Chapter III
X-ray diffraction studies

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X-RAY DIFFRACTION STUDIES

3.1 X - ray diffraction methods

In 1912 German physicist Max von Laue experimentally showed that x-rays can be diffracted by the crystal. During the same year two English physicists W.H. Bragg and W.L. Bragg (29-1) successfully analyzed the Laue experiment and were able to derive the necessary conditions for diffraction mathematically. The very famous Bragg law is given by

$$n\lambda = 2d \sin \theta \quad \ldots \quad 3.1.$$

Experimentally the Braggs law can be used in two ways. By use of the x-rays of known wave length 'λ' and measuring the angle θ one can determine the spacing 'a' in between the lattice planes of a crystal, in order to obtain the information about the crystal structure. Alternatively one can use a crystal with planes of known spacing 'd' and measure θ to determine the wavelength λ of the radiation used. X-ray diffraction is a tool for the investigation of the crystal structure of a ferrite. X-ray diffraction can indirectly reveal details of internal structure of the order of 10^{-8} cm in size.

Diffraction by the crystal is possible only when the Bragg's law is satisfied. With monochromatic radiation an arbitrary setting of a single crystal in a beam of x-rays may not produce any diffracted beams. For this Bragg's law must be satisfied. This can be made possible by continuously varying either λ or θ during the experiment. The way in which these quantities are varied gives rise to the three important diffraction methods, including the Laue method mentioned.

TABLE 3.1

Method	λ	θ
1. Laue method	variable	fixed
2. Rotating crystal method	fixed	variable
3. Powder method	fixed	variable

The details of these methods have been discussed in literature (25-2, 26-3). Here powder method is discussed briefly.

3.1.1 Powder method

This method is widely used in the study of ferrites, as the ferrite materials are polycrystalline. This method was first developed by Debye and Scherrer (27-4) in 1919 and A.W. Hull (38-5) in 1917 independently. In this method a fine powder is used. The monochromatic beam of x-rays is collimated to fall on the specimen. The crystallites are randomly oriented hence the reciprocal lattice vector of all crystallites are oriented in all directions. The reciprocal lattice points, lie on the surface of sphere of radicles (hkl), and exists oriented by every possible values of hkl cuts the Ewald sphere as shown in Fig. 3.1.

By the geometry of Ewald sphere, if we consider two consecutive reflections the angle between them is Bragg angle and is given by

$$\emptyset_{hkl} = S_{hkl}/4 \qquad \ldots \quad 3.2$$

Measurement of S_{hkl} in mm on a photographic film gives the value of $\emptyset_{hkl}$.

Then using Bragg's condition we can calculate the interplanar distance d.

3.2 Principle and discription of the system used

The principle of this method and main features are shown in Fig. 3.2. The incident beam of x-rays is

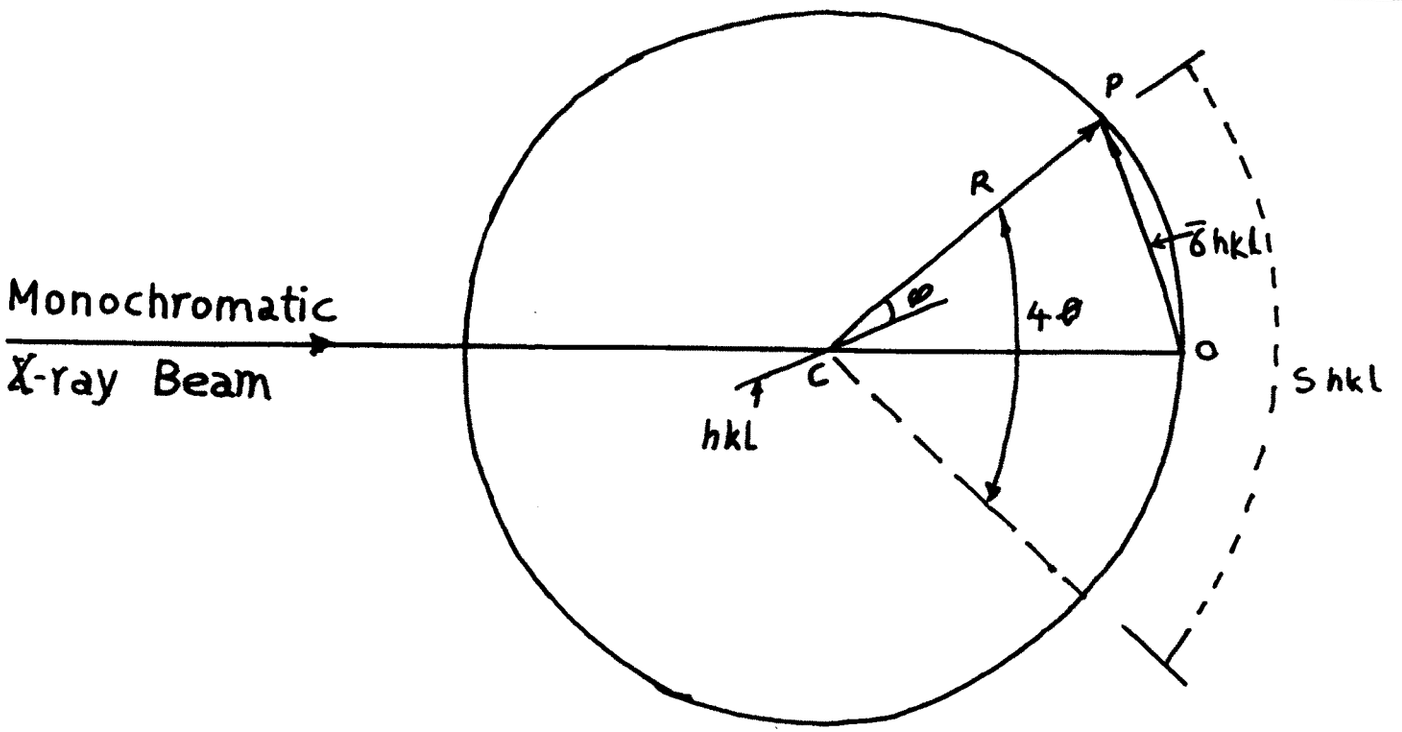
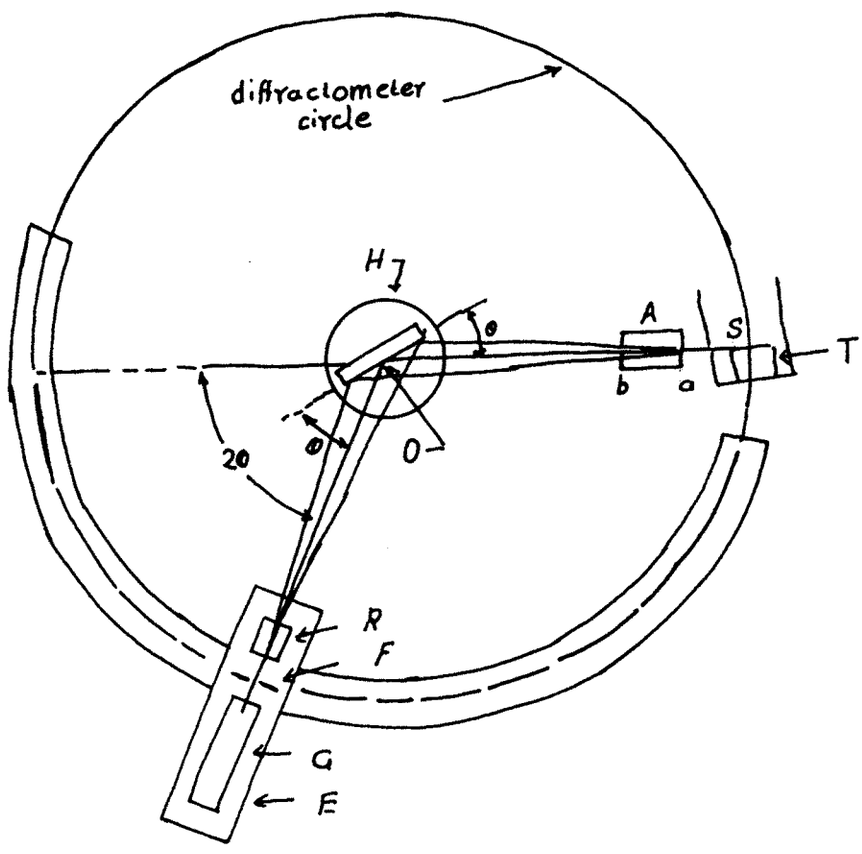


