STUDY ON THE ORDER-DISORDER PHASE TRANSITION AND LONG-RANGE ORDER PARAMETER OF Ni-Pt ALLOY

M. Phil. THESIS

BY

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DEPARTMENT OF PHYSICS

KHULNA UNIVERSITY OF ENGINEERING & TECHNOLOGY

KHULNA-920300, BANGLADESH

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KHULNA UNIVERSITY OF ENGINEERING & TECHNOLOGY
DEPARTMENT OF PHYSICS
CERTIFICATION OF THESIS WORK

A THESIS ON

STUDY ON THE ORDER-DISORDER PHASE TRANSITION AND LONG-RANGE ORDER PARAMETER OF Ni-Pt ALLOY

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has been accepted as satisfactory in partial fulfillment for the degree of Master of Philosophy in Physics and certified that the student has demonstrated a satisfactory knowledge on the field covered by this thesis in an oral examination held on April 28, 2007.

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It is to certify that this thesis, which the candidate has presented for M. Phil. degree has been done by the candidate himself and does not contain any material extracted from elsewhere or from a work published by any body else. The work of this thesis has not been presented for another degree or diploma in any other University or Institute. No other person's work has been used without due acknowledgement.

--------------------------- Supervisor

--------------------------- Candidate

To

The parents, specially
my Beloved Mother
Who teaches me without telling

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Abstract

Order-disorder phase transition of $Ni_{0.5}Pt_{0.5}$ equiatomic alloy and doped with Fe and Co with composition $Ni_{0.45}Fe_{0.05}Pt_{0.5}$ and $Ni_{0.45}Co_{0.05}Pt_{0.5}$ were studied X-ray diffraction (XRD) method. The specimens are prepared, using arc furnace, with high purity constituent elements. Ni-Pt system undergoes disorder-order transformation at high temperature from fcc (face centered cubic) structure to fct (face centered tetragonal) in the Ni-Pt alloy. Lattice parameters of the three disordered and three-ordered Ni-Pt and doped alloys were determined. A disordered alloy of all these three compositions are fcc with almost no change in lattice parameter Ni-Pt in the disordered state has lattice parameter of a=3.7468Å, while ordered one is fct having a=3.8187Å and c=3.6028Å with $\frac{c}{a}$ ratio of 0.943. A slight increase of $\frac{c}{a}$ ratio has been observed for Fe and Co doped alloys. The lattice parameter of the ordered fct phase of $Ni_{0.45}Fe_{0.05}Pt_{0.5}$ and $Ni_{0.45}Co_{0.05}Pt_{0.5}$ are a=3.8141Å, c=3.6069Å and a=3.8174Å c= 3.6154Å with $\frac{c}{a}$ ratio of 0.945 and 0.947 respectively. The average value of long-range order parameter "s" has been found to be 0.951 for the equiatomic NiPt alloy using in-situ high temperature attachment of XRD, indicating the alloy to be almost perfectly ordered. It has been calculated that out of 1000Pt sites in the crystal, 975Pt atoms occupied their places and the rest 25Pt sites were occupied by Ni atoms. It has been also observed the difference in the lattice parameter due to order-disorder transition is explained as arising from the associated change of local environment. Fe and Co doped Ni-Pt alloys have been found to be multiphase in contrast to the undoped counterpart. The phases have been identified to be FePt, FeNi, NiPt for Fe doped and CoPt, NiCo, NiPt for Co doped alloys.

CONTENTS

CHAPTER –I

Introduction

1.1. Introduction

The idea that order-disorder phenomena can exist in solid solutions was first proposed by Tammann in 1919$^{(1.1)}$. Later this phenomenon observed by Bain in 1923$^{(1.2)}$ and by Johansson and Linde in 1925$^{(1.3)}$ by means of X-ray diffraction. These works initiated extensive X-ray studies, the results of which are the basis of the modern concepts of the nature of order-disorder transformations. We know that an ordering alloy at high temperatures finds itself in a disordered state. This means that all crystallographycally equivalent crystal lattice sites are randomly occupied by the different kinds of atoms. The occupation probabilities of these sites are constants along crystal lattice directions, being equal to the corresponding atomic fractions.

Ordering leads to a "subdivision" of the crystal lattice of a disordered solution into several sub-lattices since the occupation probability i.e. the probability of finding the given kind of atom in the crystal lattice site powers to be different for the different sub-lattices although they are the same within each sub-lattice. This process yields a reduction in the symmetry of a disordered solution since crystal lattice sites of different sub-lattices which are crystallographically equivalent in the disordered state, become non-equivalent in the ordered state. Therefore the space group of an ordered alloy is always a subgroup of the space group of its disordered alloy.

A large number of binary substitutional alloys are ordered at low temperatures and disordered at high temperatures$^{(1.4\ -\ 1.10)}$. A binary alloy which is in the ordered state, the constituent atoms A and B occupy definite lattice sites at random. In the disordered state, like atoms are often adjacent to each other (AA or BB pairs), where as ordering commonly makes all nearest neighbours unlike. The order-disorder transition in magnetic alloys is interesting because atomic ordering and magnetic ordering are closely related phenomena characterized by well defined transition temperatures. There has been much interest in alloys which undergo a critical phase transition from ordered state to disordered state, since most of the physical properties of the alloys strongly depend on the atomic distribution on the lattice sites.

Ni-Pt system exhibits order-disorder transition having disordered phase with fcc structure at high temperature and undergoes ordering below 630°C in the sequence of simple cubic ($L1_2$) shown in fig-1.1 and face centered tetragonal ($L1_0$) shown in fig-1.2. Face centered tetragonal and simple cubic structure at the stoichiometric compositions Ni_3Pt, NiPt and $NiPt_3$; respectively (1.11) like the prototype Cu-Au system. Since the long-range ordered that requires some mention is the effect of change in composition. Since the ratio of corner sites to face centered sited in the $AuCu_3$ lattice is 1:3, if follows that perfect order can only be attained when take place in alloys containing less than 25 atomic percent gold.

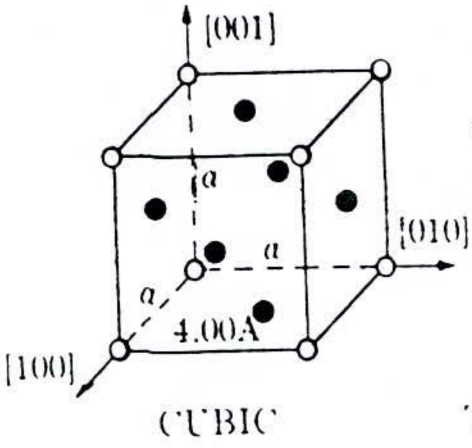


Fig- 1.1 : Face Centered Cubic

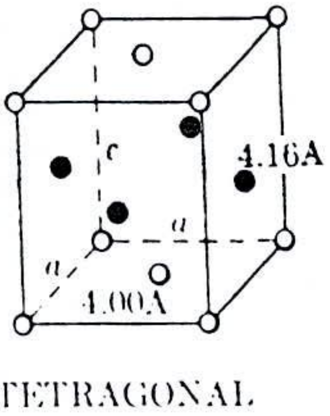


Fig- 1.2 : Face Centered Tetragonal

The gold-copper atoms of $AuCu_3$ above a critical temperature of about 395°C, are arranged more or less at random on the atomic sites of a face centered cubic lattice as illustrated in fig- 1.3 (a) and fig- 1.3 (b).

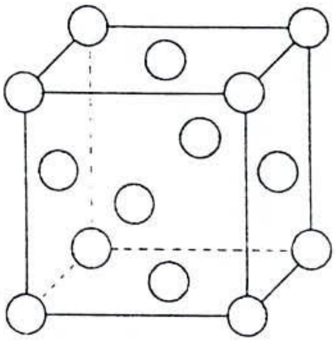


Fig-1.3 (a) : Disordered

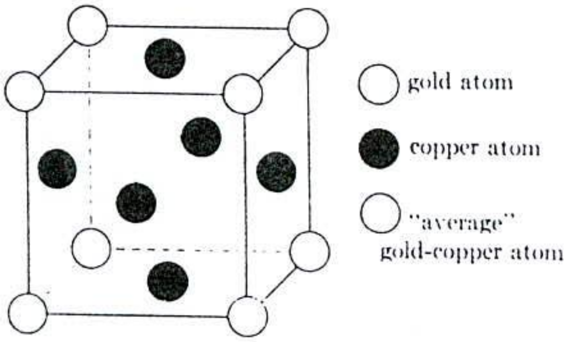


Fig-1.3 (b) : Ordered

If the disorder is complete, the probability that a particular site is occupied by a gold atom is simply $\frac{1}{4}$, the atomic fraction of gold in the alloy, and the probability that it is occupied by copper. These probabilities are the same for every site and considering the structure as a whole, we can regard each site as being occupied by statistically "average" Gold-Copper atom. Below the critical temperature, the gold atoms in a perfectly ordered alloys occupy only the corner positions of the unit cube and the copper atoms the face centered position. As illustrated in fig- 1.4(a) and fig- 1.4(b). Both structure are cubic and have practically the same lattice parameters.

