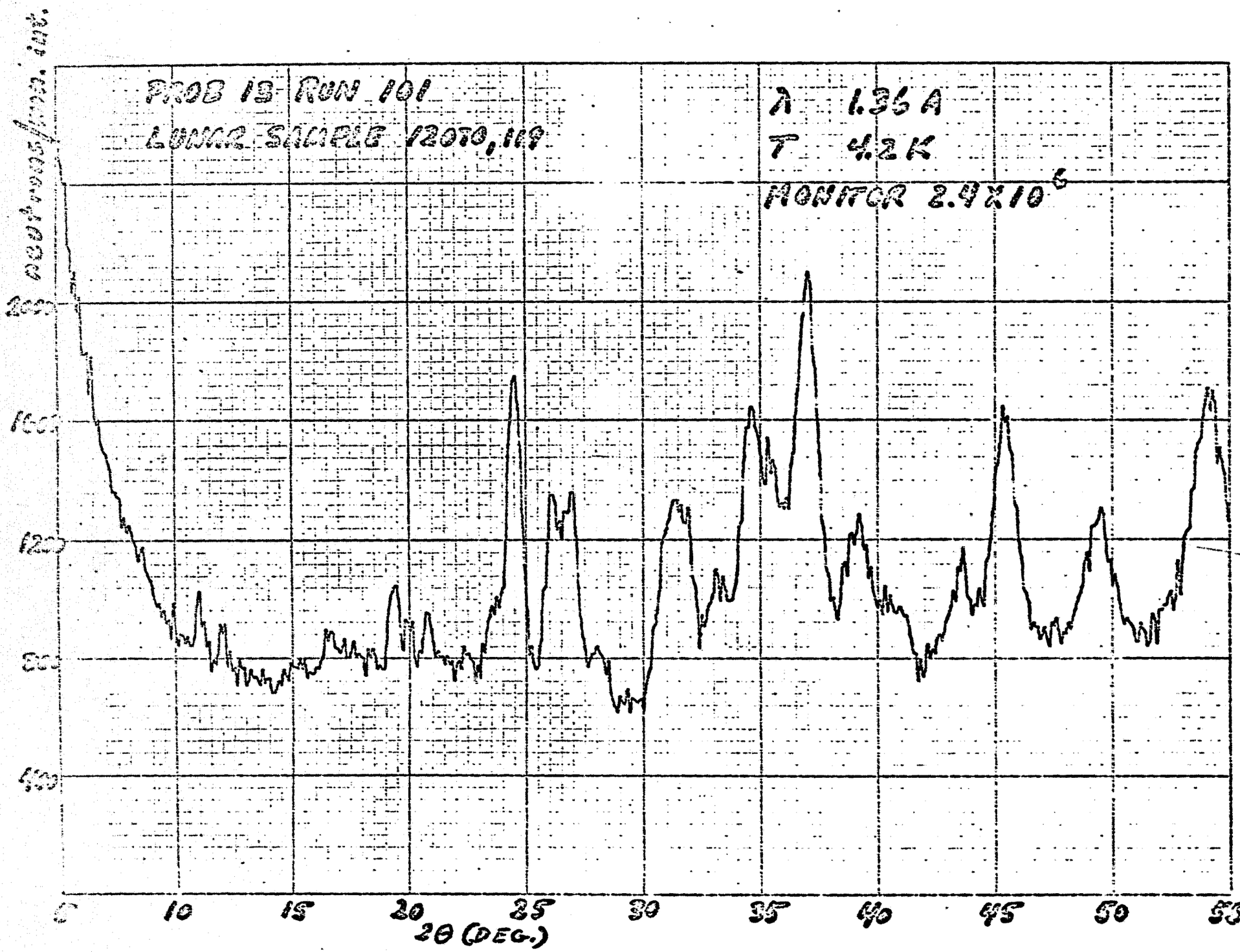
PROB 13 RUN 101
LUNAR SAMPLE 12070,119
λ 1.36 A
T 4.2 K
MONITOR 2.4 X 10^6
2000
1600
1200
800
400
10
15
20
25
30
35
40
45
50
55
2θ (DEG.)