Fig: 3.1: Ewald's Sphere.



3·2: PRINCIPLE OF THE X-RAY DIFFRACTOMETER

allowed to pass through the slit A of the collimator. As the crystallites are randomly oriented, a reflection of particular position is due to a set of atomic planes which satisfy Bragg's condition. The diffracted beam gets converged and focussed at a slit F, which further enters the counter G, With the help of special slit B the diffracted beam is then collimated. The counter G is connected to a count rate meter and out put of the circuit is fed to a last automatic recorder which registers counts per second versus 2θ. The location of the centroid of the recorded peak gives 2θ for corresponding Bragg reflection. However in modern x-ray diffractometer, proportional or scintillation counter is mounted which records automatically a graph of intensity of x-rays with respect to the Bragg angle. The main advantage of the diffractometer over the Debye Scherrer method is it gives a quantitative measure of intensity.

In the present case diffraction patterns were recorded by using Philips PW - 1710 diffractometer available at common facility center Shivaji University Kolhapur. The CuK radiations with wavelenth λ = 1.5418 A° was used. The samples were scanned within the range 2θ between 10° - 85°.

3.4. Analysis of the Diffractograms

The X-ray powder pattern of all the samples were recorded using Cu Kα radiation of wavelength 1.542 A°. The lattice parameters for each ferrite sample was determined using the following procedure, by standerd techniques described in the book by cullity. We anticipate our ferrite samples to be either of hexagonal or cubic lattice type.

Analysis for hexagonal structure

Hexagonal unit cell is characterised by two variables a and c. The plane - spacing equation is

$$1/d^2 = 4/3 \left[(h^2 + hk + k^2) / a^2 \right] + l^2/c^2 \quad \ldots 3.1$$

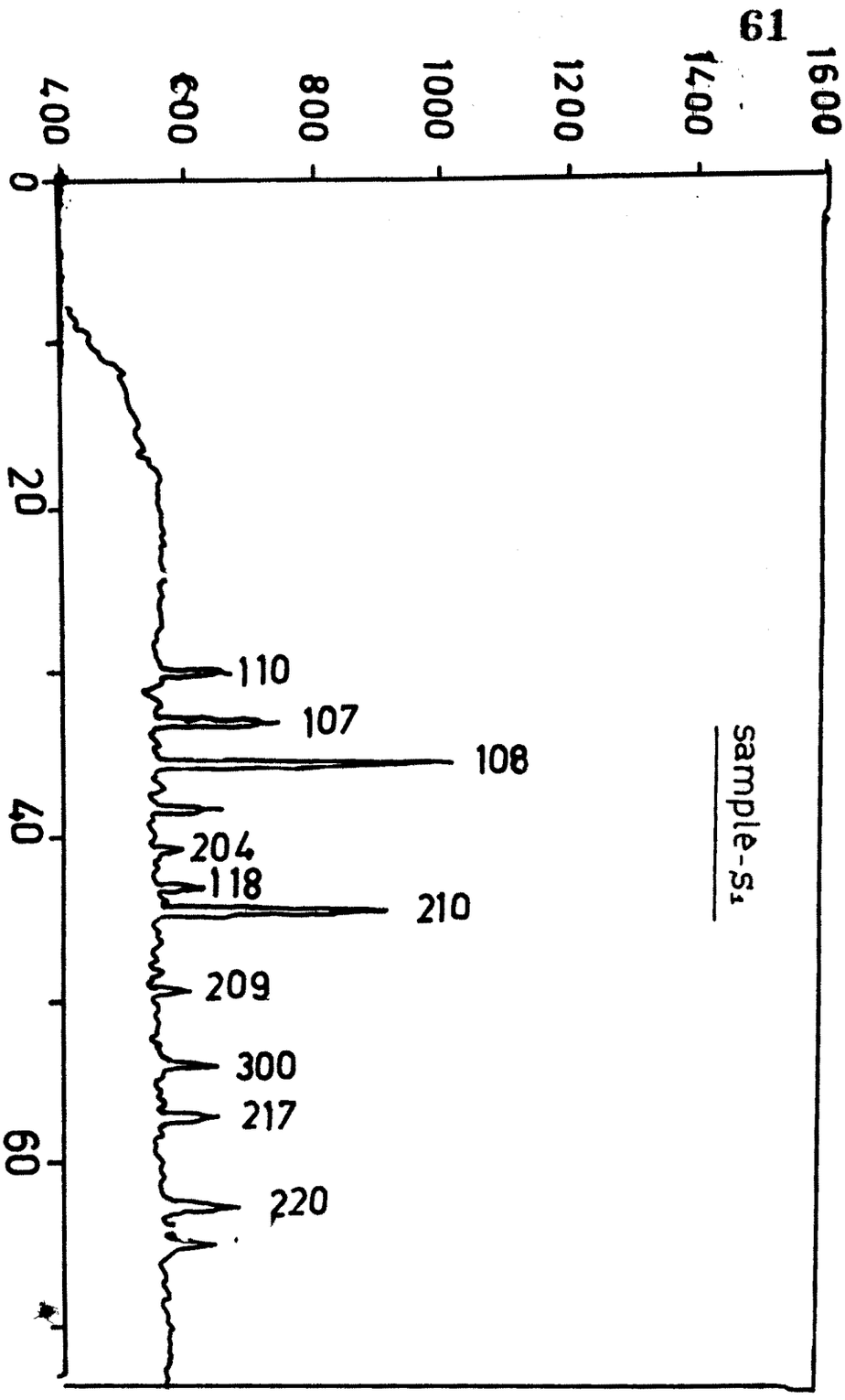
combination of the Bragg law and plane spacing equation gives