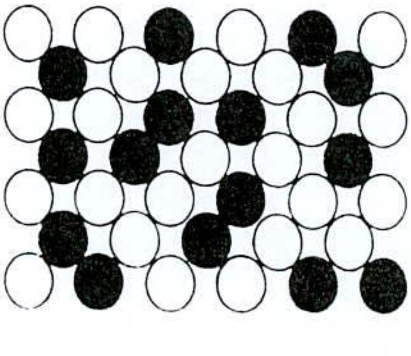


Fig-1.4 (a) : Disordered

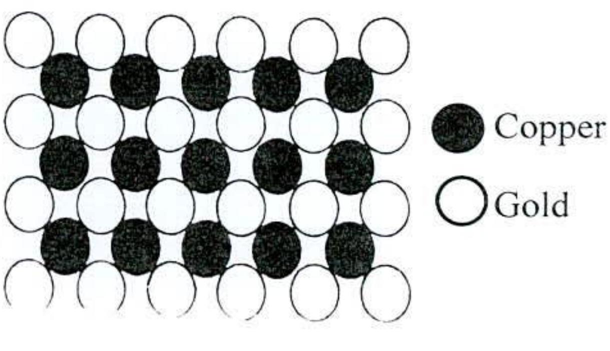


Fig-1.4 (b) : Ordered

Fig- 1.5 shows the partial binary phase diagram of Ni-Pt alloys, where $L1_2$- type Ni_3Pt and $L1_0$- type Ni-Pt order structures exist in the composition ranges from x=0.18 to 0.35 and from x=0.36 to 0.75 respectively. $L1_0$ is a layered structure, which is built up of (001) planes alternately containing only Ni or Pt atoms along the C-exis ($a=b\neq c$) with tetragonal symmetry. It has been observed that the degree of ordering i.e. long–range order parameter "s" has strong influence on the magnetic properties. The equi-atomic Ni-Pt alloy, atomic ordering completely destroys the spin orders, i.e. disordered alloy is ferromagnetic while ordered on is paramagnetic (1.12-1.13). Similarly fig-1.6, fig-1.7, fig-1.8 and fig- 1.9 are shows the partial binary phase diagrams of Fe-Ni, Fe-Pt, Co-Ni and Co-Pt alloys are respectively.