FIG. 2

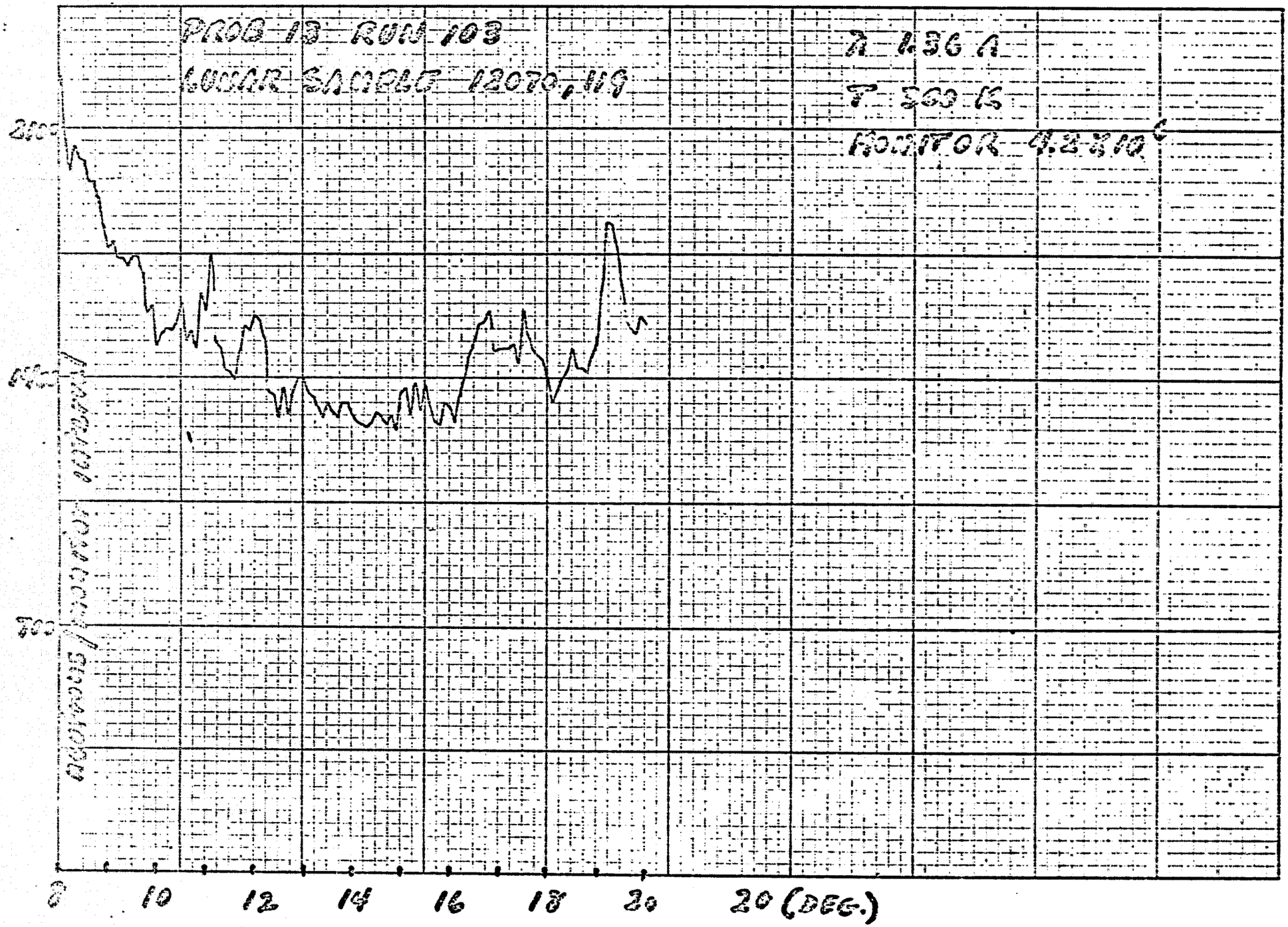
PROB 13 RUN 103
LUNAR SAMPLE 12070, 119
λ 1.36 A
T 360 K
MONITOR 4.2 X 10^6
2100
1400
700
8
10
12
14
16
18
20
20 (DEG.)