$$\sin^2 \theta = A (h^2+hk+k^2) + Cl^2 \quad \ldots 3.2$$

where

$$A = \lambda^2/3a^2 \qquad C = \lambda^2/4c^2$$

The permissible values of (h^2+hk+k^2) are 1, 3, 4, 7, 9, etc. First divide $\sin^2\theta$ values by the integers 1,3,4, etc and tabulate results. Then examine these numbers, looking for quotients which are equal to one another or equal to one of the observed $\sin^2\theta$ values. The corresponding peaks are (hk0). Then put tentatively A = $\sin^2\theta$ value. Then using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600
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1000
1200
1400
1600
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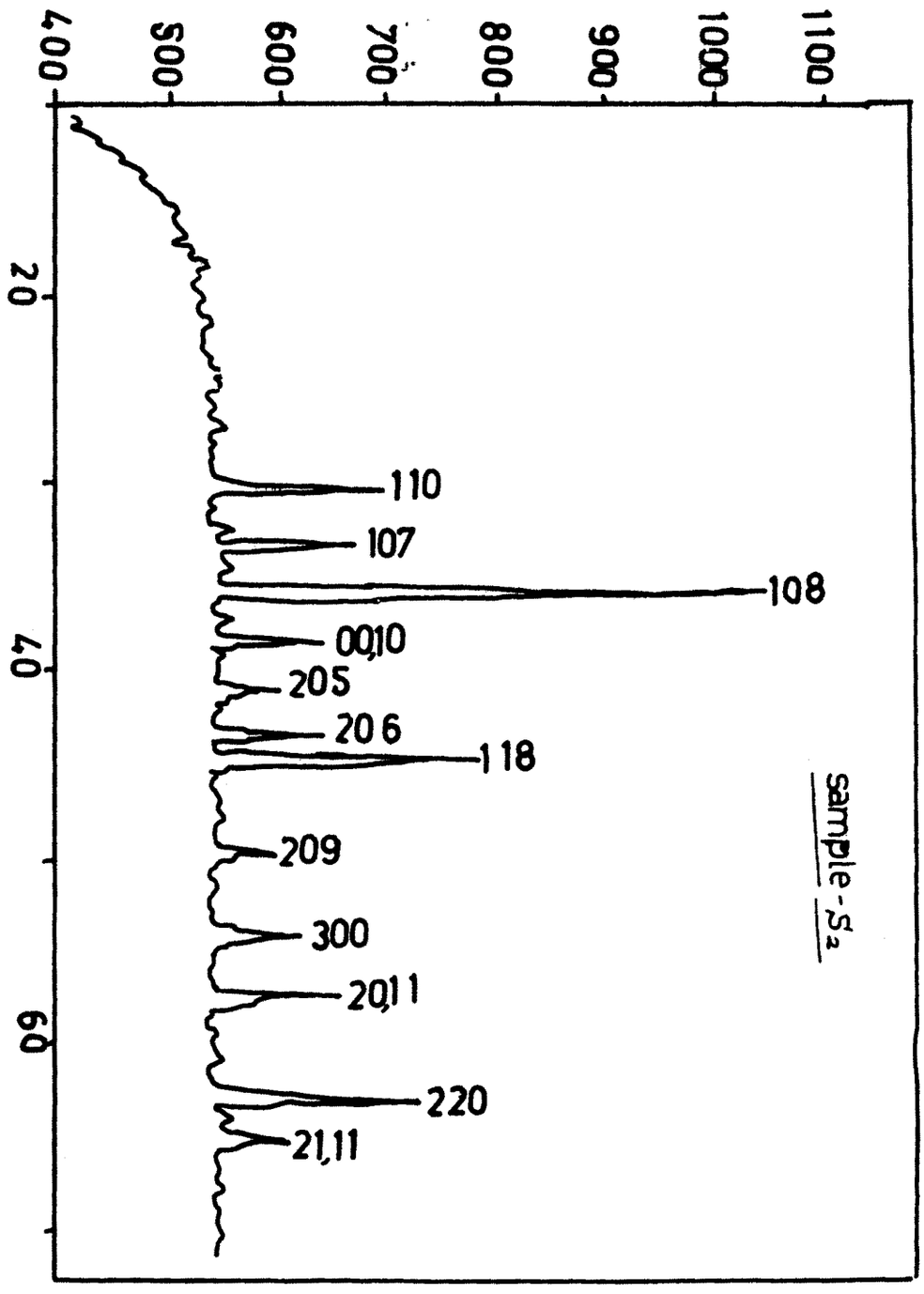
110
107
108
204
118
210
209
300
217
220
sample-S1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800
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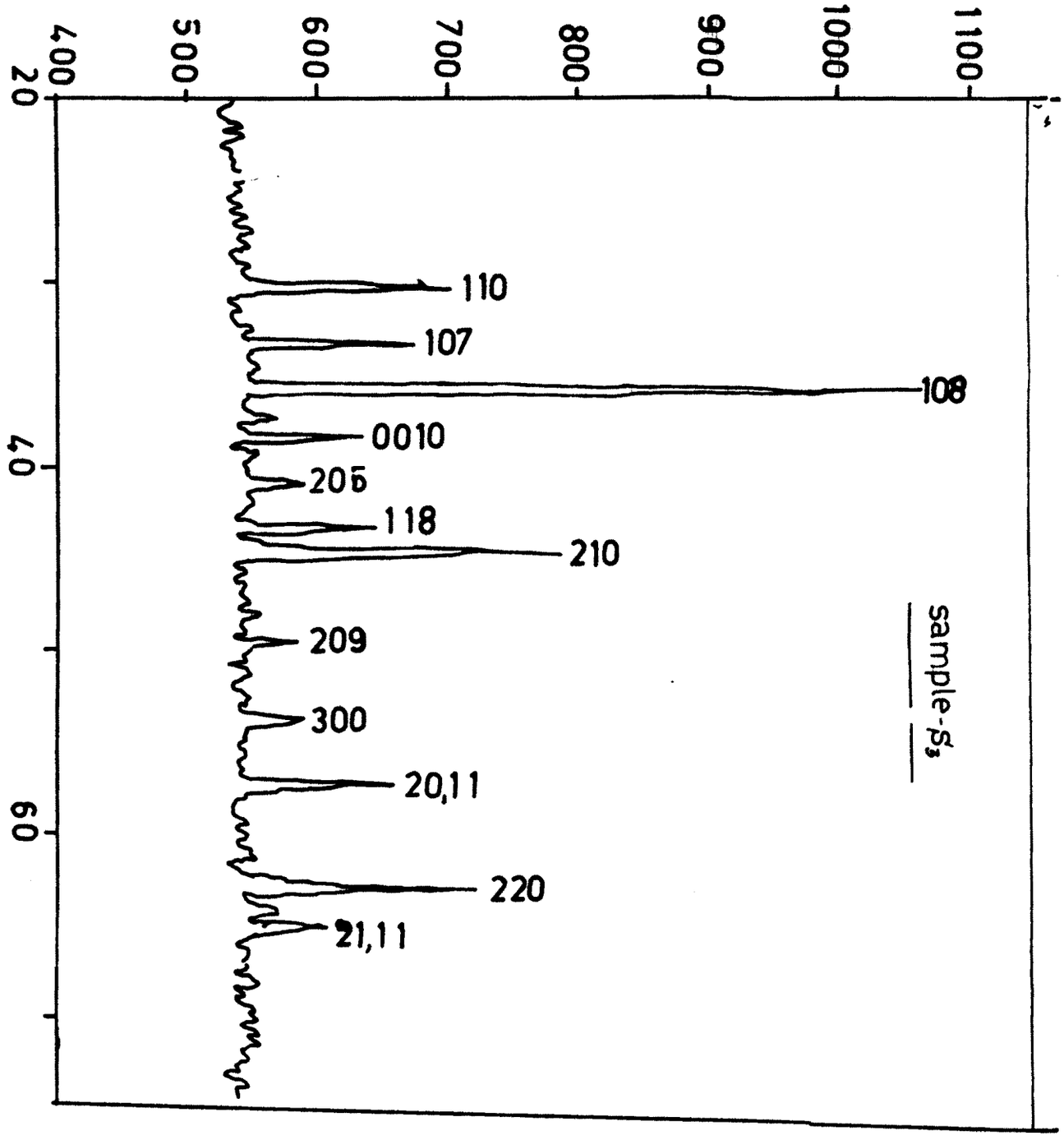
108
0010
205
206
118
209
300
2011
220
2111
sample-S2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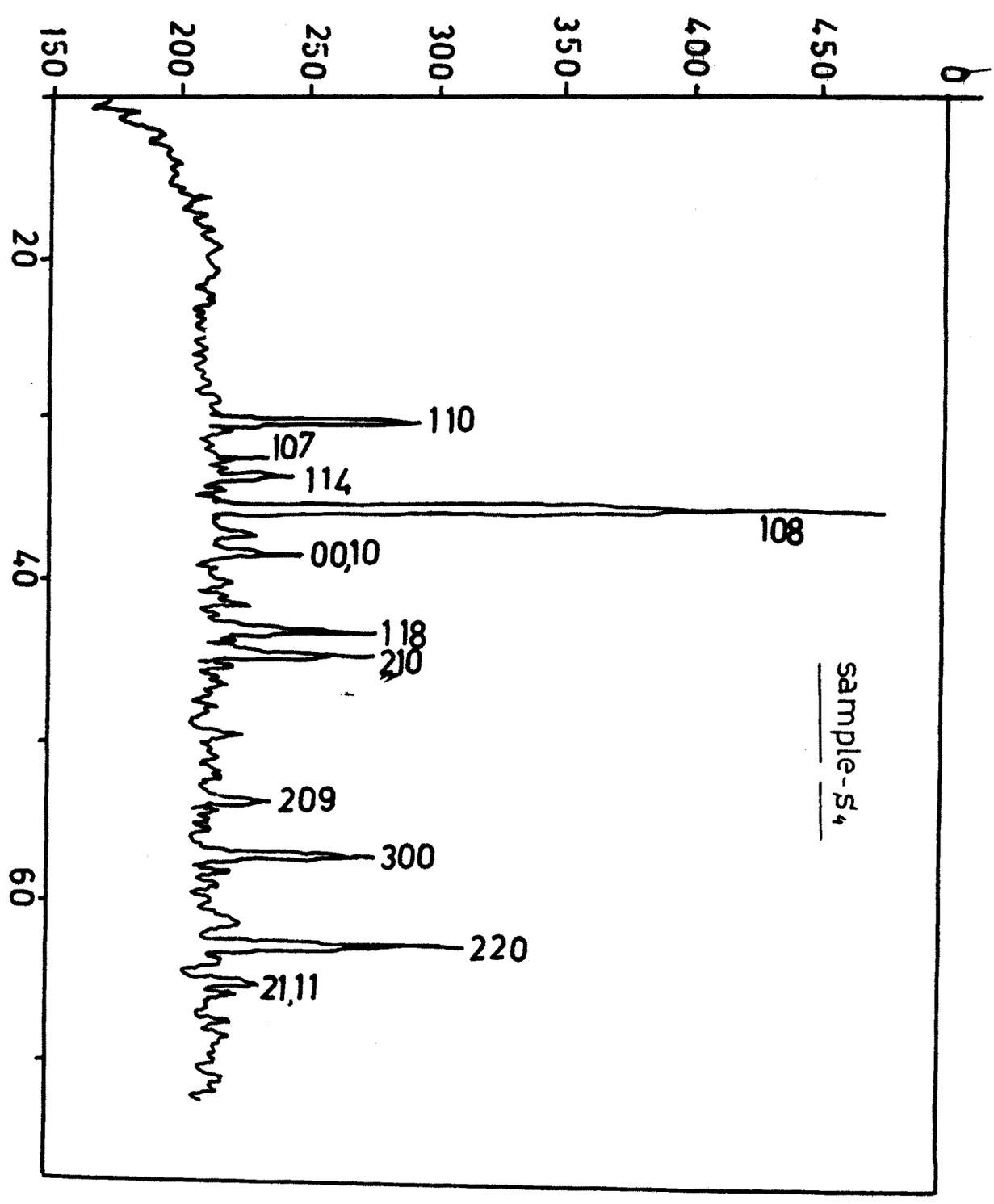
107
108
0010
205
118
210
209
300
20,11
220
21,11
sample-S3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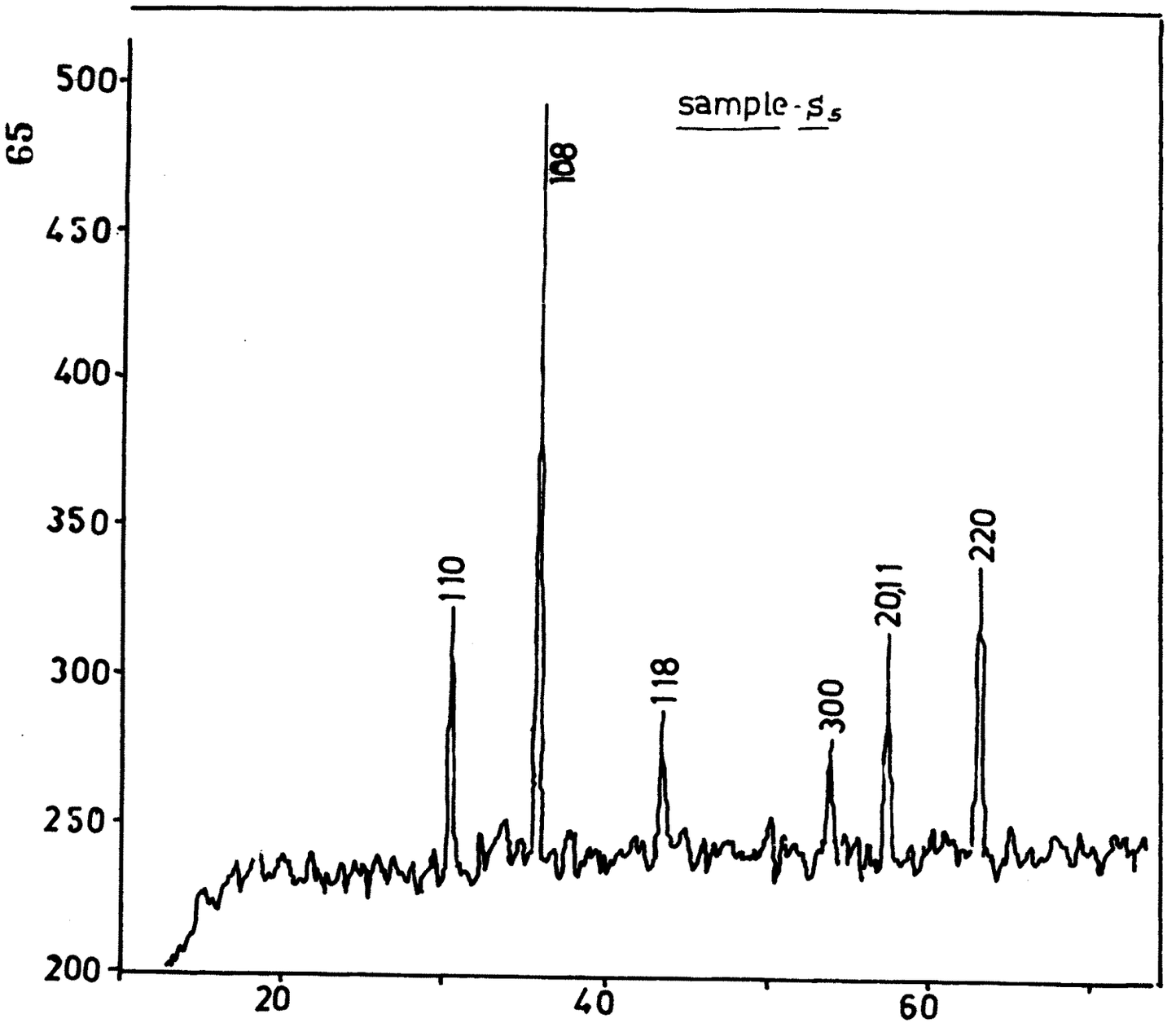
209
300
220
21,11
sample-S4


