CHAPTER - II

PREPARATION OF FERRITES AND X-RAY DIFFRACTION STUDY.

PREPARATION OF FERRITES AND X-RAY DIFFRACTION STUDY

A) THE METHODS OF PREPARATION OF FERRITES BY CERAMIC METHOD :

2.1 Introduction :

Ferrites are industrially important materials due to their electrical and magnetic properties. Therefore, preparation and manufacturing of ferrites is important. The ferrites are generally prepared by two methods; one chemical method and the other by standard ceramic technique. Due to some limitations of chemical method, most of the time standard ceramic technique is useful.(1,2,3) Also this technique is economic. The ceramic technique involves mechanism of solid state reaction and other stages which have been discussed in the articles to follow.

2.2 : Mechanism of Solid State Reaction :

The polycrystalline ferrites are generally formed by solid state reaction. To start with the mechanism of solid state reaction; the homogenous mixture of metal oxide (MO) and ferric oxide (Fe_2O_3) are heated at the elevated temperature. The mechanism is based on diffusion between divalent metal oxide MO and Fe_2O_3. In the initial stage of reaction, there is only one phase boundary between reactants; viz. divalent metal oxide MO and Fe_2O_3. In the further stage, after nucleation of the ferrite, initial phase boundary can be replaced by two different boundaries, one between Fe_2O_3 and MFe_2O_4 and other between MO and MFe_2O_4. In continuation with the reaction, reactants are transported through the ferrite phase. The transfer mechanism can be discussed by three ways which attribute to the ferrite formation. According to Wanger(4,5) in the first mode of transfer mechanism, only cations migrate in the opposite directions with oxygen ions are essentially stationary. In the second mode of transfer mechanism, diffusion of one cation is compensated by an associated flux of anions instead of another counter cation migration. The third mode of transfer mechanism involve diffusion of iron through ferrite layer in the reduced state Fe^{2+}.

2.3 (a) : Preparation of Ferrite Composition : The various methods for preparation of ferrite composition, in the required proportion are as follows:

i) Oxide Method : This method is widely used for preparation of ferrite at the commercial level. The starting (raw) material viz. divalent metal oxides and Fe_2O_3 of highest degree of purity, in the appropriate proportion as per need of final product, are mixed together. The mixing is generally performed by wet milling, for a long period in the rubber lined pot using stainless steel balls. Some times the attritor and the vibratory ball mill are used to do the mixing in short time. After milling the mixture is dried and pressed into a suitable shape before pre-sintering. The pre-sintering is done at the elevated temperature.

ii) Decomposition Method : In this method instead of using oxides as the starting materials, salts like carbonates, nitrates and oxalates are used. These salts are mixed by milling in the appropriate proportions and then pre-heated in air so as to form oxides by thermal decomposition. The oxides formed by this method have ability to undergo solid state reactions(6) readily. The other details of the method are similar to oxide method.

iii) Hydroxide Precipitation : This method is useful in order to avoid the lengthy milling process.involved in dry mixing. The method is based upon simulteneous precipitation of required oxides from solution. The essential requirements of this methods are, knowledge of solubility product and quantitative understanding of chemical process. The successful attempt had been made by Economous(7) for preparation of ferrites. Yig(8) had been prepared by hydroxide precipitation method. Recently(9) Cu-Ni ferrite have been prepared by precipitation method.

iv) Oxalate Precipitation : This method is preferable for two reasons. Firstly, precipitation can be carried out using ammonium oxalate which does not have any residue and secondly most of the metal oxalates are very similar in crystal structure. Therefore, precipitation tends to produce mixed crystals which contains the metallic cations in the proportion in which they were present in the solution. Thus mixing in the correct ratios can be achieved on a molecular scale.(7).

2.3 (b) : Pre-Sintering : Pre-sintering is a slow solid state reaction in which reactants partly react to form final product. The amount of reaction depends on reactivity of component as well as the pre-sintering temperature.(10) The purpose of pre-sintering is, to decompose carbonates and higher oxides in order to reduce the evolution of the gas in the final sintering process. Secondly to assist in homogenezing the material and lastly to control the shrinkage of the material which would occur during the final firing.

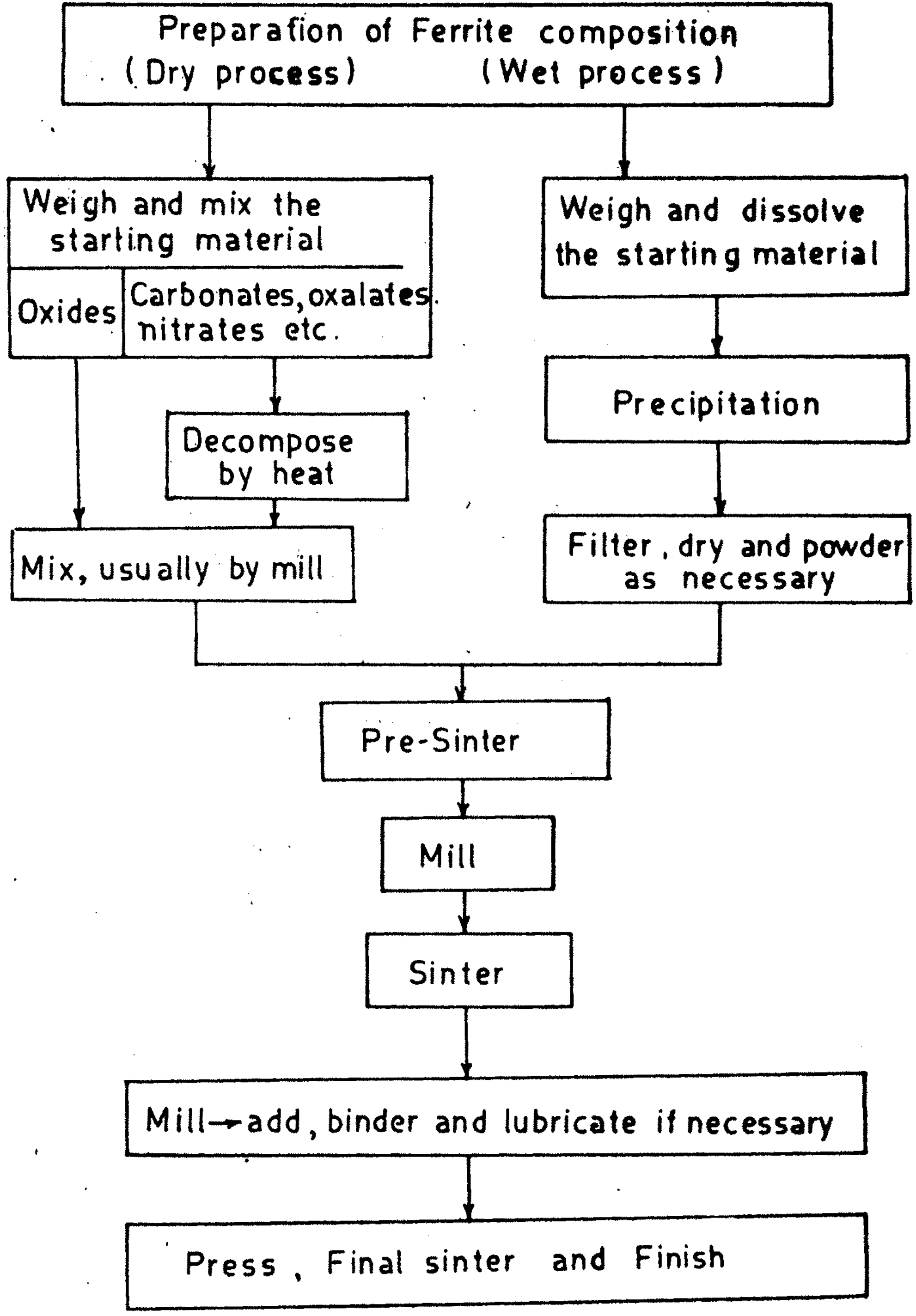
Before the pre-sintering the mixture of the requisite proportions of metal ions and Fe_2O_3 are taken. The proper care is to be taken particularly when preparing magnetic oxides containing ions of variable valance states like Fe, Mn, Cu and Co. For this, careful control of the furnace atmosphere is essential. Also appropriate partial pressure of oxygen in the furnace may be maintained through out the firing cycle; so that stiochiometry and desired valance state may be achieved. After completion of long heat treatment reacted material is subjected to next process.

2.3 (c) : Powdering and Pressing : The pre-sintered reacted material is powdered by different process like milling. The fine powder is usually mixed with one of the binder such as 1% polyvinyl alcohol or 1% ammonia alginck solution. This solution volatizes afterward. The compact and desired shape is done by high pressure technique. The pressure may be employed about several tons persquare inch (i.e. up to 10^8 Nm^{-2}). The compacted material is finally subjected to "sintering".