FIG. 3(a)

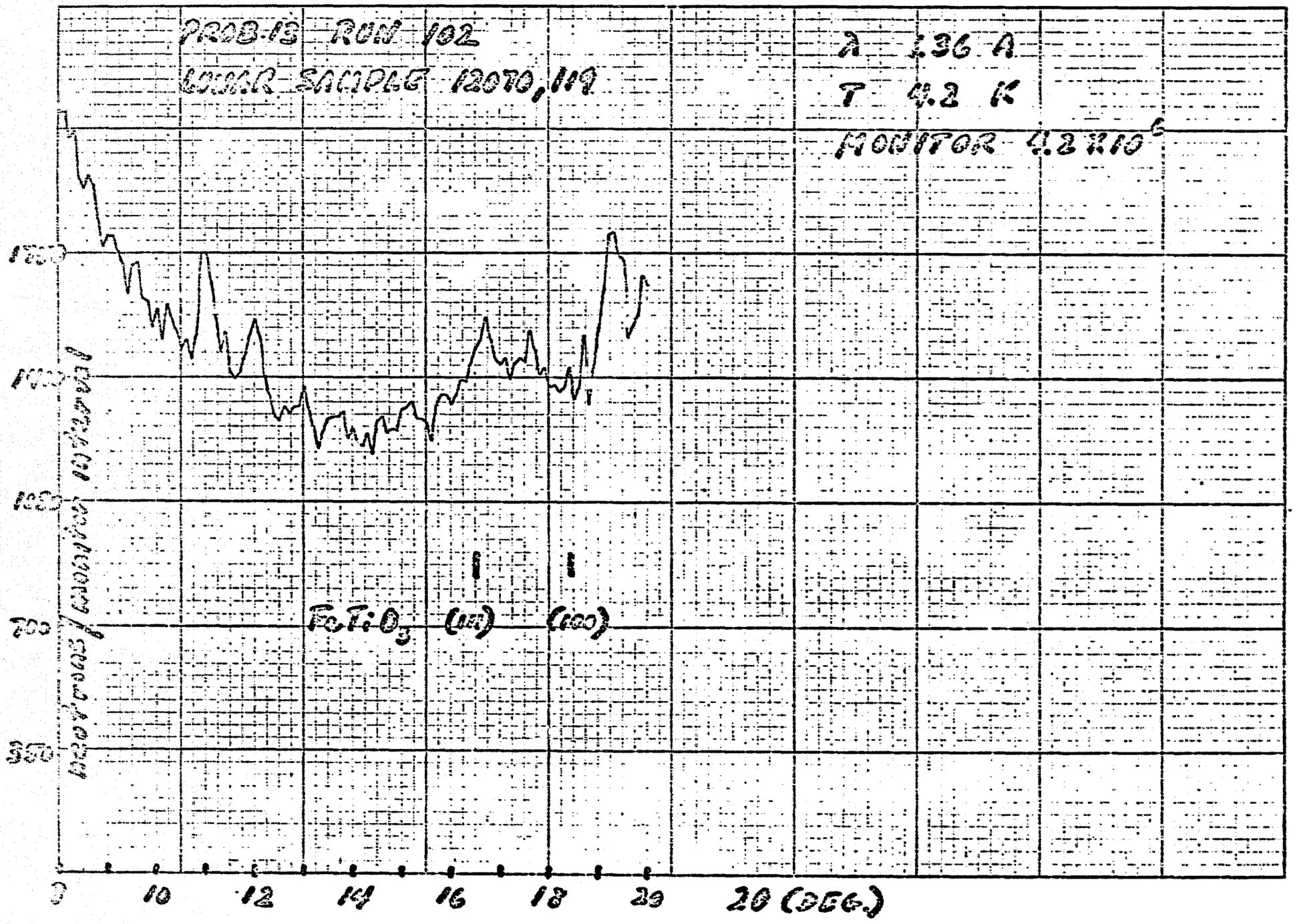
PROB-13 RUN 102
LUNAR SAMPLE 12070,119
λ 1.36 A
T 4.2 K
MONITOR 4.2 X10^6
FeTiO3 (111) (100)
neutrons/monitor interval
1750
1400
1050
700
350
0
10
12
14
16
18
20
2θ (DEG.)