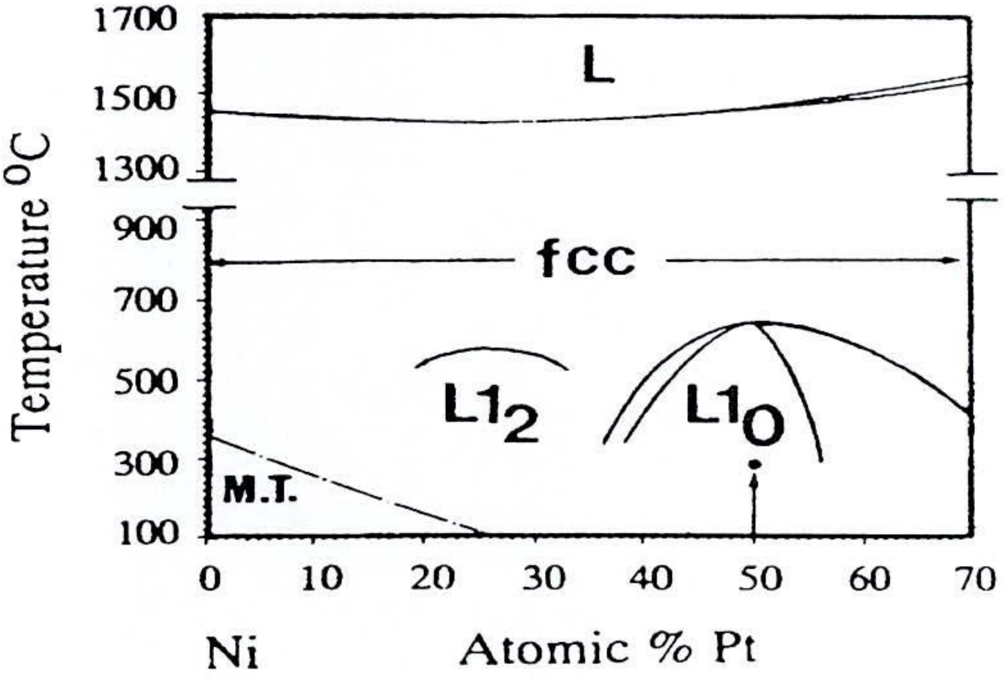


Fig-1.5: Binary alloy phase diagram of Ni-Pt alloy

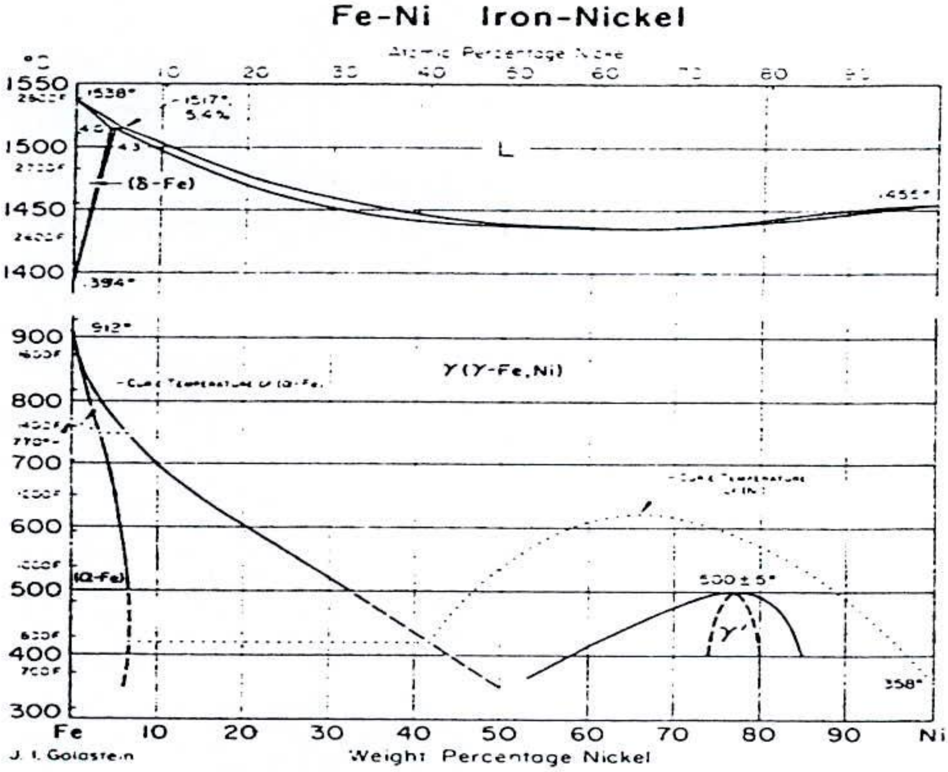


Fig-1.6: Binary alloy phase diagram of Fe-Ni alloy

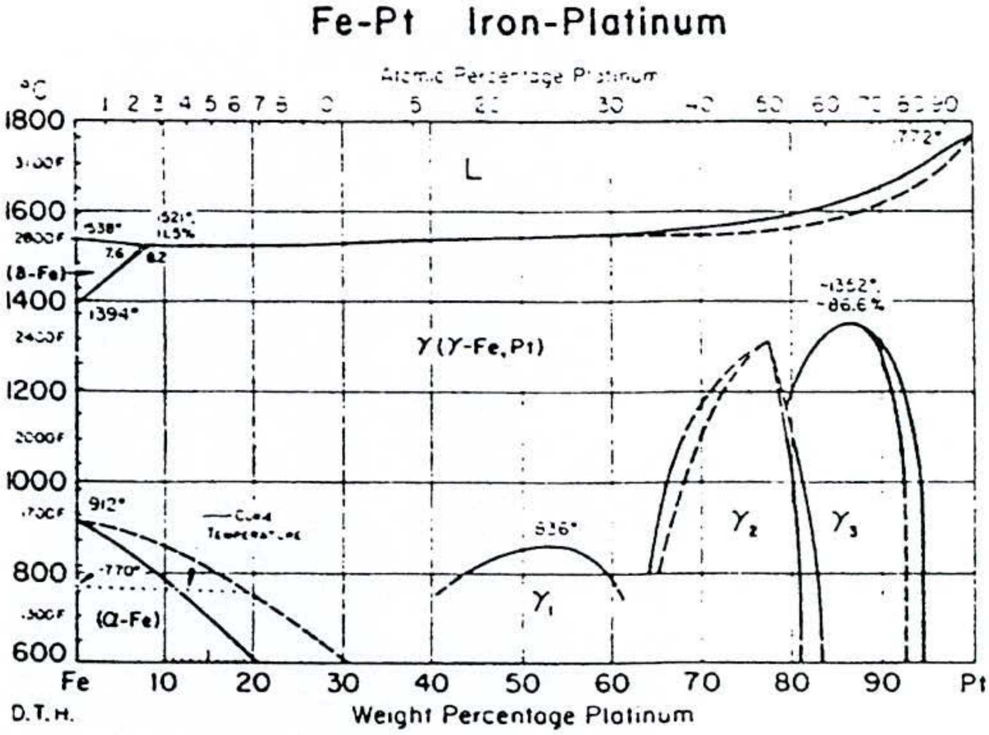


Fig-1.7: Binary alloy phase diagram of Fe-Pt alloy

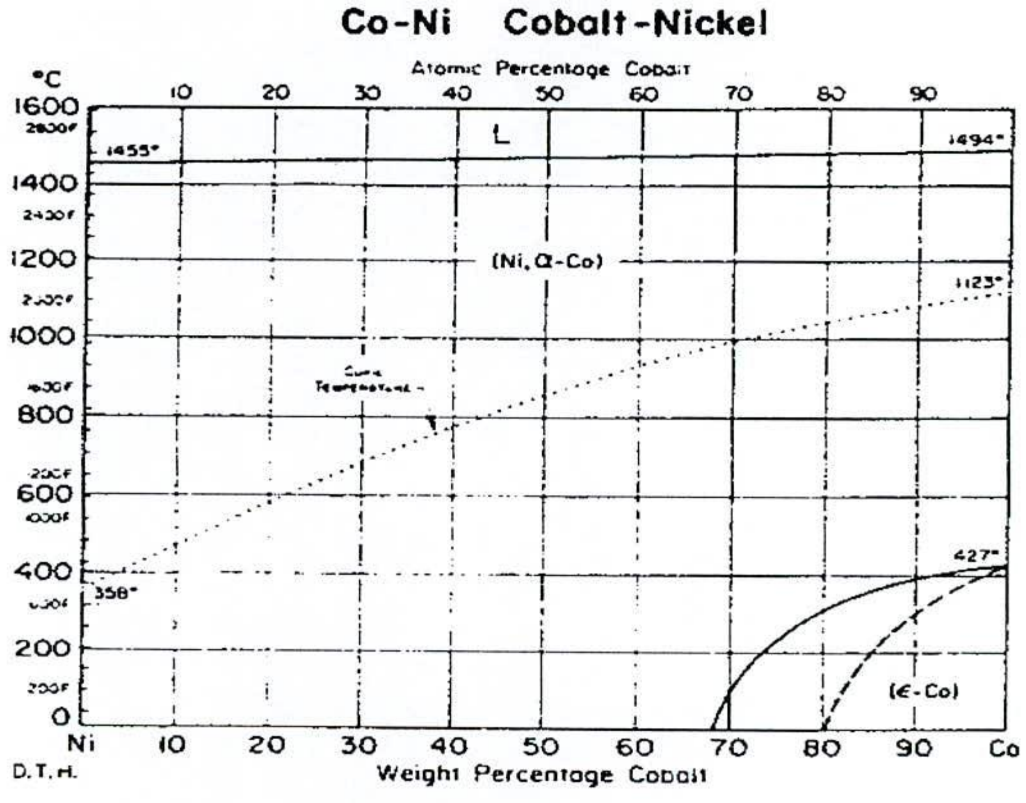


Fig- 1.8: Binary alloy phase diagram of Co-Ni alloy

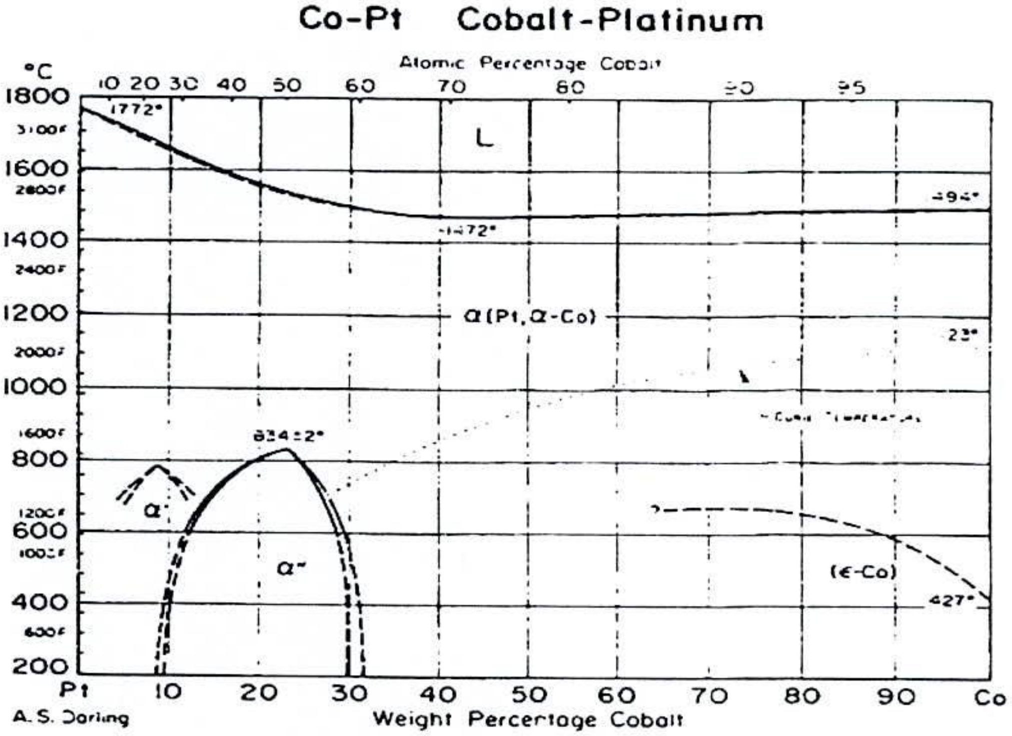


Fig- 1.9: Binary alloy phase diagram of Co-Pt alloy

In the present study X-ray diffraction method is used to determine the crystal structures, lattice parameter, $\frac{c}{a}$ ratio, average long-range order parameter "s" of Ni-Pt alloy and interpreted the results with theoretical and existing literature values.

Diffraction work has been done on disordered binary alloys to understand their structural fluctuations by analyzing the short-range order (SRO) diffuse scattering intensity quantitatively. Short-range order in some Ni-based binary alloys has been studied on the system of Ni-Cr, Ni-Mo, Ni-Fe, Ni-Al and Ni-Pt [1.14 – 1.17]. Temperature dependence of atomic relaxation time has been measured for both the order-disordered states of Ni-Pt alloys [1.18]. They have observed the important slowing down effects in the vicinity of the order-disorder transition temperature (T_p). Intensity of ordered Ni-Pt state has been measured after long annealing at 610°C (1.19). The long and short range order parameters of Ni-Pt alloy have been measured at different temperature (1.20). Sample preparation and their characterization is a vital part in the investigation of the magnetic properties in the ordered and disordered states. Small amount of impurity can effect the true evaluation. Therefore, high purity constituent elements with purity 5N have been used to prepare good quality samples. Ordering the samples is another important factor for comparing the ordered and disordered phases quantitatively. Ordering of the Ni-Pt alloy and their doped system has been done on the basis of the phase diagram and the information available from previous reports (1.18-1.21). The knowledge of the ordering kinetics of similar systems has been used of in the preparation of ordered and disordered samples. Ordered and disordered phases can be identified X-ray diffraction. In the present work X-ray investigations have been employed to identify the ordered and disordered phases. The presence of sharp super-lattice lines in the X-ray pattern conclusively determined the ordered structure of the alloys. The diffraction line from planes of unmixed indices are called fundamental lines. Since they occur at the same position and with the same intensities in the patterns of both ordered and disordered alloys. The extra lines which appear in the pattern of an ordered alloys, arising from planes of mixed indices, are called super-lattice lines and their presence is direct evidence that ordering has taken place.