2.3 (d) : Sintering : The sintering process is a sort of solid state reaction, consists of heating of the compacted material at temperature up to 1350°C. At this temp mobility is sufficient to permit the decrease of the free energy associated with the grain boundaries. The final microstructure together with the oxygen content and the distribution of the cations are greatly affected by time and temperature of sintering, the partial pressure of oxygen or any other sintering atmosphere and the cooling rate. Therefore, to achieve desired micro-structure and cation distribution in the final product, affecting factors should be controlled appropriatly. Also during the course of sintering densification and grain growth occurs simultaneously. The grain growth mechanism during the process of sintering is an interesting mechanism. Extensive reviews on grain growth and sintering are available.(11,12)

After sintering the solid mass can be designed in required shape by cutting and grinding. The cutting can be done with help of thin diamond slitting wheel or by use of ultrasonic machine with a knife edge cutting head. The final

Flowchart of the stages in the ferrite preparation.



finish may be done by surface grinding with a carborundum wheel.

B) PREPARATION OF FERRITE SAMPLES :

2.4 : The mixed ferrites containing divalent copper and nickel ions have been prepared by standard ceramic technique. The details of the steps followed have been presented in the following sub-sections.

2.4 (a) : General formula : The general formula for the mixed ferrite system is,

$$Cu_x\,Ni_{1-x}\,Fe_2O_4$$

where x = 0.0, 0.2, 0.4, 0.6, 0.8 & 1.0.

2.4 (b) : Starting Materials : The pure copper oxide (CuO) and ferric oxide (Fe_2O_3); supplied by "Riedel-De-Hean, AG Seeize-Honouer", Germany were used as starting materials. Also due to unavailability of pure nickel oxide; AR grade nickel nitrate ($NiNO_3$) was used to obtain nickel oxide (NiO). The decomposition of $NiNO_3$ was done by pre-heating of $NiNO_3$ in air at 700°C for 6 hours. Thus,

$$NiNO_3 \xrightarrow[\text{6 hr.}]{\text{700°C in air}} NiO + NO_2\uparrow$$

The purity of NiO was confirmed by chemical methods.

2.4 (c) : <u>Weighing</u> : To prepare desired samples from the $Cu_x Ni_{1-x} Fe_2O_4$ series, for x = 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 molecular weights of oxides and atomic weights of elements are necessary. The molecular weights of relevant oxides and atomic weights of elements required for further calculations are tabulated in the following table.

Oxide/Element	Molecular Weight/Atomic weight (In gms.)
CuO	79.5394
NiO	74.7094
Fe_2O_3	159.6922
Cu	63.54
Ni	58.71
O	15.9994

In order to prepare each sample of 15 gms, the requisite oxides were weighed on semi-microbalance according to molecular percentage. The necessary calculations were done by considering relevent chemical formula of the sample. The specimen calculations for the sample $Cu_x Ni_{1-x} Fe_2O_4$ with x = 0.2 has been represented as follows.

The chemical formula of the sample is

$Cu_{0.2} Ni_{0.8} Fe_2O_4$

To prepare the sample of 15 gm, we have considered the simple reaction

$$Cu_{0.2} + Ni_{0.8} + Fe_2O_4 \longrightarrow Cu_{.2}Ni_{.8}Fe_2O_4$$

By using molecular weights and atomic weights of relevant oxides and elements, with x = 0.2, above equation may be written as,

$$(79.5394)(0.2) \text{ gm of } CuO + (74.7094)(0.8) \text{ gm of } NiO + 159.6922 \text{ gm of } Fe_2O_3$$

$$= (63.54)(0.2) \text{ gm of } Cu + (58.71)(0.8) \text{ gm of } Ni + 175.6916 \text{ gm of } Fe_2O_4$$

$$= (12.708 \text{ gm of } Cu + (46.968) \text{ gm of } Ni + (175.6916) \text{ gm of } Fe_2O_4$$

$$= (235.3676) \text{ gm of } Cu_{.2}\,Ni_{.8}\,Fe_2O_4$$

or (15.9078) gm of CuO + (59.7675) gm of NiO + (159.6922) gm of Fe_2O_3

$$= (235.3676) \text{ gm of } Cu_{.2}\,Ni_{.8}\,Fe_2O_4$$

For 15 gm of $Cu_{.2}\,Ni_{.8}\,Fe_2O_4$, we had divided by a factor, 15.691173 through out, which had been obtained by dividing to the total molecular weight of sample $Cu_{.2}\,Ni_{.8}\,Fe_2O_4$ i.e. to the R.H.S. value, 235.3676 by 15 gm.

$$\therefore \left(\frac{15.90}{15.69}\right) \text{ gm of } CuO + \left(\frac{59.76}{15.69}\right) \text{ gm of } NiO + \left(\frac{159.6922}{15.691173}\right) \text{ gm of } Fe_2O_4 ?$$

$$\simeq 15 \text{ gms } Cu_{.2}\,Ni_{.8}\,Fe_2O_4$$

Thus for preparation of $Cu_xNi_{1-x} Fe_2O_4$ (with x = 0.2), of 15 gm; 1.013 gm of CuO, 3.80 gm of NiO and 10.17 gm of Fe_2O_3 were used.

The values of molecular weights taken for other samples with x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0 have been presented in the following table.

X	Molecular weight of CuO in gms.	Molecular weight of NiO in gm	Molecular weight of Fe_2O_3 in gm
0.0	-	4.78	10.21
0.2	1.01	3.80	10.17
0.4	2.01	2.84	10.13
0.6	3.01	1.88	10.09
0.8	4.00	0.94	10.05
1.0	4.98	-	10.01

2.4 (d) : Pre-sintering : The oxides Fe_2O_3, NiO and (or) CuO in the proportions relevant to each sample, according to molecular percentage were mixed thoroughly in an agate morter with acetone. The mixture was then allowed to dry in atmosphere. The dry mixture of each samplewas taken in platinum crucible and pre-sintered at 700°C for twenty four hours. Then the samples were furnace cooled by switching off the furnace. The temperature of the furnace was measured with the help of calibrated alumel-cromel thermocouple and D.R. potentiometer.

2.4 (e) Grinding : The pre-sintered samples were taken out of platinum crucible and were then converted in to very fine and homogeneous powder by ball-milling with acetone for two hours. The samples were dried at 100°C and again milled without acetone. The samples then transferred to platinum crucible for sintering.

2.4 (f) Sintering : The samples in the form of homogeneous powder were fired within the range 1050°C to 950°C with reference to respective samples having x = 0 to x = 1, in the $Cu_x Ni_{1-x} Fe_2O_4$ series; 40 hours. During the course of sintering, temperature was increased up to reaction temperature in order to maintain final micro structure, content of oxygen and the distribution of cations as indicated in the article (2.3:d). After the firing cycle the samples were furnace cooled. The samples were supposed to be homogeneous, also solid state reaction was supposed to be completed after sintering.

2.4 (g) : Pellet formation : One gram of each sample was taken into agate-morter for regrinding. The wet mixing was done by using polyvenyl acetate (PVA) as binder. The mixture was then allowed to dry in air. With the help of die of 1 cm diameter, pellets were formed by hydraulic press with hydraulic pressure about 15 tons for ten minutes.

2.4 (h) : Final Sintering : The final sintering of the samples was done in the pellet form in order to reduce porosity which ultimately lead to high densification of sample as well as to control grain growth and other crystal defects. For the final sintering pellets were again fired at 1050°C to 950°C for relevent samples, by increasing temperature of the furnace slowly, upto firing temperature. The samples were then kept at the firing temperature for 24 hours. After firing cycle samples were furnace cooled. The above mentioned temperature and time factors are reported and confirmed to be sufficient for completion of solid state reactions. The final confirmation of sample preparation and crystal structure were done by X-Ray diffraction study which is discussed in the next section.

The physical densities of the samples were measured and are tabulated as follows; for the series $Cu_xNi_{1-x}Fe_2O_4$ with x = 0.0, 0.2, 0.4, 0,6, 0.8 and 1.0

x	Physical density (ds) in gm/cm^3
0.0	2.932
0.2	3.563
0.4	3.685
0.6	3.586
0.8	3.427
1.0	3.648

C) X-RAY DIFRACTION STUDY :

2.5 : Introduction :

X-ray diffraction technique is an esteemed and well established tool for the study of the crystal structure. The details of X-ray diffraction study in short has been presented in the next section. In order to confirm the crystal structure of ferrites and for determination of lattice parameter of spinel structure, we have been carried out X-ray diffraction studies of the series of $Cu_xNi_{1-x}Fe_2O_4$ ferrite.