65
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350
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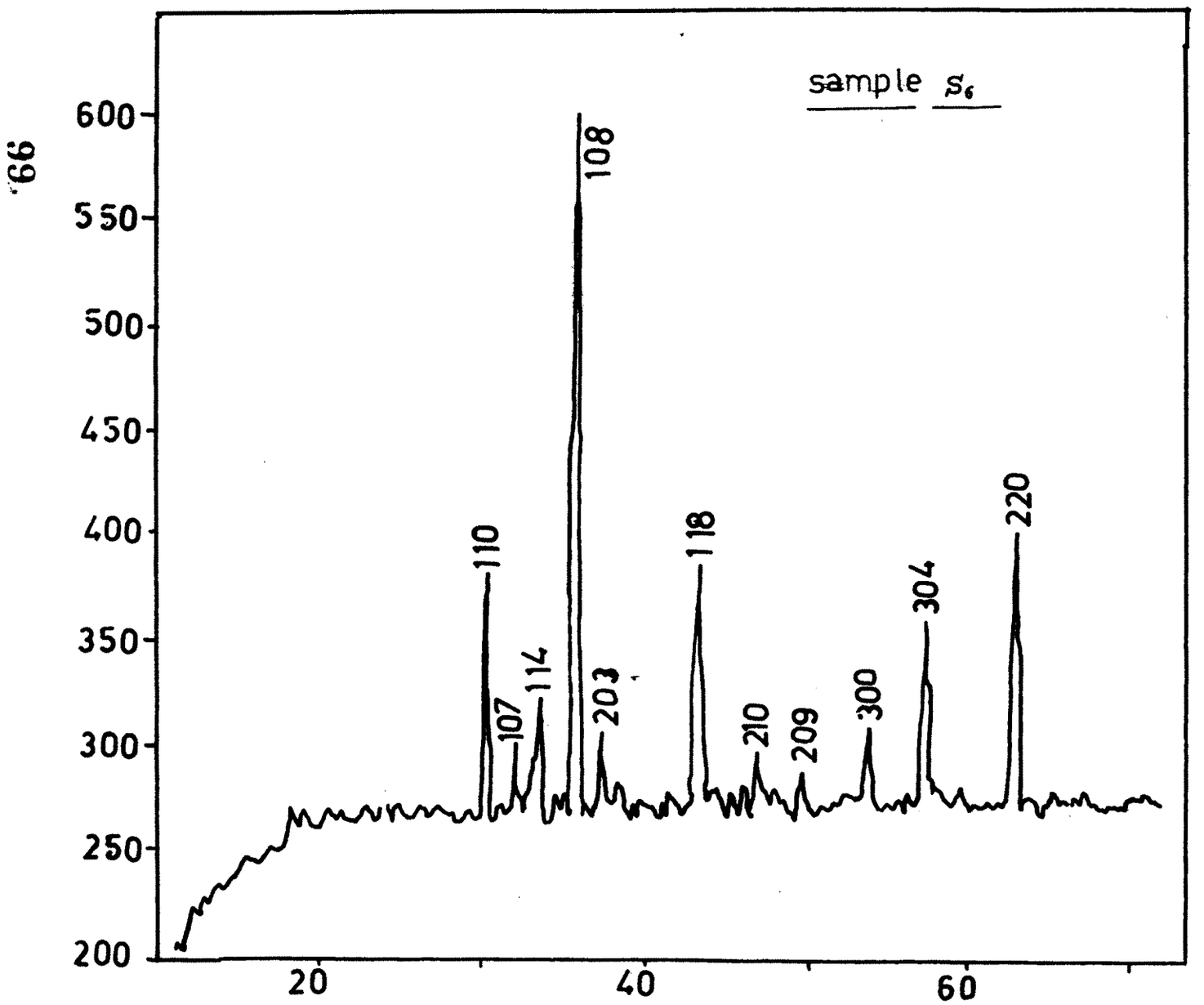
250
200
20
40
60
sample - S5
110
108
118
300
2011
220