FIG. 3(b)

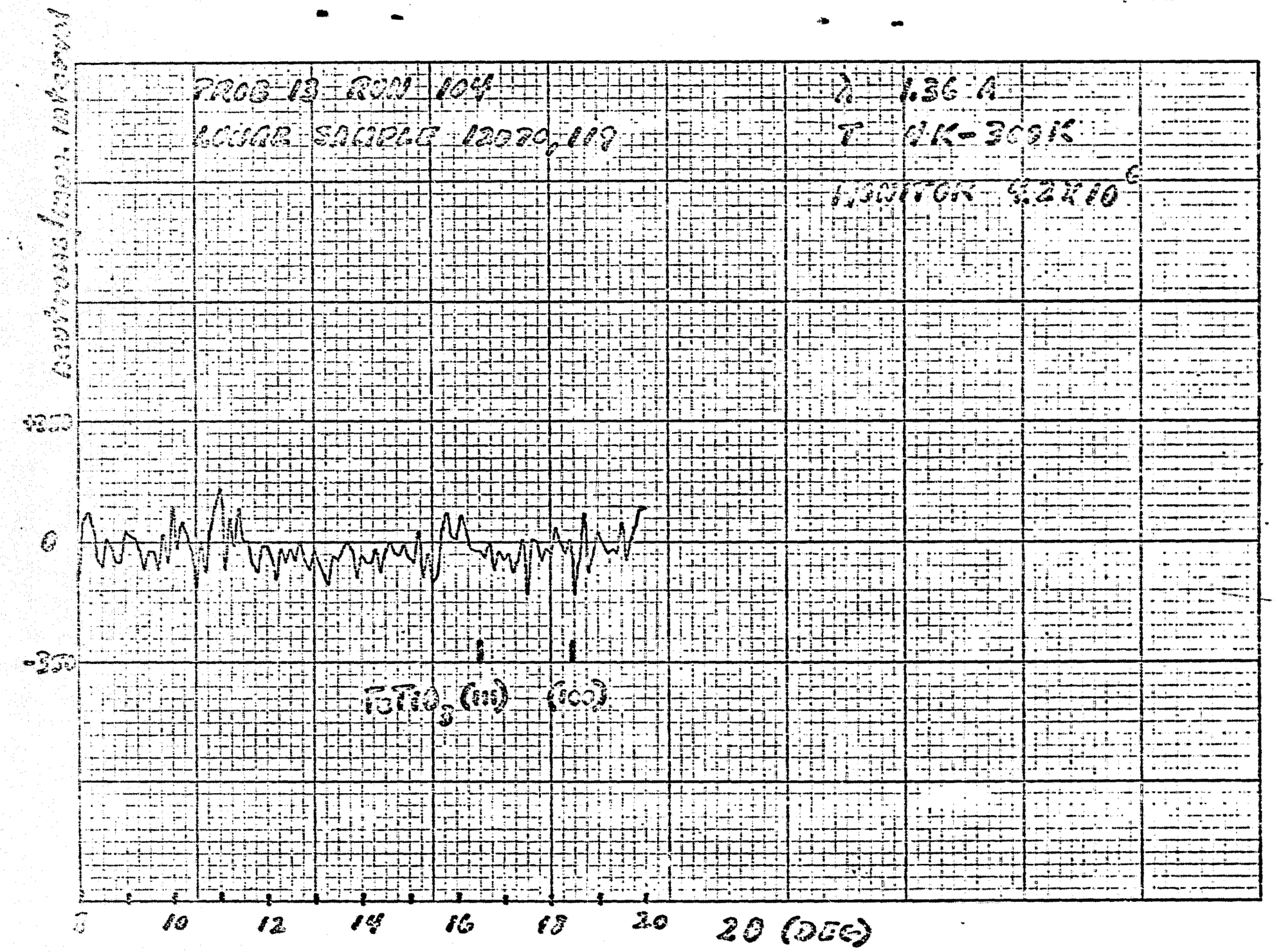
PROB 13 RUN 104
LOWAR SAMPLE 12070, 119
λ 1.36 A
T 4K-300K
MONITOR 4.2X10^6
0
-350
FeTiO3 (111)
(100)
10
12
14
16
18
20
2θ (DEG)