2.6 : Brief Survey :

2.6 (a) Condition for X-ray diffraction :

The regular three dimensional arrangement of unit cells in the crystals can be regarded as three dimensional diffraction grating for X-rays. According to Bragg(17) diffraction is possible only when the wave length of X-rays is comparable with inter planer distance. The Bragg's law is,

$$n\lambda = 2\, d' \sin\theta \quad \text{------------} \qquad (2.61)$$

where d' is the interplaner distance.

n, is the integral number.

$$\theta < \sin\theta < 1 \quad \Rightarrow n\lambda < 2\, d' \quad \text{----} \qquad (2.62)$$

since, n = 1, is the least value of n in the diffraction condition, for any observable angle $2\,\theta$,

$$\lambda < 2\, d' \quad \text{----------------} \qquad (2.63)$$

Bragg's law can be rearranged as,

$$\lambda = 2\, \frac{d'}{n} \sin\theta \quad \text{-----------} \qquad (2.64)$$

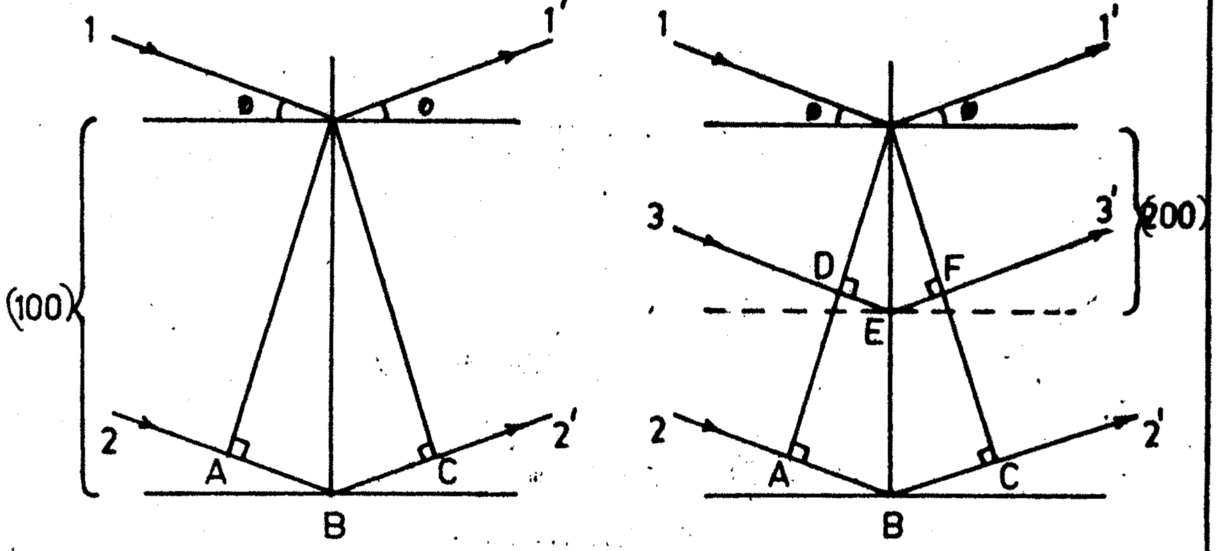


Fig.: 2·1a

Fig.: 2·1b

Fig.: 2·1 : The Application of Bragg's Low.

The coefficient of λ being unity, a reflection of any order can be conveniently considered as the first order reflection from planes real or imaginary, spaced at a distance $\frac{1}{n}$ of the previous spacing. For convenience, replacing $\frac{d'}{n}$ by d, we get,

$$\lambda = 2\, d \sin\theta \qquad \text{---------------} \qquad (2.65)$$

The applicability of the law can be illustrated from Fig.2.1. The number of whole wave lengths lying in the path difference between rays scattered by adjacent (hkl) plane is known as the order of diffracted beam. Fig. (2.1 a) represents the 2^{nd} order (100) reflection. If there is no real plane midway between the (100) planes, it can be imagined as in Fig. (2.1 b) forming 1^{st} order reflection for adjacent (200) planes. In the same way (300), (400) etc. reflections may be equivalent to the 3rd, 4th etc. order from the (100) planes. Thus the 4th order reflection from (hkl) planes of spacing d' may be viewed as a first order reflection from (nh nk nl) planes of spacing $d = \frac{d'}{n}$. This suits with the definition of Miller indices of planes parallel to the (hkl) planes with $\frac{1}{n}$ spacing of the latter.

The number of diffraction directions $2\theta_1$, $2\theta_2$, $2\theta_3$ etc. can be traced and photographed from the (100) planes by using a monochromatic incident beam at the angle θ_1, θ_2, θ_3 etc. which produce first, second, third etc. order reflections. The diffraction from other planes is also expected. The combination of Bragg's law and the plane spacing expression of a particular crystal under investigation predict the diffraction. angles for any set of planes.

For the cubic crystal(18), the interplanner distance in (hkl) set of plane is,

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \qquad \text{------------} \qquad (2.66)$$

where a denotes the unit cell size. Combining with the Bragg's law, we have,

$$\sin^2\theta_{hkl} = \frac{\lambda^2}{4a^2}(h^2 + k^2 + l^2) \qquad \text{------} \qquad (2.67)$$

The equation become representative of Bragg' angles for diffraction occuring from the planes (hkl) for known value of λ. For tetragonal crystal(18),

$$\sin^2\theta_{hkl} = \frac{\lambda^2}{4}\left(\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}\right) \qquad \text{----} \qquad (2.68)$$

where a and c are axes of tetragonal.

Thus the diffraction direction as predicted by equations (2.67) and (2.68) are determined solely by the shape and size of the unit cell. The converse of this statement is most important as far as the crystal analysis is concerned. The measurements of directions of diffracted beam speculated the shape and size of crystal's unit cell while their intensities gives the information regarding the positions of atoms. For the structural analysis of Crystal, from the diffraction pattern, diffracted angles 0 can be measured. For the known value of wavelength λ of X-rays used, interplanner distance d can be calculated by Bragg's law; $\lambda = 2\ d\ \text{Sin}\ \theta$.

2.6 (b) Experimental Diffraction Methods :

i) Laue Method(19) : In this method a single crystal is held stationary (θ is fixed) in the path of X-rays of continuous wavelength (λ is variable). The crystal selects out and diffracts the discrete values of λ for which the planes have interspacing d, satisfying the Bragg law. The diffraction pattern due to Laue Method consists of spots. This method is convenient for the rapid determination of crystal orientation and symmetry. The Laue Method is practically never used for crystal structure determination.

ii) Rotating Crystal Method : A single crystal rotates (θ is varied) about a fixed axis in a monoenergetic beam (λ is fixed) of X-rays. The variation in θ brings different atomic planes into position for reflection. In a course of rotation of the crystal, the beam get diffracted whenever the value of θ satisfies the Bragg equation. A modified rotating crystal method can be used for structure determination when the available specimen is a single crystal. Several variations of the rotating - crystal method are in common use(20).

iii) Powder Method and Its Principle : The powder method of X-ray diffraction was first developed by P.Debye and P.Scherrer(21) in 1916 and independently by A.W.Hull(22) in