sample S_6
600
550
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108
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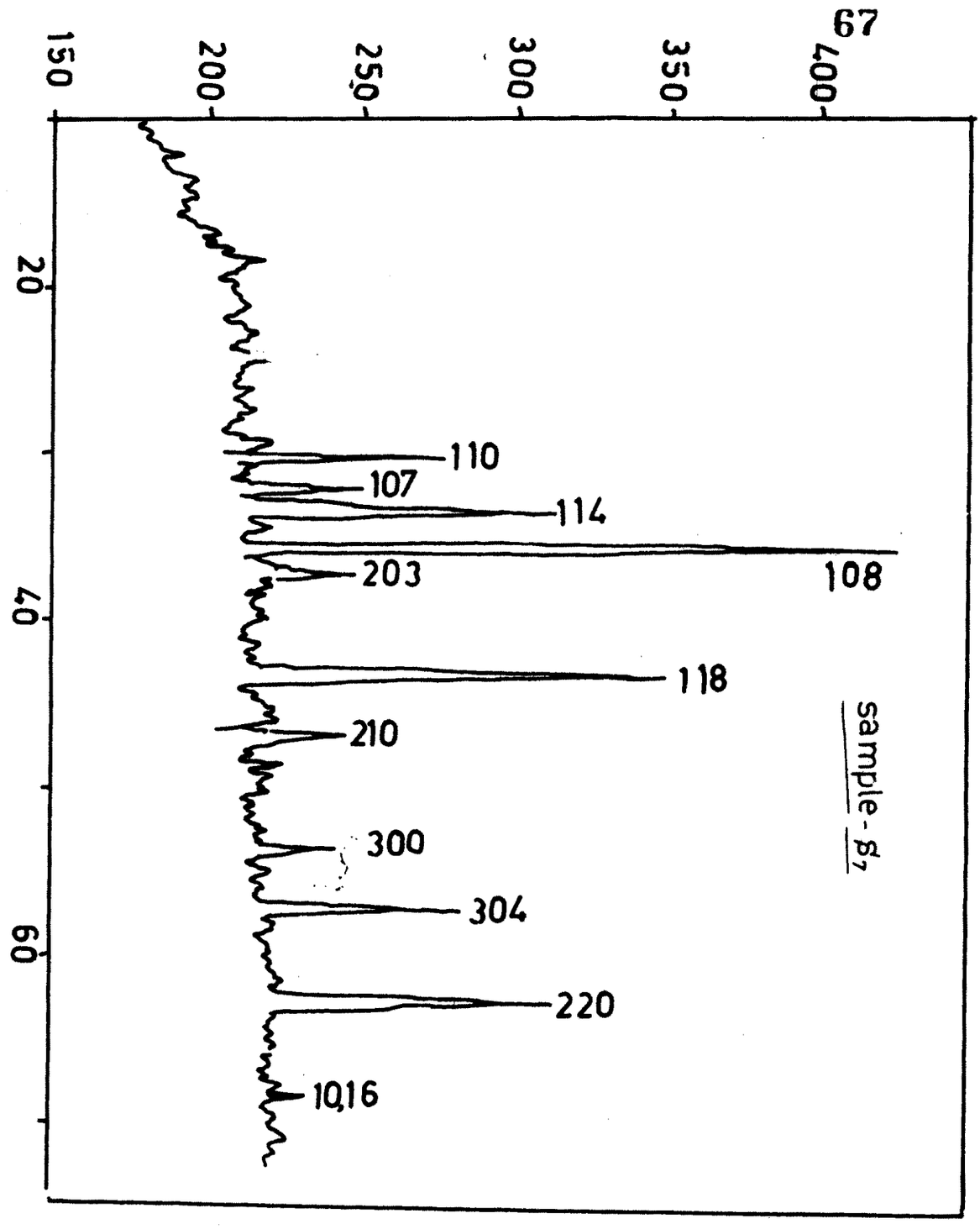
209
300
304
220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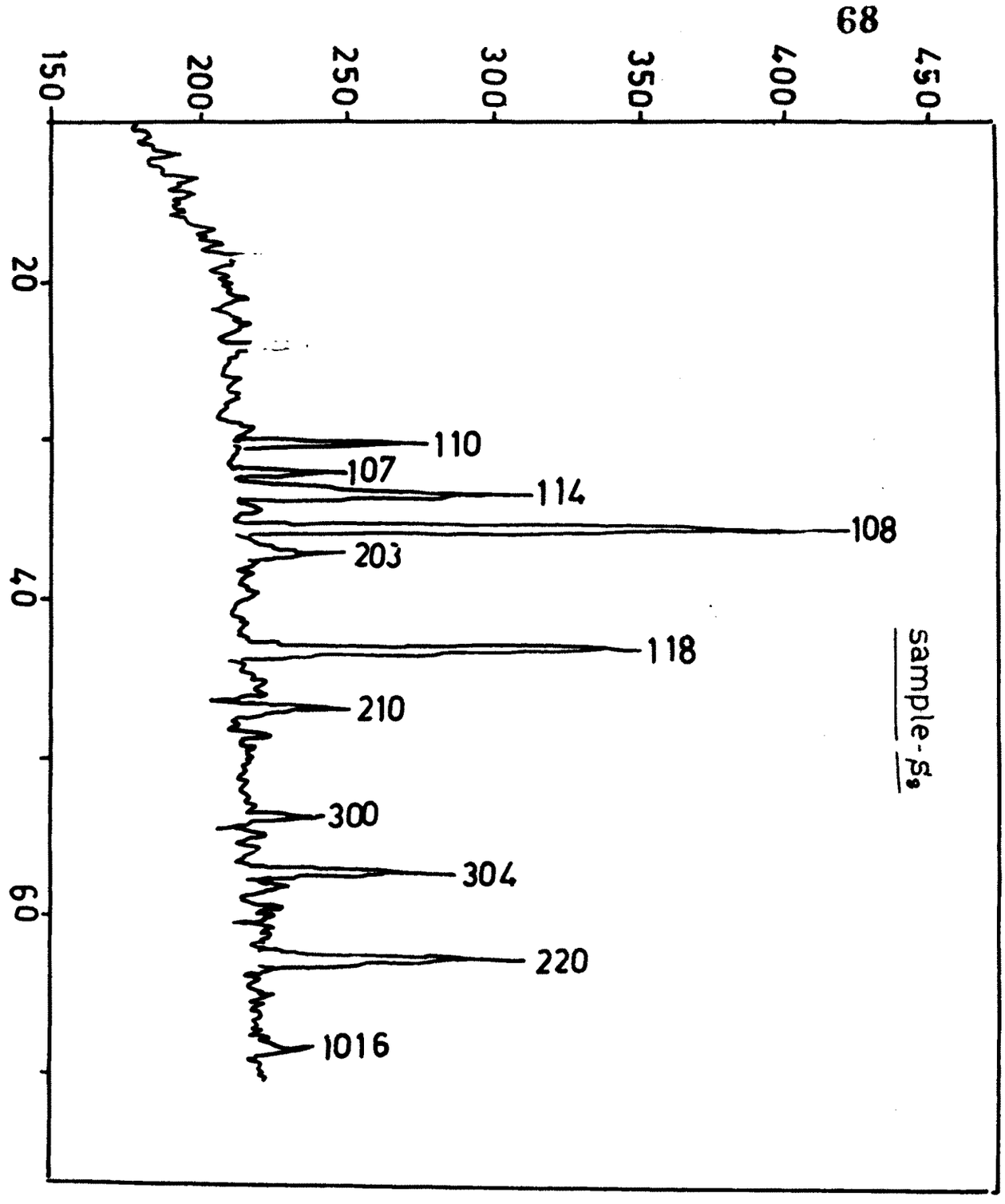
107
114
108
203
118
210
300
304
220
10,16
sample - g_7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210
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1016
sample-Si