FIG. 3(c)

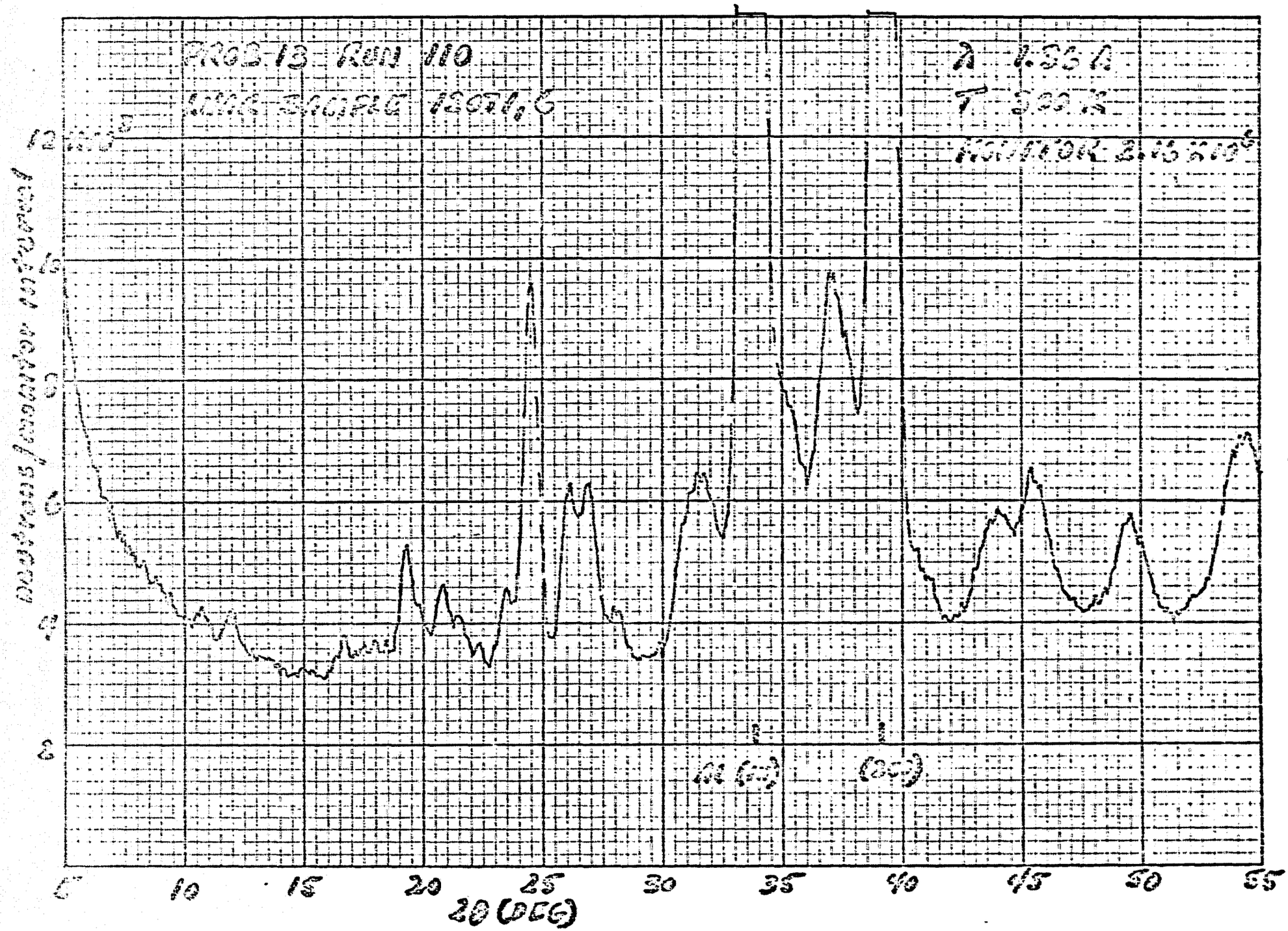
PROB 13 RUN 110
λ 1.36 A
T 300 K
neutrons/monitor interval
2θ (DEG)
5
10
15
20
25
30
35
40
45
50
55
2
4
6
8
10
12