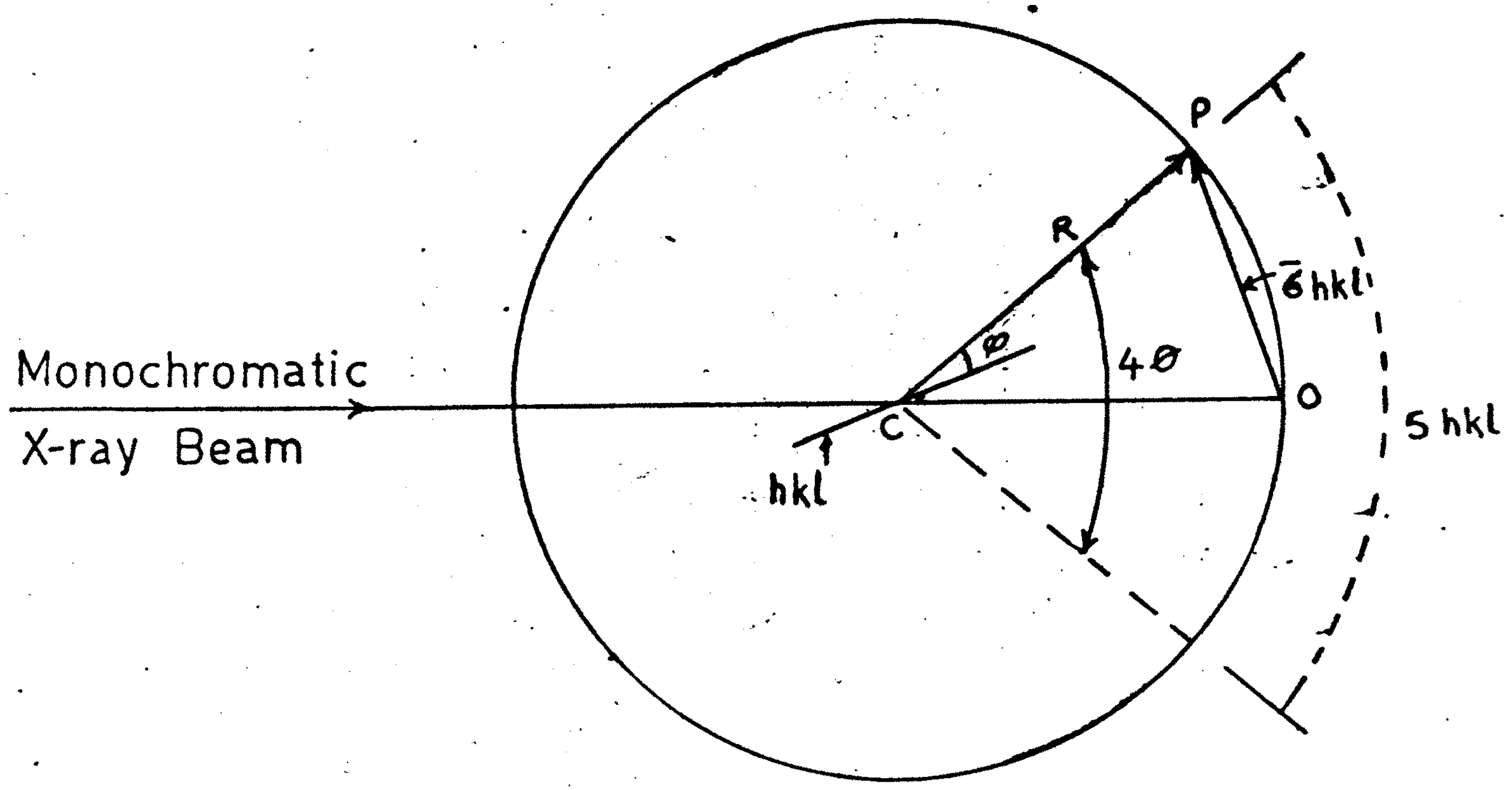


Fig. 2·2(a) Ewald's Sphere.

1917. This method can be used properly to get the knowledge of structural information about the sample under investigation.

In this method the film is placed on the cylindrical surface of D.S. camera and the specimen holder rotates about the axis of the camera in a mono-energetic beam of X-rays. The small amount of smoothly ground powder can be coated on the surface of a fine glass fibre with a glue or petroleum jelly. The specimen prepared is then mounted in its holder by proper adjustments.

The crystallites in a powder get completely randomly oriented so that the reciprocal lattice vectors of all the crystallites point in all the directions. The reciprocal lattice points lie on the surface of sphere of radices (hkl). Each reciprocal lattice sphere oriented by every possible values of hkl. cuts the E Wald's sphere Fig. 2.2 a. A narrow film strip Fig.2·2(b)is used to record the representative portion of the cuts.

By the geometry of Ewald's sphere,

$$4\,\theta_{hkl} = \frac{S_{hkl}}{R}$$

If we consider the two consecutive reflections, the angle between them is the Bragg angle which can be readily written as,

$$\theta_{hkl} = \frac{S_{hkl}}{4}$$

The measurements of S_{hkl} in mm on photographic film give the values of θ_{hkl}.

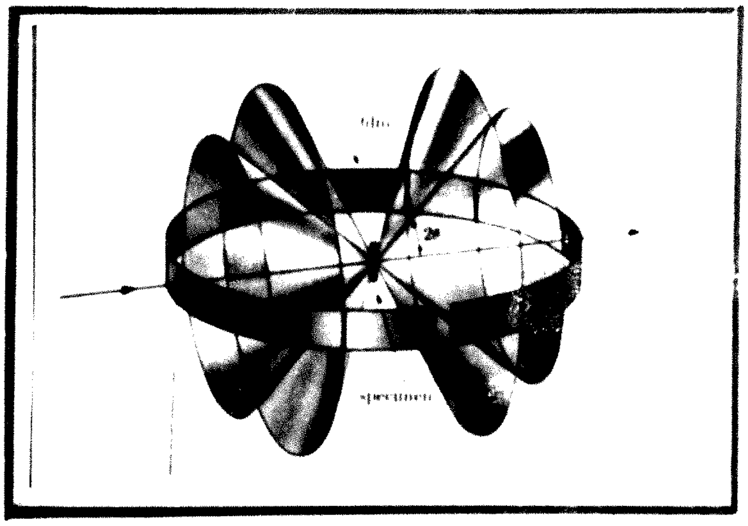


Fig. 2.2 b

X-ray diffractometer schematic

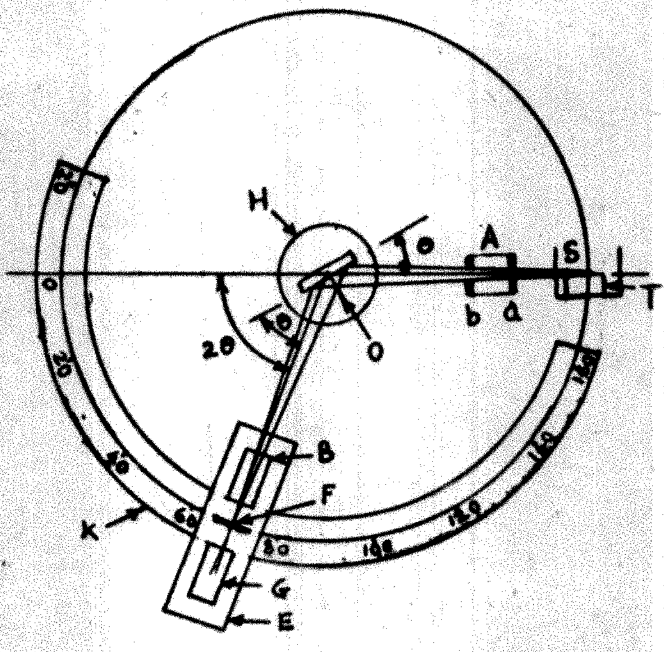


Fig. 2.3

Using Bragg's law,

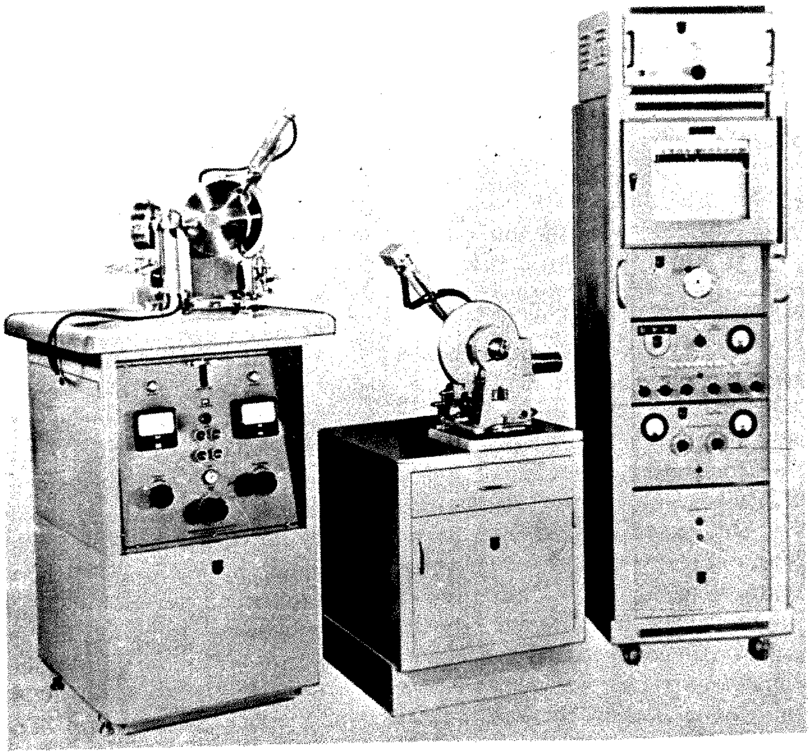
$$2\ d_{hkl}\ \mathrm{Sin}\ \theta_{hkl} = \lambda \quad \text{----------} \qquad (2.69)$$

the interplaner distances d_{hkl} can be determined.

iv) X-Ray Diffractometer and its principle.