A detail study of magnetic properties of NiPt doped with Fe and Co system showed that ordered alloys are highly anisotropic with the manifestation of large hysteresis effect with very high coercivity incontrast with, the undoped NiPt alloy(1.12). This has been explained as due to some second phases which could not identified since some extra Bragg diffraction peaks other than the ordered NiPt fct phase. The aim of this thesis has been to investigate experimentally the effect of atomic order-disorder on the order parameter, lattice parameter and phase formed during ordering of Nickel-Platinum alloys and iron and cobalt doped Nickel-Platinum alloys. To investigate lattice parameter of the sample of Debye-Scherrer experiment Nelson-Rally method has been used.

1.2. Objective of the present work

a) Preparation of Ni-Pt alloy ingot and alloys doped with Fe and Co.

b) Determination of crystal structure of fully ordered and disordered state of the alloys after adequate thermal treatment keeping the sample in side the oven of the diffractometer.

c) X-ray Debye-Scherrer experiment would be carried out on thin needle like samples.

d) Lattice parameter of the sample would be determined from the data of Debye-Scherrer experiment using Nelson-Really method.

e) Order-disorder phase transition temperature would be determined from the X-ray high temperature experiment (in-situ).

f) Long-range order parameter "s" has been determined from the in-situ X-ray high Temperature data by comparing the like Paris of fundamental and super-lattice reflection peak intensities.

g) Experimentally determined parameters such as lattice constant crystal structure and long-range order has been compared with the available literature values as affected by thermal treatment around the order disorder phase transition temperature.

CHAPTER 2

Order-Disorder Phenomena

2.1 Order-disorder phenomena

The order disorder phenomena is possible in interstitial as well as is substitutional solutions. There is no difference in principle between them since one can always consider an interstitial solution as a substitutional one composed of interstitials and vacant interstices. The host atoms in interstitial solutions do not take part in an ordering reaction. They form an immobile frame.

2.1.1. General characteristics

Order-disorder phenomena, in metallic alloys and compounds, belong to the class of co-operative phenomena of considerable intrinsic interest to physicists. There has been much interest in alloys, which undergo a critical phase transition from ordered to disordered states since most of the physical properties of the alloys strongly depend on the atom distribution on the lattice sites. In many binary alloys, usually those which exhibit complete or nearly complete miscibility, at particular compositions there can exist below a critical temperature, T_c, an "ordered" lattice (superlattice) and above T_c a "disordered" lattice (2.1-2.7).

The idea that order-disorder phenomena can exist in solid solutions was predicted by G. Tammann in 1919 (2.8) on CuAu alloy on the basis of chemical evidence and latter on in 1925 Johansson and Linde(2.9) confirmed the ordered structure of CuAu from X-ray pattern. These works initiated extensive X-ray studies, the results of which are the basis of the modern concepts of the nature of order disorder transformations. In the disordered state in most substitutional solid solutions, the two kinds of atoms A and B are arranged more or less at random on the atomic sites of the lattice. By "ordered" is meant that the lattice, sites are grouped into sublattices, each of which is occupied predominantly by one species of atoms. Simple superlattices in binary alloys with cubic structure occur near composition corresponding to stoichiometric ratios of atoms like A_3B, AB, AB_3 etc. Ideally, at sufficiently low temperatures this long range order should extend throughout each single crystal. However, at low temperature the ordering process is too slow and at high temperature the disturbing thermal agitation is too large to allow the ideal condition ever to be attained. The ordered state in an actual single crystal (or grain) should be imagined as consisting of many small volumes within which the order is very high but varying in a discontinuous manner at the boundary between these volumes. Each of these volumes can be thought of as separately nucleated during the transition from a random to an ordered solid solution. Clearly, the over-all degree of order in a crystal at equilibrium depends upon the size of these blocks of high order and it changes with temperature and with deviation from the stoichiometric composition which corresponds to an ideal complete order.

For sometime it was believed that the order-disorder transformation is homogeneous transformation; i.e., the two states cannot co-exist in equilibrium. Now mounting evidence (2.3, 2.10, 2.11) points to the conclusion that this is not true and that many, if not all, ordering reactions are heterogeneous and similar to the conventional phase transitions.

The ordering process is very conveniently described in terms of a change in the number of nearest neighbours of each kind of atoms. The ordering usually leads to a preferential formation of mixed bonds AB rather than AA or BB. In the disordered state like atoms are often adjacent to each other i.e., they prefer AA or BB bonds. On the basis of thermodynamics it can be shown that an ordered arrangement of atoms in an alloy may produce a lower internal energy compared to a disordered arrangement, particularly if the segregation of atoms to designated atomic sites occurs at relatively low temperatures where entropy, associated with randomness, plays a lesser role. The thermodynamic criterion for an alloy to be orderable is

$$E_{AB} < \frac{1}{2}\left(E_{AA} + E_{BB}\right) \qquad 2.1$$

Where E_{AA} and E_{BB} represent energies of like pairs of atoms and E_{AB} represents the energy of the unlike pair. The physical significance of this criterion is that atomic ordering is feasible only when the bond energy of the unlike atom pair is less than the mean bond energy of the two kinds of like atom pairs. On the other hand, if $E_{AB} > \frac{1}{2}\left(E_{AA} + E_{BB}\right)$, system will tend to form mixtures of two A and B rich solid solutions, in which like atom pairs dominate.

2.1.2. The long range order Parameter

The terminology appropriate to the description of crystal structures, let us now go on to consider crystals containing various quantities of a metal B added to a metal A, to form 'substitutional solid solution'. An alloy are often very similar to those of the pure A metal sure only that some of the lattice sites are now occupied by B atoms rather than by A atoms, *i.e.* the formation of this kind of AB alloys. For a long time it was thought that this substitutions was a purely random process and that there was no particular regularity or order in the arrangement of the substituted B atoms on the lattice site of the AB crystals.

Suppose then that the lattice of a given crystal may be sub divided into two sub-lattices symmetrically related to each order in this way, *i. e.* there are N-lattice points of which $\frac{N}{2}$ are of type a and $\frac{N}{2}$ are of type b, the nearest neighbors of a sites being b sites and vice versa. Let us also suppose that there are N atoms of which $\frac{N}{2}$ are of type A and $\frac{N}{2}$ are of type B. We may then characterize states of long range order- as measured by the tendency for atoms to arrange themselves on their 'own' sub-lattice by a parameter 'S' defined by the relation.

$$S=\frac{(\text{A on a})\text{state of order 's'}-(\text{A on a})\text{random}}{(\text{A on a})\text{perfect order}-(\text{A on a})\text{random}}$$

$$=\frac{(\text{B on b})\text{state of order 's'}-(\text{B on b})\text{random}}{(\text{B on b})\text{perfect order}-(\text{B on b})\text{random}} \qquad 2.1$$

Where the brackets indicate the number of atoms in the ordered state specified by the subscript. The random state being of course the state of long-range disorder. The 'second equality' follows from the first is a simple consequence of the self evident facts that A atoms are not on a sites are on b sites, and all sites not occupies by A atoms are occupies by B atoms. Determine the distribution of A and B atoms on a and b from eq^n(2.1) in terms of the parameter S. The results of this very simple calculation are given by

$$\text{Number of A atoms on a sites} = \frac{1}{2}(1+S)\frac{N}{2}$$

$$\text{Number of A atoms on b sites} = \frac{1}{2}(1-S)\frac{N}{2}$$

$$\text{Number of B atoms on a sites} = \frac{1}{2}(1-S)\frac{N}{2}$$

$$\text{Number of B atoms on b sites} = \frac{1}{2}(1+S)\frac{N}{2}$$

For S= 1 all the A atoms are on a sites and all the B atoms are on b sites and so S= I characterizes the state of perfect order for this kind of structure.