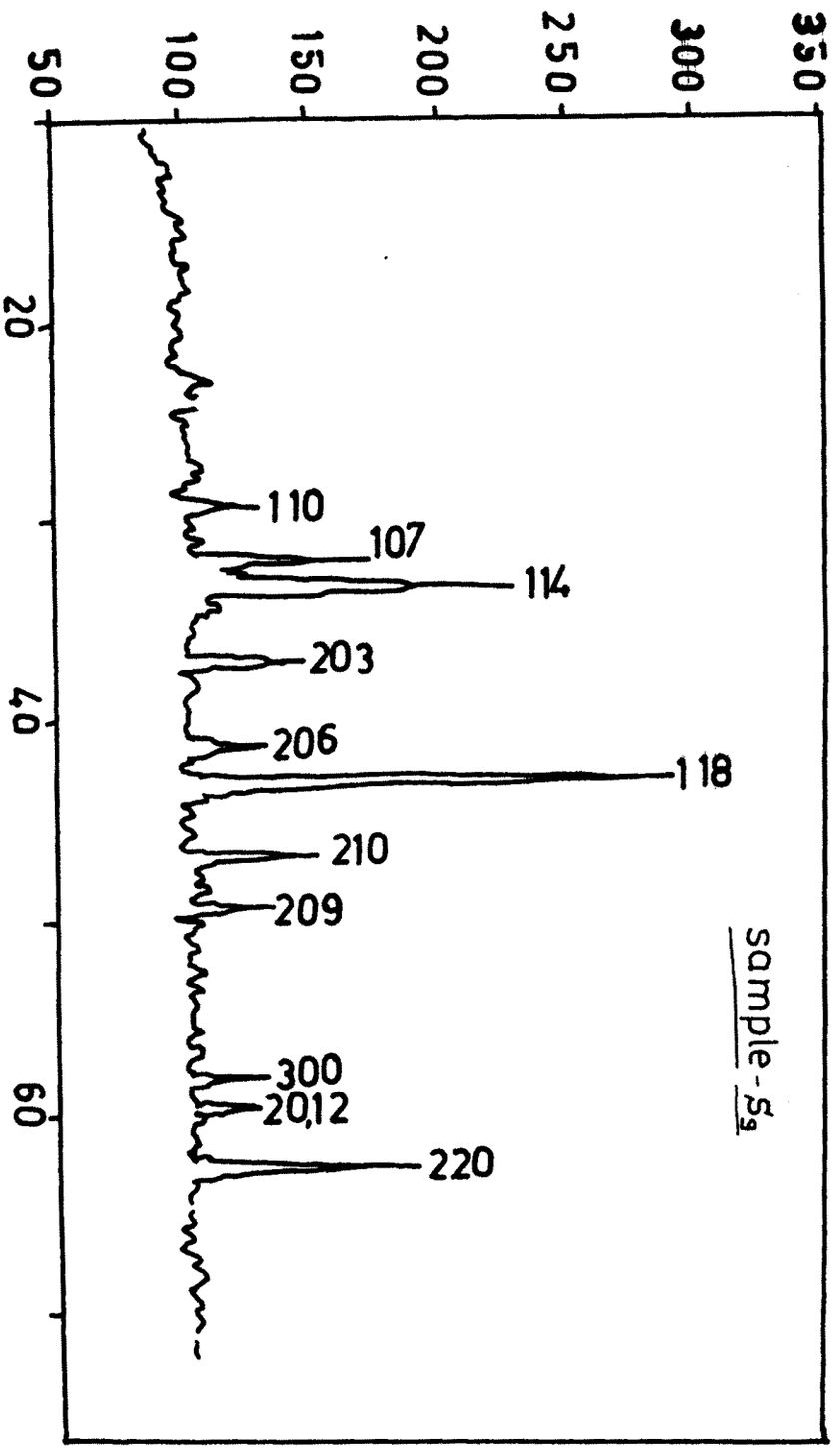
50
100
150
200
250
300
350
20
40
60
110
107
114
203
206
118
210
209
300
20,12
220
sample-S5