The film in a Debye-Scherrer is replaced by a movable counter in an X-ray diffracto-meter. The principle of the method and main features of the diffractometer are shown in Fig. 2.3. The incident beam of X-rays, free from $K_{\alpha'}$ radiations made by use of a filter is allowed to pass through the Slit 'A' of the collimeter. The K_α radiations thus fall on the sample powder kept in a holder 'C' and get reflected by Crystal planes satisfying the Bragg's law. As the crystallites are randomly oriented, a reflection at the particular position is due to a set of atomic planes which satisfy the Bragg's condition. The diffracte beam from the set of parallel planes of the specimen get converged and focused at a slit 'F', which further enters the counter 'G'. With the help of a special slit B, the diffracted beam is collimated. The counter 'G' is connected to a counter rate-meter. The output of the circuit is fed to a fast automati recorder which register the counts per second versus the angle '2θ'. The location of the centroid of the peak registered gives the values of $2\theta_{hkl}$ for the corresponding Bragg's reflection.

The carriage 'E' supports the receiving slits and the counter. The carriage 'E' is free to rotate about an axis 'C'. The angular position '2θ' of the carriage and hence that of the counter G may be noted on the graduated circular scale 'K'. The mechanical coupling of 'E' and 'H' is made, so that the



rotation of the counter G through an angle 2θ degrees moves the specimen (C) through an angle θ degrees. It also ensures that the complimentary angles of incidence and reflection from the flat specimen are always equal to each other, each being half the total angle of diffraction. This type of arrangement is necessary to satisfy the focusing conditions. The power driven counter moves with constant angular velocity about the axis of the diffractometer for any desired angular range from 1° to 160°. The main advantage of the diffractometer over the Debye - Scherrer powder method is that it gives a quantitative measure of the intensity.

2.7 Experimental :

The X-ray diffraction of ferrite system $Cu_xNi_{1-x}Fe_2O_4$ (with $x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) were taken by using Philips make P.W. 1051, P.M. 9920 X-ray diffractometer. The samples of $Cu_x Ni_{1-x} Fe_2O_4$ were used in the fine powder form. With the proper skill powder could be moulded in the screens of sample holder so as to form plain surface of the specimen. Mo target was used for $Cu_x Ni_{1-x} Fe_2O_4$ series. The wavelength of MoK_α being 0.71069 A°. The speed of chart was 1 cm. per 1 degree rotation angle. The recording had been made from 9° to 32° of 2θ. The reflections were indexed by usual method.

2.8 X-Ray Characterization, Results and Discussion :

In the Fig.2.4(a) to Fig.2.4(f) are given the x-ray diffractograms of the series of mixed ferrites $Cu_xNi_{1-x}Fe_2O_4$. The well defined x-ray diffraction peaks show a perfect crystalline single phase formation of samples. In table 2.1(a) to 2.1(f) are given the 'd' values, corresponding phanes of reflections (h,k,l), crystal structure and lattice parameters. The ferrites are the spinels (having what is known as spinal structure) and can have the following planes, as (111), (220), (311), (222), (400), (422), (333), (511) for cubic structure(18) and (111) (202) (220) (113) (311) (222), (004), (400), (422), (333), (511), (404) and (440) for tetragonal structure.(23) Our observations are, therefore, compared with the allowed ones and thus preparation is confirmed. We have not observed any irrelevent planes. The much interesting part of it is as follows. The $NiFe_2O_4$ is a well known cubic lattice while $CuFe_2O_4$ is a tetragonal one. When a mixture of these two is done to give rise to a composition $Cu_xNi_{1-x}Fe_2O_4$, it is interesting to see how is the crystal structure of the resultant product.

After correctly indexing the reflections the lattice parameter (a) for all the compositions have been determined. Fig.2.5 shows a variation of lattice constant with composition in the ferrite system. It can be seen that the lattice parameter increases with increasing copper content in the system. A linear relation is exhibited which suggests that Vegard's(24)

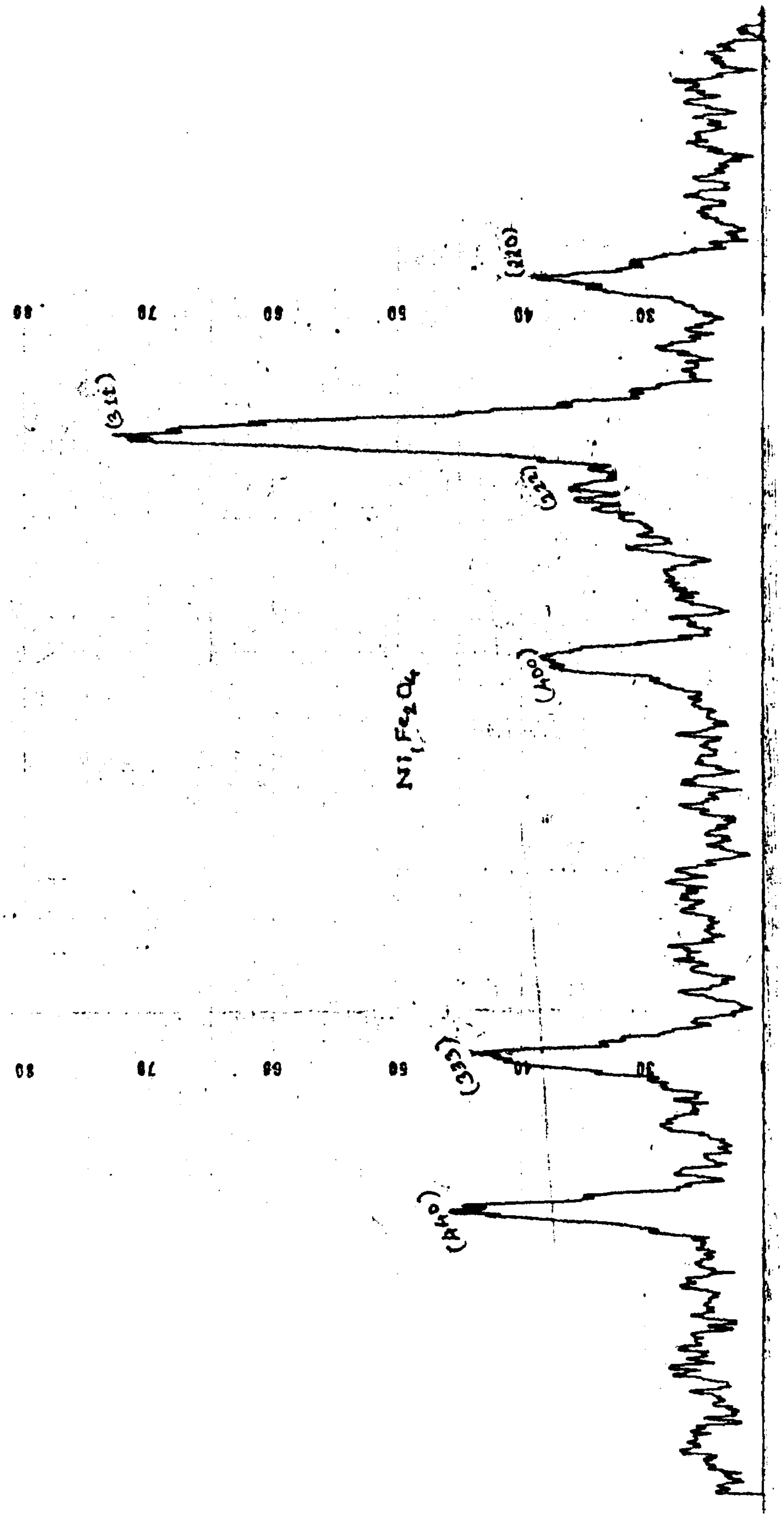
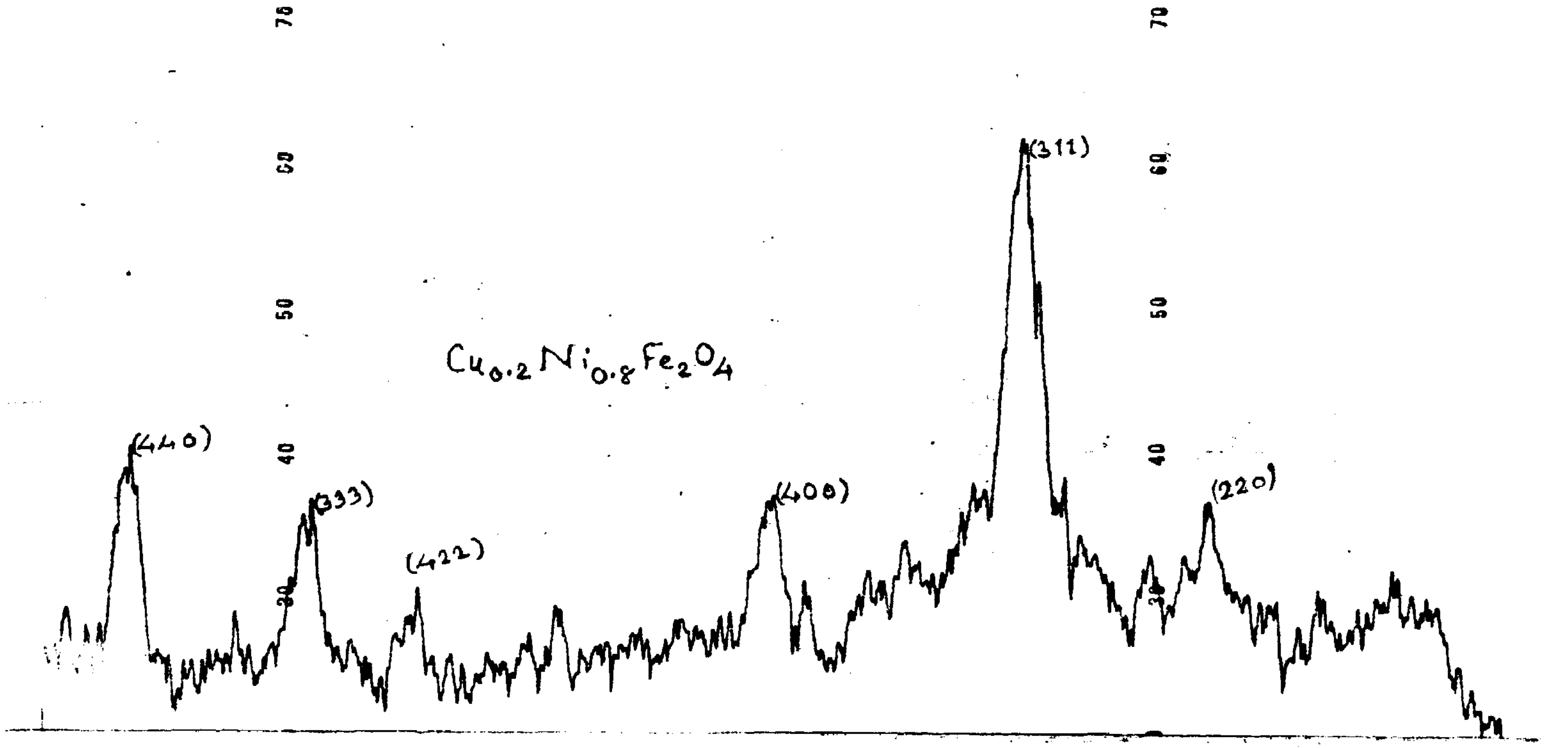