For S = 0 there are equal numbers of A atoms on both a and b sites and equal numbers of B atoms on a and b sites, S = 0 therefore characterizing the state of complete long range disorder where the distinction between a and b sites has effectively disappeared.

To regard the parameter S as satisfying the inequality $0 < S < 1$, negative values of S being regarded as corresponding simply to a different labeling of the sub-lattices but to essentially the same physical situation.

Intermediate values of S clearly characterize intermediate states of order where the tendency for atoms to arrange themselves on there own sub-lattice has not been completely destroyed, the parameter S thus gives a quantitative measure of what may be called "the degree of long range order" for this kind of structure.

With perfect order at a low temperature the mathematically probability of finding an A atom on a sites and B atoms on b sites in unity. At higher temperature, however, the probability that an a site is occupied by an A atom will be reduced to a fraction of unit, say p. The departure from perfect order can be described, according to Bragg and Williams by means of the long range order parameter, S.

$$S=\frac{P-r}{1-r} \tag{2.3}$$

Where r is the fraction of A atoms in the alloy. According to eq^{n} (2.3), S varies from one to zero as order decreases.

For an AB alloy of fractional composition n_A, n_B $[n_A + n_B = 1, n_A \leq n_B]$, there are now no longer necessarily $\frac{N}{2}$ atoms of each kind but rather n_AN of type A and n_BN of type B. The numbers of A and B atoms on a and b sites in the state of order 'S' are calculated the distribution is now given by

Number of A atoms on a sites = $n_A(1+S)\frac{N}{2}$

Number of A atoms on b sites = $n_A(1-S)\frac{N}{2}$

Number of B atoms on a sites = $(n_B - n_A S)\frac{N}{2}$

Number of B atoms on b sites = $(n_B + n_A S)\frac{N}{2}$

Here S = 1 corresponds to the state of best possible ordered based on two equivalent sub-lattices; *i. e.* when all the atoms are on a sites and all the nearest neighbors of A atoms are B atoms.

For S = 0 equal numbers of A atoms are on a and b sites, *i. e.* the distribution is completely random and corresponds to complete disorder; the parameter S given a quantitative measure of what may again be regarded as 'The degree of long range order.

2.1.3. The Short- Range Order Parameter

The parameter S defined above tells us something about how, on the average, the A(B) atoms are distributed on a particular sub-lattice. Values of S > 0 indicate that there is preferential ordering of the A(B) atoms on one of the sub-lattices to the exclusion of the other, this preferential ordering being given the name 'long range order'. The linear chain of A and B atoms illustrates below is considered separately are each perfectly ordered (S=1)

-------------AB AB AB ⋮ BA BA BA---------------

Order structure for which S = 0, a value which suggests disorder. This kind of difficulty associated with what is called a 'change step' boundary- shown dotted … is part of an intrinsic difficulty.

For the moment we will ignore configuration such as the one illustrated and suppose that S=0 does in fact imply that there is no tendency for A and B atoms to separate into different sub-lattices over any extended region of the crystal.

The value S=0 does not preclude order entirely, there may still be a tendency for A atoms to surround them-selves with nearest neighbor B atoms and vice versa a even through there is no overall tendency for the A(B) atoms to separate into one particular sub-lattice, such ordering is called local or short range ordering and is illustrated in terms of a linear chain below

------------A BBBA BB A B A BB AA B AAA BA BB A BA---------------

where it is readily found by counting that the number of A and B atoms an any one particular sub-lattice are approximately S = 0.

The nearest neighbors of A(B) atoms are preponderantly B(A). A parameter of σ giving a quantitative measure of an aspect of this kind of ordering may be defined as follows.

A quantity q equal to the fraction of the nearest neighbor pairs in the configuration under consideration which consist of unlike atoms, the short range order parameter σ is then defined by

$$\sigma = \frac{q - q(\text{random})}{q(\text{maximum}) - q(\text{random})} \text{-----------} \qquad 2.4$$

Where q (random) and q (maximum) are the values of q for complete disorder and best order repetitively.

σ = 1 for perfect order and σ = 0 for complete disorder and takes intermediate values for intermediate states of order.

σ is explicitly defined in terms of nearest neighbors pairs and since, in part, it tells how, on the average, particular A(B) atoms are surrounded by nearest neighbor B(A) atoms, σ is called the 'short-range order parameter'.

σ may take negative values, these negative values being associated with configurations in which there is a tendency for the atoms to form clusters of A (or B) atoms; when the number of A-B nearest neighbor pairs is less than the number for the random configuration.

In the linear chain illustrated S=0 and σ =0.68 indicating a fairly high degree of local ordering, it is also to be noted that although in the first linear chain illustrated S=0 and the parameter S fails to indicate the order σ is very nearly equal to unity of the value for perfect order.

Perfect order the values for S and σ are related in that S= σ =1 and knowledge of σ gives us knowledge of S and vice versa, this is true for no other configuration values of $S < 1$ ($\sigma < 1$) do not allow value of σ (S) to be inferred. So σ is defined in such as way that it would become unity for perfect order and Zero for randomness.

Actually instead of reaching Zero on disordering 'a', usually remains 'a' definite value above T_c. In terms of the relationship between atoms 'a' measures the state of order in the immediate vicinity of a given order in the immediate vicinity of a given atom, unlike the long range order parameter, S, which deals with the whole lattice.

2.1.4. Crystallography

The necessary condition for the second order phase transition in an ordering allow of possible only if any fundamental reciprocal lattice vector cannot be obtained by combining any three ordering wave vectors of the star $\{K_o\}$ generating ordering. For second-order transition leads, in particular, to a very important conclusion obtained by Landau "any crystallization reaction is always a first order transition".

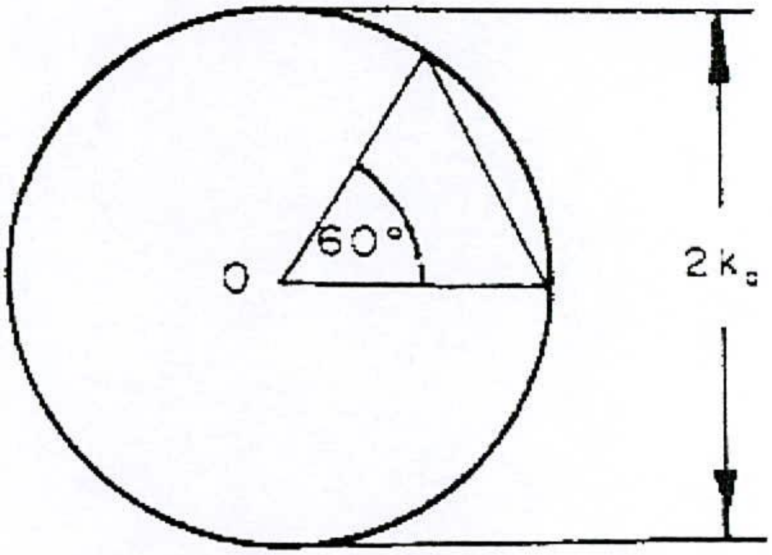


Fig- 2.1: Relationship between the vectors of the star at a liquid crystal phase transition,

Atomic ordering changes the crystal structures of the alloys and compounds. FeCo alloy is bcc in the disordered state and forms ordered $L2_0$ (superlartice) structure after atomic ordering. The ordered $L2_0$ structure corresponds to CsCl structure in which iron atoms occupy only corner sites and Co atoms only the cube center sites. In this ordered structure, each atom has eight unlike nearest neighbors. Again Ni_3Fe. Fe_3Pt, Co_3Pt and Ni_3Pt alloys are fcc in the disordered state and form super lattices corresponding to Ll_2 structures on ordering. This structure is equivalent to four interpenetrating simple cubic lattices. In Ll_2 ordered structure all A atoms are accommodated at the corners of the unit cells and all B atoms at the face centers of the unit cells. Another type of ordered structure Ll_0 is found in alloys of FeNi, FePt, CoPt and NiPt and they are all fcc in the disordered state. Ordering of all these equiatomic AB alloys in the fcc lattice necessitates the segregation of atoms of each species alternately on the (001) planes leading to a change in the original structure from fcc to an ordered face-centered tetragonal (fct) $L1_0$ superlattice. Each atom has eight nearest neighbours of opposite kind in the adjacent (001) planes, and four of the same kind in its own (001) plane at a slightly greater distance, since the axial ratio, c/a, is usually less than unity. Another type of superlattice DO_3, is found in ferromagnetic Fe_3Al and Fe_3Si alloys in which the bcc lattice is accompanied by an enlargement of the unit cell by a factor of 8, i.e, unit cell of an ordered alloy in the bcc lattice contains 8 original unit cells of the disordered bcc structure. Four common types of superlattices found in ferromagnetic alloys are given in table- 2.1(1.12).