FIG. 4

FIG. 5

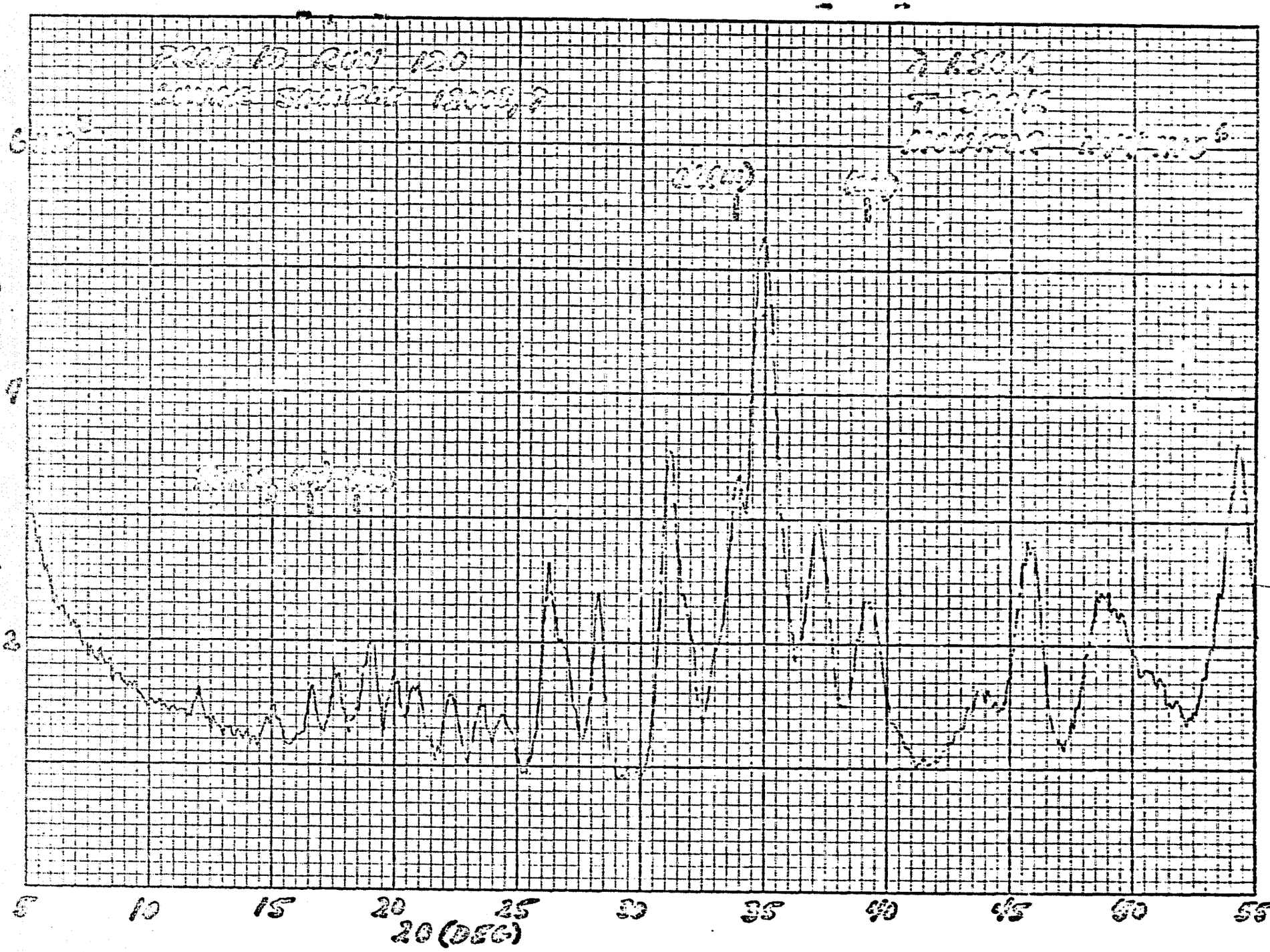

FIG. 6