Fig 2.4 (a)



$Cu_{0.2}Ni_{0.8}Fe_2O_4$

Fig 2.4 (b)

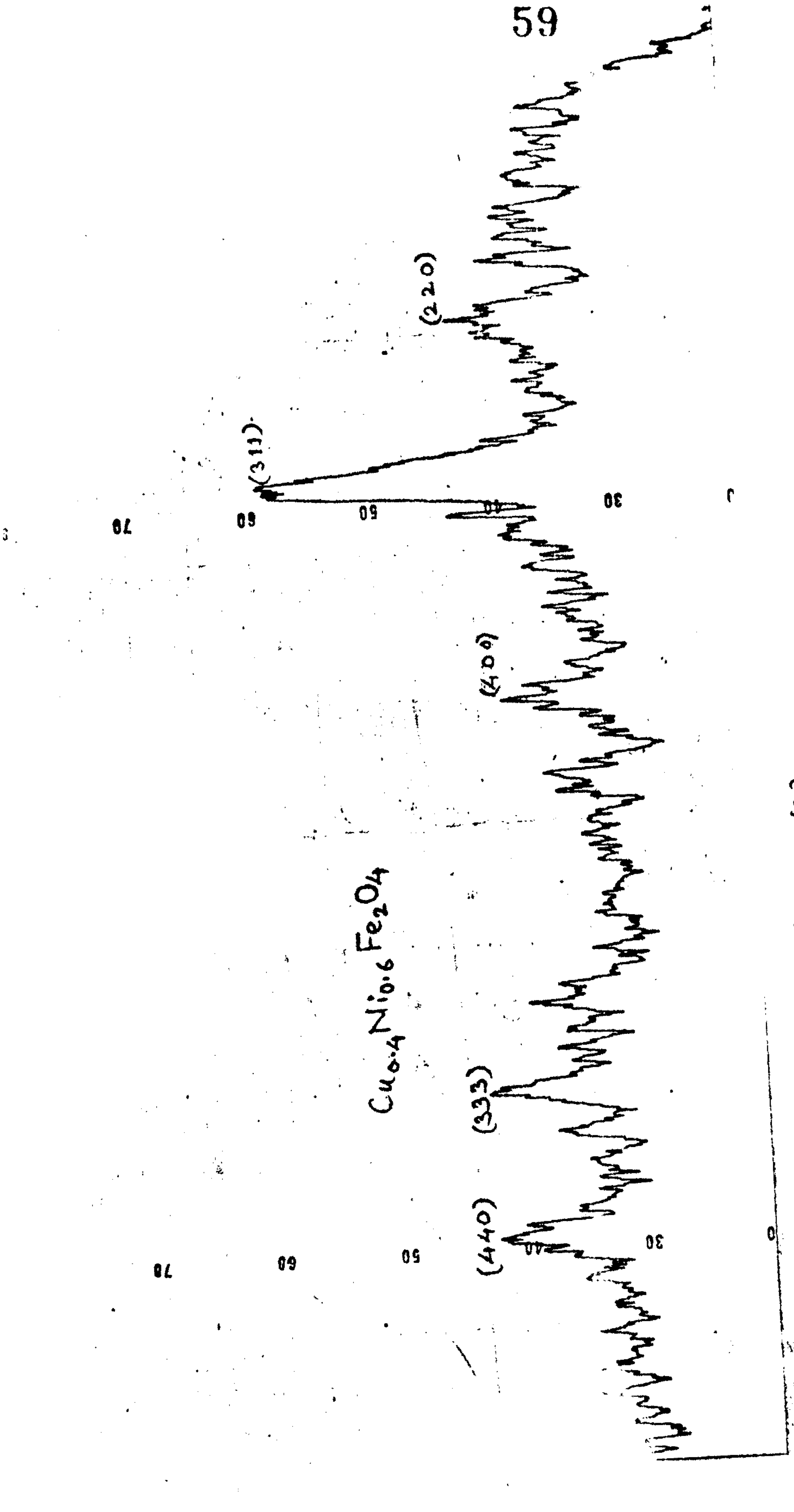


Fig 2.4 (c)