Table- 2.1

Four common types of super lattices observed in ferromagnetic alloys

Type	Crystal Structure	No. of atoms per unit cell	Coordinates of atoms in the unit cell	No. of possible distinct domains	Examples
$L1_0$	Face-centered tetragonal	4	2A in $(000, \frac{1}{2}\frac{1}{2}0)$ 2B in $(\frac{1}{2}0\frac{1}{2}, 0\frac{1}{2}\frac{1}{2})$	6	FePt, CoPt, NiPt, FePd
$L1_2$	Face-centered cubic	4	1B in (000) 3A in $(0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}, 0\frac{1}{2}\frac{1}{2})$	4	Ni_3Fe, Ni_3Mn, Fe_3Pt, Pt_3Fe, Pt_3Co, Ni_3Pt, Pd_3Fe
$L2_0$	Body-centered cubic	2	1A in (000) 1B in $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	2	FeCo
DO_3	BCC with unit cells 8 times larger than those in the disordered lattice	6	4B in (000) f.c. 4A in $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ f.c. 8A in $\pm(\frac{1}{4}\frac{1}{4}\frac{1}{4})$ f.c.	4	Fe_3Al, Fe_3Si

2.2. Order-disorder Transition Kinetics in Alloys

The existing experimental methods for studying diffusion processes are based on the measurements of the dissolution of concentration in homogeneities whose space dimensions greatly exceed inter-atomic ranges. The ordered and disordered state of an alloy is an important factor in structural analysis. An alloy is completely ordered at absolute zero. It becomes less ordered as the temperature (T_c) is reached, above which the structure is disordered. In the ordered state the constituent atoms of the alloy arrange themselves in an orderly periodic manner. So it is called that a long-range order exists in the structure which is order over many inter-atomic distances. The transition temperature marks the disappearance of this long-range order but some short-range order or co-relation among near neighbors may persist above the transition (2.13).

If an alloy is quenched rapidly from high temperature to a temperature below T_c, metastable condition may be produced in which a non-equilibrium disorder is frozen in the structure and the constituent atoms arrange themselves more or less randomly. The degree of order can be investigated experimentally by X-ray diffraction. The disorder structure has the diffraction line as if lattice points were all occupied by only one type of atoms because the effective scattering power of each plane is equal to the average of the scattering powers of the constituent atoms.

The order structures has extra diffraction lines in addition to the fundamental diffraction lines, not possessed by disordered structure. These extra lines are called the superstructure reflections. The existence of superstructure reflection is the evidence of ordered structure. Several types of ordered structures are found in the crystalline materials. Among others

Cu_3Au (LI_2), CuAu I (LI_0), CuPt (LI_1) and CsCl (B_2) type ordered structures are common in the binary alloy systems.

2.2.1. Kinetics of Ordering

The knowledge of the kinetics of the order-disorder transition has been provided by the investigation of the ordering process under cooled of the disordered alloys or the disordering process is overheated of the ordered alloys. The kinetics may be infered from the evolution of heat, the change of some line on an X-ray photograph, or the variations of electrical resistance, magnetic susceptibility, or some other physical property (2.14). The time at which the equilibrium state has been observed to vary markedly from one system to another and to depend on the actual temperature T and on the difference between T and critical temperature, T_C of the system.

An alloy as a thermodynamic system will tend to make its free energy minimum. It will do so if sufficient time is given for this equilibrium to be attained. Now at finite temperature, the enthalpy H is greater than the free energy G of the system by an amount given by absolute temperature T times of the entropy S'.

$$G = H - TS' \qquad 2.4$$

At high temperature the increase in entropy, hence the corresponding disorder will be favoured so long as the associated increase in the internal energy is more than compensated by the reduction of free energy by the entropic part.

A disordered state can be obtained if the alloy is cooled rapidly enough from the high temperature so as to inhibit the formation and growth of ordered regions. The nucleation for ordered regions involves the diffusion of atoms. In order to overcome local energy barriers of the disordered alloy which is in a meta-stable state the atoms must get sufficient thermal energy. The number of atoms available with necessary activation energy is controlled by the Boltzman factor $e^{-E_\alpha/kT}$, where E_α is the appropriate activation energy for diffusion. The time required for ordering should thus vary exponentially with temperature.

This is expressed by the Arrhenius law,

$$\tau(T) = \tau_0 e^{E_\alpha/kT} \qquad 2.5$$

where τ_0 is a constant of the order of 10^{-13} - 10^{-14} second. Dahmani *et. al.* (2.15) and Berg *et. al.* (2.16) found $\tau_0 = 1.3 \times 10^{-13}$ and 6×10^{-14} sec and E_α = 2.48 and 3.12 eV for $Ni_{0.5}Pt_{0.5}$ and $Co_{0.25}.Pt_{0.75}$ respectively. The exponential dependence of relaxation time on temperature makes the choice of annealing temperature very critical. The annealing time on the other hand has a linear relation with ordering. This is because annealing time is proportional to the number of attempts made by an atom to overcome the local energy barriers.

For a particular alloy number of distinct domains that can be formed plays an important role in sustaining a meta-stable micro structure. An aggregate can not sustain a meta-stable state when the number of different types of domains is less than four. When this number exceeds four the system is more likely to maintain the meta-stable micro structure according to Bragg (2.17).

In order to prepare an ordered magnetic alloy properly we must know the time rate at which the equilibrium state of order or disorder is approached, since there are marked variations in the rates at which super lattices form in different alloys. If the ordered state is preferred for the product of the alloy, the temperature and time for the ordering treatment must be chosen according to the specific kinetics. On the other hand if a disordered state is desired, we have to know first whether or not the ordering transition can be suppressed by quenching. So the knowledge of the kinetics of order-disorder transition is thus extremely important in the preparation of the alloy product.

2.2.2. The Effect of Temperature on the Order-Disorder Transformation

To investigate the effect of increase of temperature on the x-ray superstructure lines of an originally well ordered alloy crystal at low temperatures. It is found that, starting with a well ordered crystal at a low temperature, the superlattice lines are quite intense. As the temperature is increased, however, how superlattice lines become relatively weaker with respect to the main lattice lines and finally disappear completely and rapidly as a particular temperature known as the 'critical' temperature of the particular alloy is approached. As the temperature is now decreased from above the critical temperature the reverse process happens, the superstructure lines first appear at the critical temperature find become more intense, at first rapidly and then more slowly as the temperature is decreased. For the present purpose, and for the sake of clarity, this description of the effect of temperature and interpretation ignored a detailed discussion of actual X-ray investigation of the effect of temperature on ordered structure is given my thesis.

Let us now see if we can, by slightly anticipation the detailed treatment to suggest a possible interpretation of these temperature effects.

Two dimensional structure containing equal numbers of atoms A and B. The perfectly ordered structure is illustrated in fig- 2.2; it is clear that the ordered structure itself defines two kinds, a and b, of lattice site A atoms arranging themselves on a sites and B atoms on b sites in the perfectly ordered structure. This concept of a and b sites defined by the perfectly ordered structure allows the definition of a measure of the amount of order that is associated with any arrangement of atoms in the crystal, in particular, define two kinds of order. The first, called long range order, measures how many of the a (b) sites are occupied by A (B) atoms, the second, called short range or local order, measures how well, on the average, A atoms are surrounded by nearest neighbor B atoms. It is clear immediately that the long range order, will be intimately related to the intensities of the super lattice lines for the ordered structures, since the intensities of these lines will be (with qualifications) greater the more complete the separation of A and B atoms onto a and b sites, i.e., the greater the long range order.