TABLE 3.1a

Silver Lanthanum Ferrite			S_1		S_2		S_3		S_4	
d(A)	Ret.	hkl	d_{obs}	d_{cal}	d_{obs}	d_{cal}	d_{obs}	d_{cal}	d_{obs}	d_{cal}
2.94	M	110	2.95	2.95	2.94	2.94	2.94	2.94	2.95	2.95
2.75	S	107	2.70	2.79	2.69	2.70	2.69	2.70	2.74	2.79
2.61	S	114	-	-	-	-	-	-	2.67	2.63
2.51	M	108	2.52	2.53	2.51	2.53	2.51	2.53	2.50	2.53
2.42	M	203	-	-	-	-	-	-	-	-
2.30	VW	00,10	2.34	2.34	2.34	2.34	2.34	2.34	2.34	2.34
2.22	M	205	2.20	2.24	2.20	2.23	2.20	2.23	-	-
2.118	VW	206	2.09	2.13	-	-	-	-	-	-
2.067	VW	118	2.02	2.07	-	-	2.08	2.07	2.08	2.077
1.910	VVW	210, 00.12	1.84	1.82	-	-	2.02	1.924	2.02	1.931
1.800	VVW	209	-	-	1.89	1.819	1.89	1.819	1.80	1.82
1.686	M	300	1.68	1.70	1.69	1.697	1.69	1.697	1.61	1.70
1.652	M	217	-	-	-	-	-	-	-	-
1.620	M	304	-	-	-	-	-	-	-	-
1.606	MS	20,11	1.60	1.63	1.60	1.632	1.60	1.632	-	-
1.524	VVW	20,12	-	-	-	-	-	-	-	-
1.464	MS	220 & 10,15	1.47	1.47	1.47	1.470	1.43	1.470	1.48	1.47
1.412	VVW	21,11	1.45	1.42	1.43	1.427	1.43	1.427	1.43	1.42
1.372	VW	10,16	-	-	-	-	-	-	-	-
1.48	W	313	-	-	-	-	-	-	-	-

TABLE 3.1b

Silver Lanthanum Ferrite			S_4		S_7		S_8		S_9	
d(A)	Ret.	hkl	d_{obs}	d_{cal}	d_{obs}	d_{cal}	d_{obs}	d_{cal}	d_{obs}	d_{cal}
2.94	M	110	2.95	2.95	2.96	2.96	2.96	2.96	3.06	3.005
2.75	S	107	2.70	2.79	2.79	2.77	2.79	2.77	2.79	2.81
2.61	S	114	2.67	2.63	2.67	2.63	2.67	2.63	2.68	2.673
2.51	M	108	2.52	2.53	2.52	2.53	2.52	2.51	-	-
2.42	M	203	2.41	2.42	2.42	2.433	2.42	2.43	2.42	2.469
2.30	VW	00,10	-	-	-	-	-	-	-	-
2.22	M	205	-	-	-	-	-	-	-	-
2.118	VW	206	-	-	-	-	-	-	2.18	2.165
2.067	VW	118	2.09	2.07	2.09	2.069	2.09	2.069	2.10	2.097
1.910	VVW	210, 00.12	1.94	1.93	1.94	1.938	1.94	1.938	-	-
1.800	VVW	209	1.84	1.82	-	-	-	-	1.84	1.840
1.686	M	300	1.70	1.70	1.70	1.709	1.61	1.639	-	-
1.652	M	217	-	-	-	-	-	-	-	-
1.620	M	304	1.61	1.63	1.62	1.639	-	-	-	-
1.606	MS	20,11	-	-	-	-	-	-	-	-
1.524	VVW	20,12	-	-	-	-	-	-	1.55	1.56
1.464	MS	220 & 10,15	1.48	1.47	1.48	1.480	1.48	1.480	-	-
1.412	VVW	21,11	-	-	-	-	-	-	-	-
1.372	VW	10,16	-	-	1.36	1.392	1.36	1.392	-	-
1.48	W	313	-	-	-	-	-	-	1.48	1.41

Table 3.2

Nickel aluminate ferrite		Sample 85
d	2θ	dobs
2.951	30.3	2.9465
2.522	35.6	2.5154
2.086	43.1	2.0865
1.7020	53.8	1.7062
1.6052	57.2	1.6093
1.4739	62.74	1.4792
1.278	72	1.2757

a = 8.3460 A°

$A = \lambda^2/3a^2$ find out a. To find out value of c we must use the equation $Sin^2\theta - A(h^2+hk+k^2) = Cl^2$.

Analysis for Cubic structure

For cubic system the plane spacing equation is

$$1/d^2 = (h^2 + hk + k^2)/a^2 \quad \ldots \quad 3.3$$

combining equation (3.3) to Bragg's law we have

$$Sin^2\theta = \lambda^2/4a^2 (h^2+hk+k^2)$$

It can be written as

$$\frac{Sin^2\theta}{(h^2+hk+k^2)} = \frac{Sin\ 2\theta}{S} = \frac{\lambda^2}{4a^2} \quad \ldots \quad 3.4$$

Since the sum S = (h2+hk+k2) is always integral and $\lambda^2/4a^2$ is a constant for any one pattern. The problem of indexing the pattern of a cubic substance is one of finding a set of integers S which will yield a constant quotient when divided one by one into the observed Sin 2θ values. Once set of S are found using eqn. 3.4 hkl values can be found out.

3.5 Results and discussion

The x-ray diffraction patterns of ferrite samples were obtained by using monochromatic radiation. The interplaner distance d were calculated for each sample and have been compared with silver lanthanum ferrite given in Table 3.1 a,b

Table 3.1 shows except sample S_8, d-observed, d-calculated values and d values of silver lanthanum ferrite are in good agreement (Ind. J. Pure and Appl. Phys. vol 1, (1963)). Sample S5 is decomposed into the Nickel aluminate ferrite. Table 3.2 shows the d-observed, d-calculated and d values of Nickel aluminate ferrite.

The x-ray results obtained were very conclusive mainly due to the fact that only the powder patterns could be taken easily, and the comparative table 3.1 shows remarkably good crystle lattice spacings data. X-ray results indicate that there is a close similarity between d values for silver lanthanum ferrite and other compounds except S_8 of the present series. The S_8 sample composition seems to be exhibit two different chemical phasis, such as pure Nickel ferrite and the other a non-stoichiometric mixture of unreacted element and their oxides. [illegible] table 3.3.

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