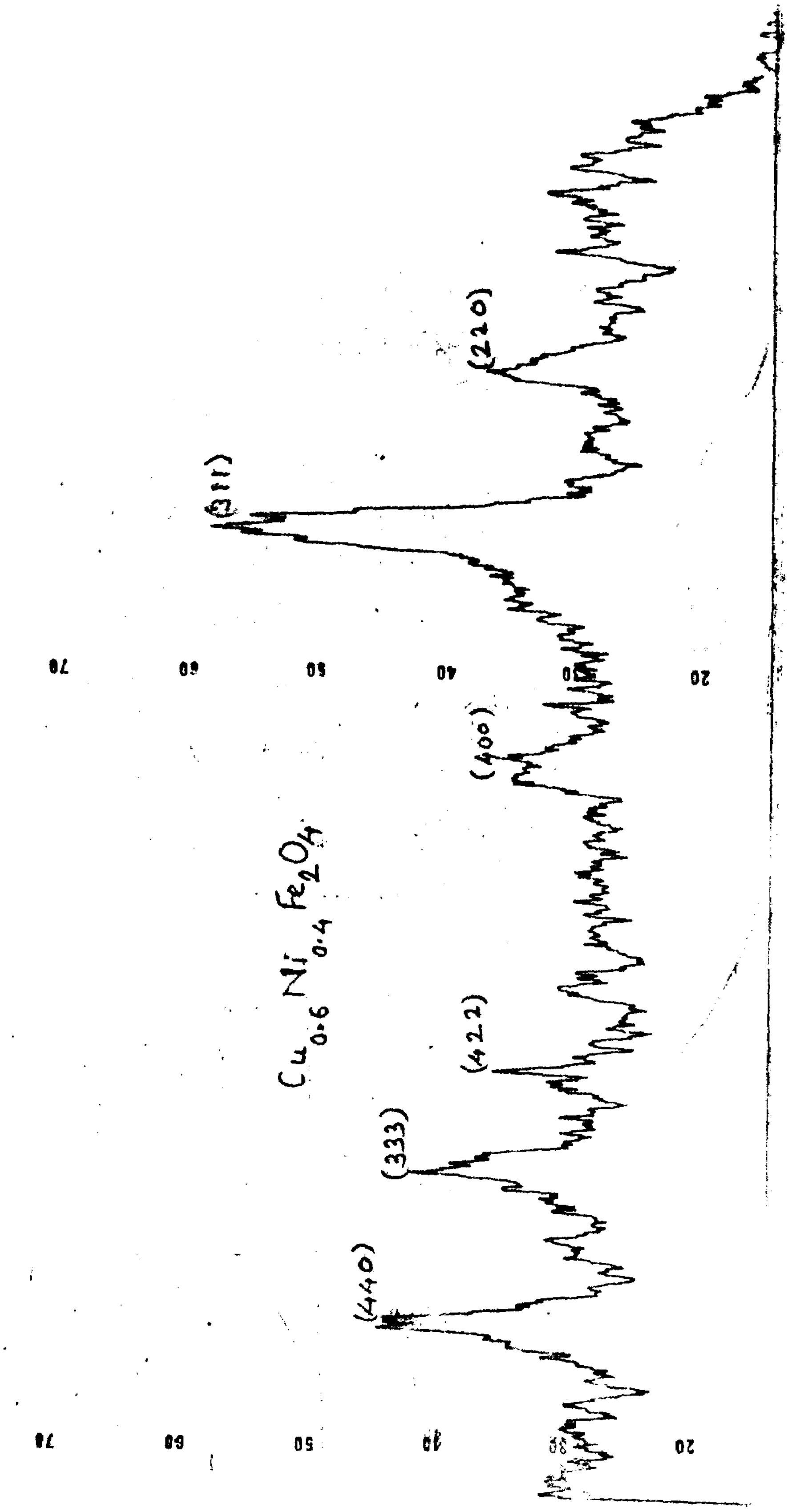

$Cu_{0.6}Ni_{0.4}Fe_2O_4$
(311)
(220)
(400)
(422)
(333)
(440)
80
70
60
50
40
30
20
70
60
50
40
30
20

Fig 2.4(d)

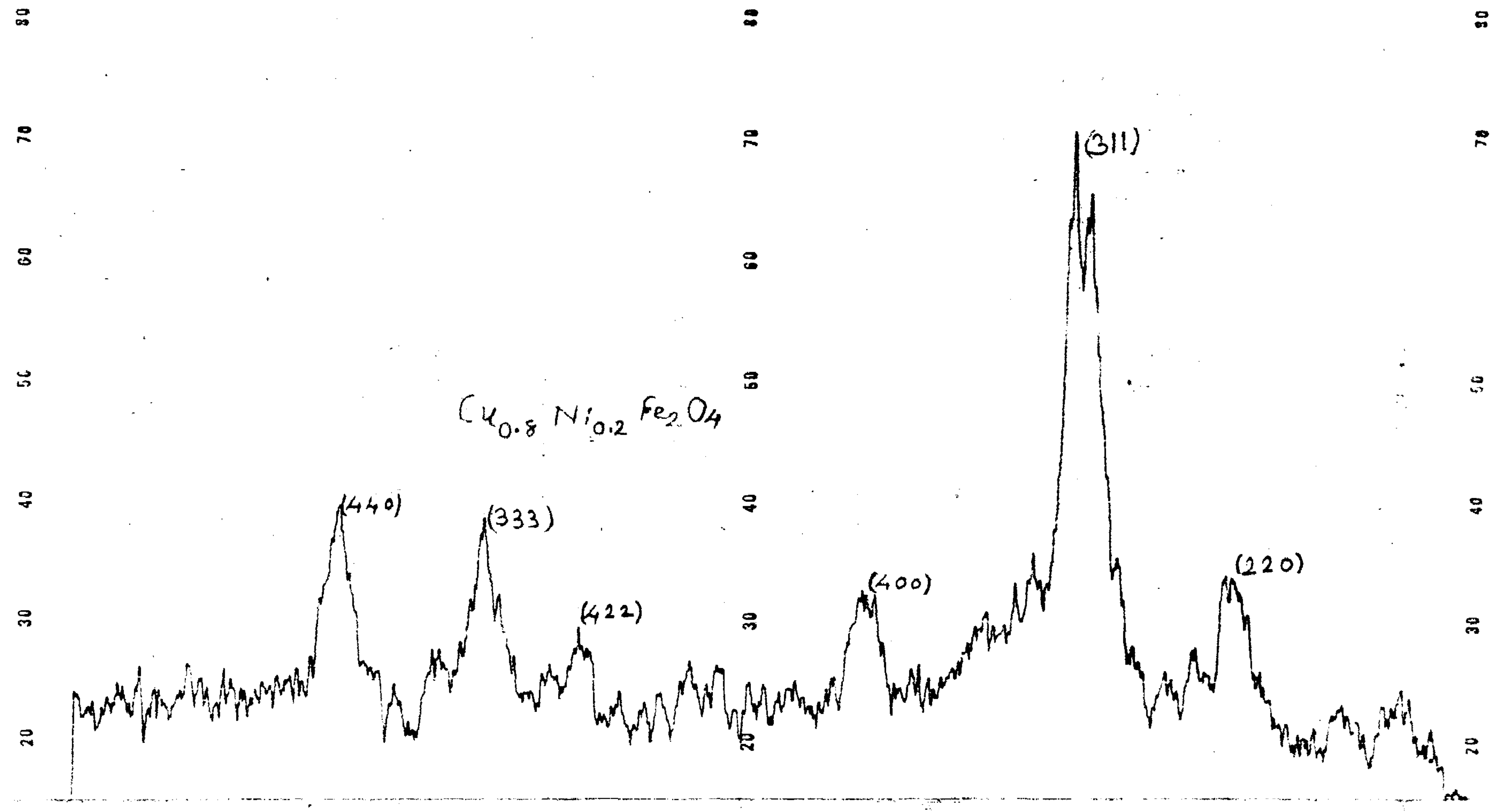


Fig 2.4(a)

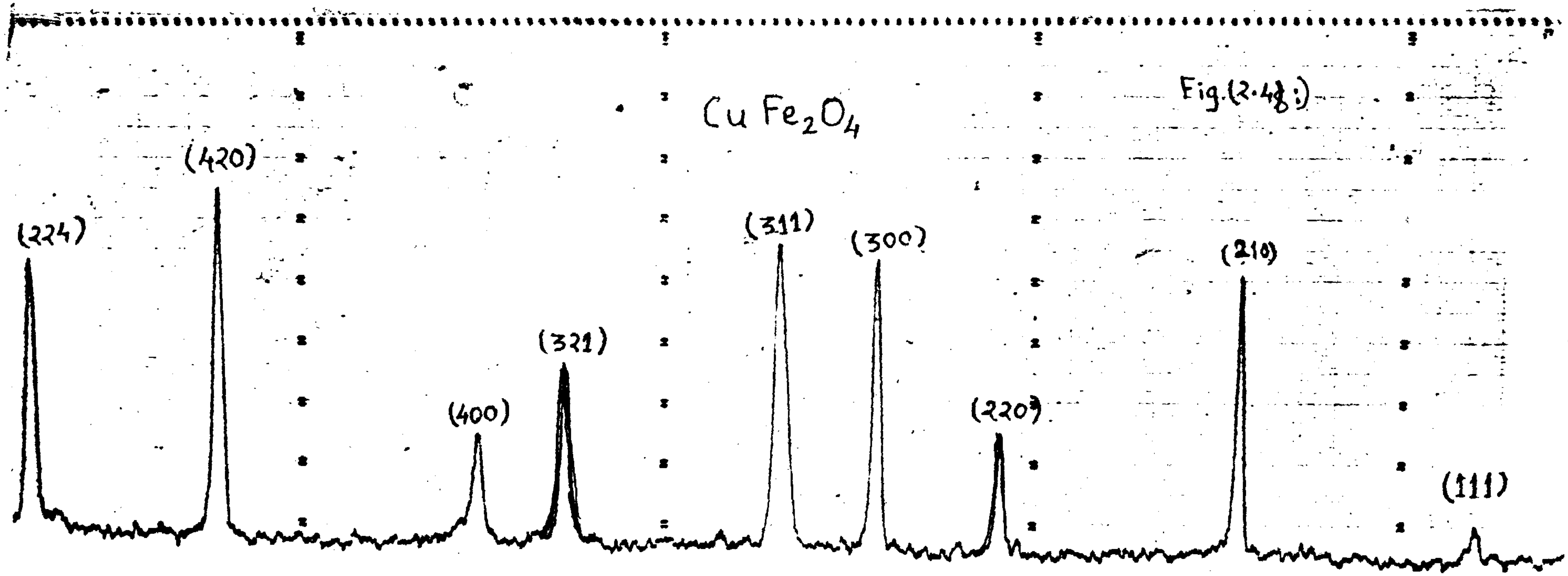


Fig. 2·4(b)