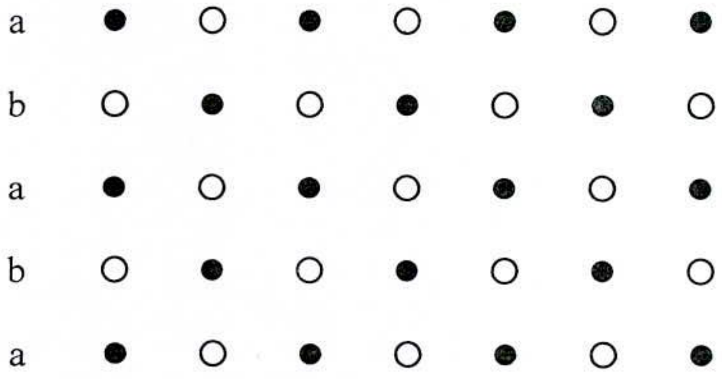


Fig. 2.2. The perfectly ordered two-dimensional AB structure

What happens when the temperature of the originally perfectly ordered structure is increased. At first the only effect will be that the amplitude of thermal vibration of the atoms about their equilibrium positions slightly increases. As the temperature is further increased, however, this effect will become larger and here and there in the perfectly ordered structure, neighboring pairs or small groups of atoms will acquire sufficient energy to break away from their original equilibrium positions in the lattice and interchange places with one another. This interchange of places will result in a number of atoms becoming 'wrong', in the sense that an atom on A atom on b site or B atom on a site is called wrong. Clearly this sort of interchange results in a decrease in the long-range order associated with the structure and hence, from what has been said above, to a decrease in the intensities of the super lattice lines, in agreement with experiment. Also, from a local point of view, the interchange results in some of the nearest neighbors of interchanged atoms now being of the same kind in opposition to the tendency to form unlike nearest neighbor. This tendency for atoms to surround themselves by unlike nearest neighbor pairs. This tendency for atoms that ultimately results in the formation of a perfectly ordered structure at low temperatures. At higher temperatures, where increasing amplitudes of thermal vibrations lead to atoms becoming ‘wrong’, this tendency of atoms to surround themselves by unlike nearest neighbors will still continue to operate and counteract disordering influences by tending to return wrong atoms to right places. At all temperatures below the critical temperature there will be an equilibrium state characterized by a definite number of wrong atoms. In this equilibrium state the rate at which right atoms go wrong under the influence of thermal agitation, is equal to the rate at which wrong atoms go right under the influence of thermal agitation together with the ordering effects of right neighbors of wrong atoms. However, a further interesting and important effect, which we have not so far taken into, account. Consider fig- 2.3, which illustrates the state of disorder in our two dimensional structure when two pairs of nearest neighbor atoms (ringed) have interchanged places. Each of the interchanged atoms has gone from a position in which it had no nearest neighbors of the same kind into a position in which it has three nearest neighbors of the same kind. To interpret the tendency to form arrangements with unlike nearest neighbors is to suppose that such arrangements have a relatively low energy associated with them, and that the presence of like neighbors increases the energy of an arrangement in proportion to the number of pairs of like neighbors. Considering again the disordered structure of fig- 2.3, it is seen that it is now possible to have an interchange (shown arrowed) in which the atoms after the interchange now have only two nearest neighbors of the same kind. From what has been said above it is clear that the energy necessary to produce this last interchange will be less than the energy necessary to produce either of the interchanges which originally led to the structure of fig- 2.3, each of which introduced three like nearest neighbors pairs.

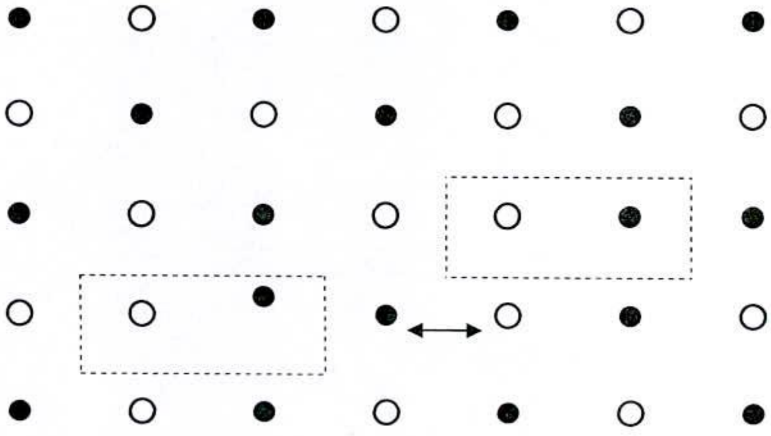


Fig. 2.3. Interchange in an already disordered structure

It is now clear that, if our suggestions and interpretations are correct, with increasing temperature there is not only increasing disorder but also increasing ease of disordering. This process would be expected to be cumulative and to lead to more and more rapid disordering until finally the long-range order disappeared abruptly and completely at some particular temperature characteristic of the particular material. Above this temperature there will be as many wrong atoms as right ones. However, short-range order will still to some extent persist even up to the highest temperatures. Thus, at least as far as the intensities of the X-ray superstructure lines are concerned.

Phenomena such as the one described above are called co-operational or cooperative phenomena. In example of binary alloy ordering, the ease of disordering depends on the degree of disorder already present. Quite generally, in systems exhibiting cooperative phenomena, subsystems cooperate to form larger subsystem of same kind in spite of influences tending to destroy them, the utility of the subsystems to cooperate depending markedly on the degree of cooperation already present. A.H. Lipson (2.18) has given a forceful and attractive analogy of the cooperative phenomenon. It may be compared to the behavior of a crowd of people, if one or two look up fixedly at the sky other may not be induced to do likewise, but if more people look upwards, the inducement to others to do so becomes greater until, when nearly everyone is looking upwards, the urge to look upwards becomes almost irresistible even in the most obstinate individual.

CHAPTER-III

Experimental

3.1 Preparation of samples

3.1.1 $Ni_{0.5}$ $Pt_{0.5}$

A polycrystalline $Ni_{0.5}$ $Pt_{0.5}$ alloy has been prepared from appropriate proportions of Ni of 99.99% purity and Pt of 99.99% purity in an arc furnace on a water-cooled copper hearth under an atmosphere of pure argon. The required amounts of the constituent elements were taken from pure metal bars or wires and weighed carefully with a sensitive electronic balance and were placed inside the furnace. Before melting the furnace chamber has been evacuated (10^{-3} torr) and flashed with argon gas, the process was repeated several times to get rid of residual air and finally kept in an argon atmosphere. A substantial amount of pure titanium getter placed in one side of the chamber was melted first, in order to absorb any oxygen present in the furnace chamber. The constituent elements were then melted in the shape of buttons and turned upside down and re-melted three times to ensure homogeneous mixer and eliminate segregation. The button shaped alloys were then taken out of the furnace and weighted. The samples were then sealed in evacuated quartz tubes and heat treated at 1050°C for seven days for further homogenization and water quenched. The weight loss after melting was less than 1% except for the concentrated alloys, and weight loss for the alloys with higher percentages of nickel have higher melting loss. However the actual composition of the alloy must be very close to the nominal values, which are shown in Table 3.1 from the alloy small amount of powder was field for X-ray measurements.

Table- 3.1: Composition of $Ni_{1-x}Pt_x$ alloy

Platinum Content x	Weight % Ni	Weight % Pt	At % Ni	At % Pt	% weight loss after melted
0.50	23.08	76.92	49.93	50.07	0.51

Table- 3.2 : Composition of $Ni_{0.5-x}Fe_xPt_{0.5}$ alloy

Iron Content x	Weight % Ni	Weight % Fe	Weight % Pt	At% Ni	At % Fe	At % Pt	% weight loss after melted
0.05	21.98	1.09	76.93	47.5	2.49	50.01	0.42

Table- 3.3 : Composition of $Ni_{0.5-x}Co_xPt_{0.5}$ alloy

Cobalt Content x	Weight % Ni	Weight % Co	Weight % Pt	At% Ni	At % Co	At % Pt	% weight loss after melted
0.05	22.00	1.16	76.94	47.51	2.49	50.00	0.88

3.1.2 Preparation of $Ni_{0.5-x}Fe_xPt_{0.5}$ and $Ni_{0.5-x}Co_xPt_{0.5}$ alloys

A pseudobinary alloy $Ni_{0.5-x}Fe_xPt_{0.5}$ with x = 0.05, and $Ni_{0.5-x}Co_xPt_{0.5}$ with x=0.05, based on equiatomic nickel-platinum have been prepared by arc melting in an argon atmosphere as described. The purity of the starting material was 99.99% for Ni, Fe and Co and 99.99% for Pt. In this alloy preparation platinum was taken in powder form and pressed with a hydraulic press in the form of pellets. Iron and cobalt was placed inside the platinum powder before pressing. It was done so to prevent any loss of Fe and Co during arc melting since the amount of Fe and Co was very small. By arc melting button shaped ingots were prepared. The ingots were re-melted at least four times in order to achieve homogeneity. Weight loss during the melting was much less than 1% in weight. The compositions of $Ni_{0.5-x}Fe_xPt_{0.5}$ and $Ni_{0.5-x}Co_xPt_{0.5}$ alloys are given in Table- 3.2 and table- 3.3 respectively. The ingots were then heat treated for homogenization at 1050°C for ten days and subsequently quenched in water. Powders for X-ray diffraction have been taken from each ingot.