Table No. 2.1 (a) : $NiFe_2O_4$

'd' in A°	Planes (h k l)	Structure	Lattice Parameter
2.935	(220)		
2.502	(311)		
2.416	(222)		
2.089	(400)	Cubic	a = 8.334 A°
1.603	(333)		
1.474	(440)		

Table No.2.1 (b) : $Cu_{0.2} Ni_{0.8} Fe_2O_4$

'd' in A°	Planes (hkl)	Structure	Lattice Parameter
2.939	(220)		
2.506	(311)		
2.418	(222)		
2.098	(400)	Cubic	a = 8.343 A°
1.698	(422)		
1.610	(333)		
1.474	(440)		

Table No.2.1 (c) : $Cu_{0.4}Ni_{0.6}Fe_2O_4$

'd' in A°	Planes (hkl)	Structure	Lattice Parameter
2.958	(220)	Cubic	a = 8.351 A°
2.522	(311)		
2.428	(222)		
2.081	(400)		
1.601	(333)		
1.476	(440)		

Table No.2.1 (d) : $Cu_{0.6}Ni_{0.4}Fe_2O_4$

'd' in A°	Planes (hkl)	Structure	Lattice Parameter
2.953	(220)	Cubic	a = 8.352 A°
2.521	(311)		
2.320	(222)		
2.083	(400)		
1.701	(422)		
1.605	(333)		
1.479	(440)		

Table No. 2.1 (e) : $Cu_{0.8}Ni_{0.2}Fe_2O_4$

'd' in A°	Planes (hkl)	Structure	Lattice parameter
2.959	(220)		
2.524	(311)		
2.403	(222)		
2.077	(400)	Cubic	a = 8.365 A°
1.702	(422)		
1.610	(333)		
1.475	(440)		

Table No. 2.1 (f) : $CuFe_2O_4$

'd' in A°	Planes (hkl)	Structure	Lattice parameter
4.843	(111)		
3.699	(210)		a = 8.377 A°
2.976	(220)		c = 8.725 A°
2.701	(300)	Tetragonal	
2.526	(311)		c/a = 1.041
2.231	(321)		
2.102	(400)		

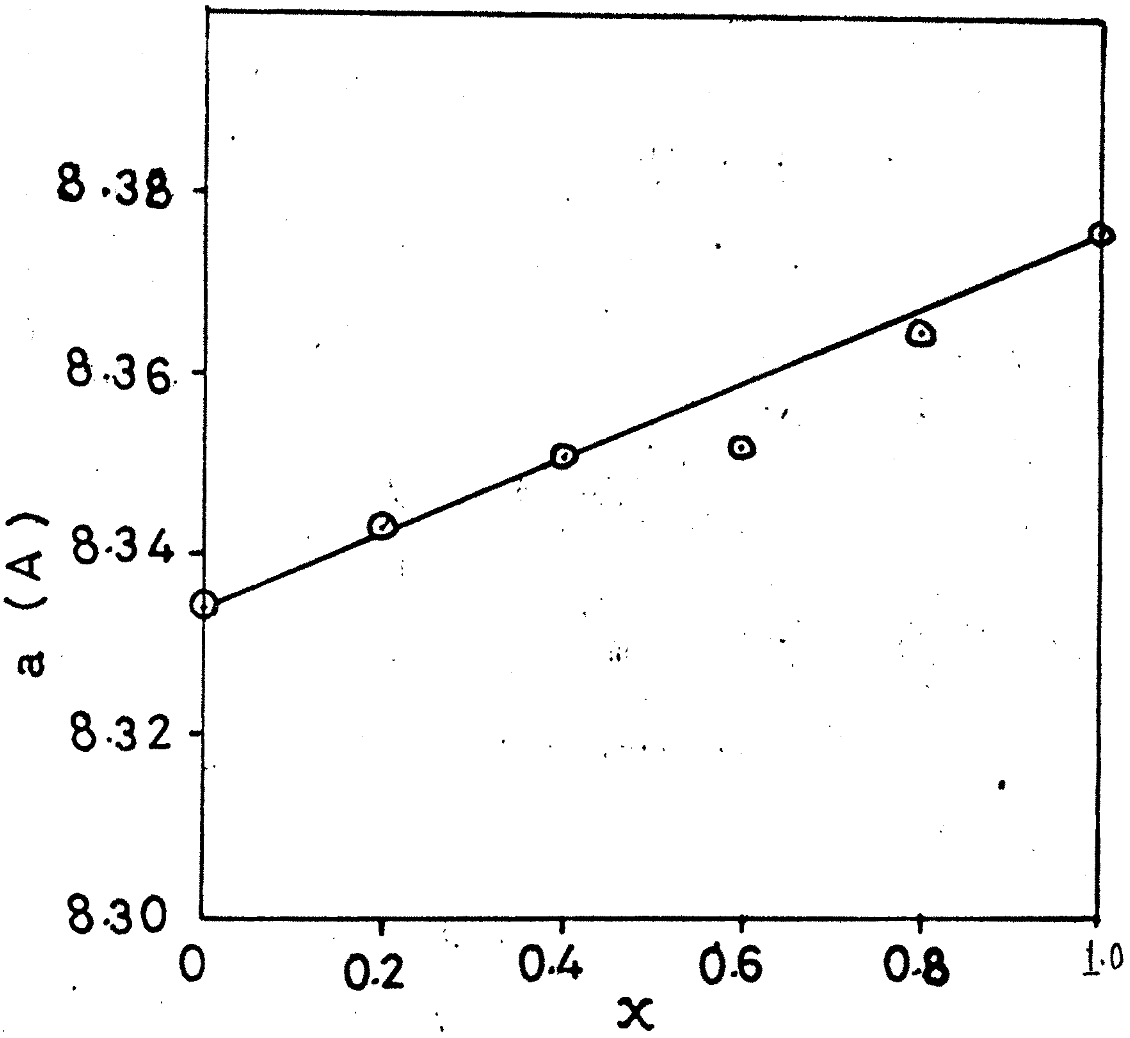


Fig. 2.5

law is obeyed by the system $Cu_xNi_{1-x}Fe_2O_4$. The lattice parameter has minimum value (a = 8.33 A^o) for $NiFe_2O_4$ and maximum (a = 8.38 A^o) for Cu Fe_2O_4. Our results are of correct order and in good agreement with the previously reported$^{(25)}$ results. Further these result look to be correct if the ionic volumes of the divalent ions are taken into consideration. The Pauling ionic radius for Ni^{2+} is 0.69 A° while that for Cu^{2+} is 0.72 A°. This therefore suggests that the lattice parameter would go on increasing with the increasing copper content.

The tables 2.1(a) to 2.1(f) show that $NiFe_2O_4$ is cubic lattice and addition of copper does not distort its lattice upto x = 0.8 i.e. for x = 0.0 to 0.8 the structure is cubic while for x = 1 it is tetragonal. It can be looked upon from another angle that if copper from $CuFe_2O_4$ is treated to be substituted by nickel to give the composition $Cu_xNi_{1-x}Fe_2O_4$, then it is interesting to comment that the moment 20% nickel ions are introduced into the general formula, the tetragonal lattice is immediately converted into a cubic one and it continues to remain cubic for further compositions. Our results are in good aggreement with P.Muthukumarasmy et al.,$^{(24)}$. However, it may be mentioned here that H.V. Kiran et al.$^{(25)}$ have pointed out for the same system that in the composition upto 20% nickel, and at 20%, itself (i.e. x = 0.8 in $Cu_xNi_{1-x}Fe_2O_4$) the structure is shown to have tetragonality.

Table No. 2.2 : Densities, System $Cu_xNi_{1-x}Fe_2O_4$

X	Physical Density gm/cm^3	X-Ray density (Ref.24)
0.0	2.93	5.38
0.2	3.56	5.37
0.4	3.68	5.37
0.6	3.57	5.37
0.8	3.43	5.37
1.0	3.65	5.37

In table 2.2 are given the x-ray density and the physical density of the samples. The X-ray density shows it is independent of the nickel content variation in the system. This may be because the Ni^{2+} is both lighter and smaller in size (Pauling radius 0.69 A°) compared with copper (Pauling radius 0.72 A°) and this may make the density independent of nickel content. However, the actual physical densities we have measured can be seen to differ a little and are smaller than the corresponding X-ray densities. This may be because of some porosity prevailent in the final pressed pellets. As is well known this may affect the electrical and magnetic properties in general which can be given consideration in the Chapters to follow.

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