3.2 Ordering of the sample

To get atomically disordered samples the spheres were sealed in evacuated quartz tubes and annealed at 1000°C for 24 hours and were quenched rapidly by crushing the quartz tubes in the iced water or salt water. This annealing also helps to eliminate the effects of plastic deformation resulting from grinding for shaping. By this drastic quenching method it is assumed that the maximum degree of atomic disorder is attained although upon quenching it is reasonable to expect the formation of some short-range chemical order (3.1). This is a quite general effect. Any solid solution, which exhibits long-range order below a certain temperature, exhibits some short-range order above that temperature. Moreover another kind of departure from randomness in a solid solution is often found known as clustering in which a tendency of like atoms to be close neighbours is observed. In fact, there is probably no such thing as a perfectly random solid solution. All real solid solutions probably exhibit either short-range ordering or clustering to a greater or lesser degree simply because they are composed of unlike atoms with particular forces of attraction or repulsion operating between them. Bardos *et. al.* (3.2) pointed out that to inhibit the ordering process, a quenching rate of approximately 6000°C per second must be employed.

Kinetics of ordering in Ni-Pt and pseudobinary (Ni-Fe)-Pt and (Ni-Co)-Pt alloys is slow since their superlattices have four and more than four distinct domains and hence quenching has been proved effective to suppress ordering. In view of the above fact it is plausible to assume that the alloys are disordered to a high degree which has indeed been confirmed by X-ray diffraction.

Ordering has been done in-situ with high temperature attachment in the XRD system model PHILIPS PW3040 X'Pert Pro Diffractometer. The sample has been heated to 650°C for half an hour then slowly cool down to 500°C with step of 10°C with holding time of 30 minuets in each step. At 500°C the sample has been kept for 1 hour and than slowly cooled down to room temperature to form perfect ordering state. Than at room temperature the diffraction pattern has been taken for analysis of the ordered state as well ordered parameter 's'.

3.2.1. Experimental Techniques for X-ray Diffraction

X-ray diffraction (XRD) is a versatile non-destructive analytical technique for identification and quantitative determination of various crystalline phases of powdered or solid samples of any compound. Our polycrystalline $Ni_{0.5}$ $Pt_{0.5}$ alloy ingots were prepared by melting 99.99% pure Pt and 99.99% pure Ni using an arc-melting furnace under vacuum (10^{-3} torr) in an argon atmosphere in the Institute of material Science, University of Tsukulsa, Japan (3.3).

Subsequently, the alloys were re-melted nine to ten times to homogenize the specimens. The weight loss after melting was less than 0.5%. Therefore, the actual composition of the alloys must be very close to the nominal values.

Thin sheets of the sample were prepared from the alloy ingot by rolling the ingot. Sharp strip like sample were cut from the thin sheet for

Debye-Scherrer experiment. After heat treatment of the samples separately to remove strain the lattice parameter of the quenched specimen in the disordered state were measured by Debye-Scherrer method using Cu-radiation. In the present case a special technique was used to determine the lattice parameter using Debye-Scherrer method. The shape of the sample was used as the same of Debye-Scherrer method sample. But in the conventional Debye-Scherrer experiement, sharp strip sample rotates and X-ray tube and camera remain fixed. In the present case, sample was kept fixed, and X-ray tube and detector were moved to the θ and 2θ ranges, respectively. Instead of film, digital data was recovered for the whole 2θ range.

After the pattern is obtained the value of 2θ is calculated for each diffraction lines set of 2θ values are the raw material for the determination of the lattice parameters of the unit cell.

A PHILIPS PW3040 X'Pert PRO X –ray diffractometer was used for the lattice parameter determination in the Material science Division, Atomic Energy Center, Dhaka shown in fig. 3.1, Fig. 3.2 shows the inside view of the X'Pert PRO XRD System and Fig. 3.3 shows a sample on the sample holder.

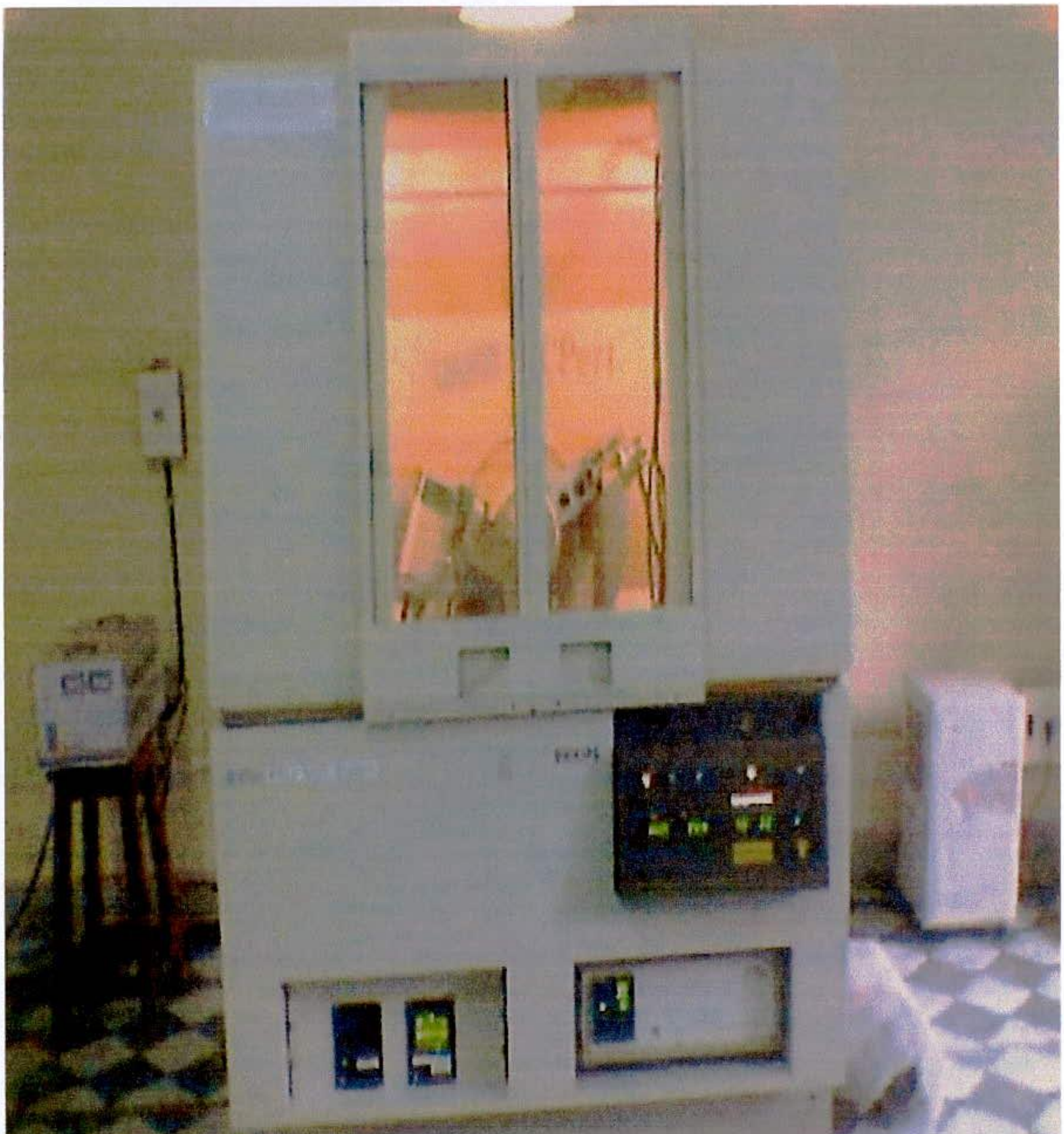


Fig:3.1. PHILIPS X-Pert PRO XRD System

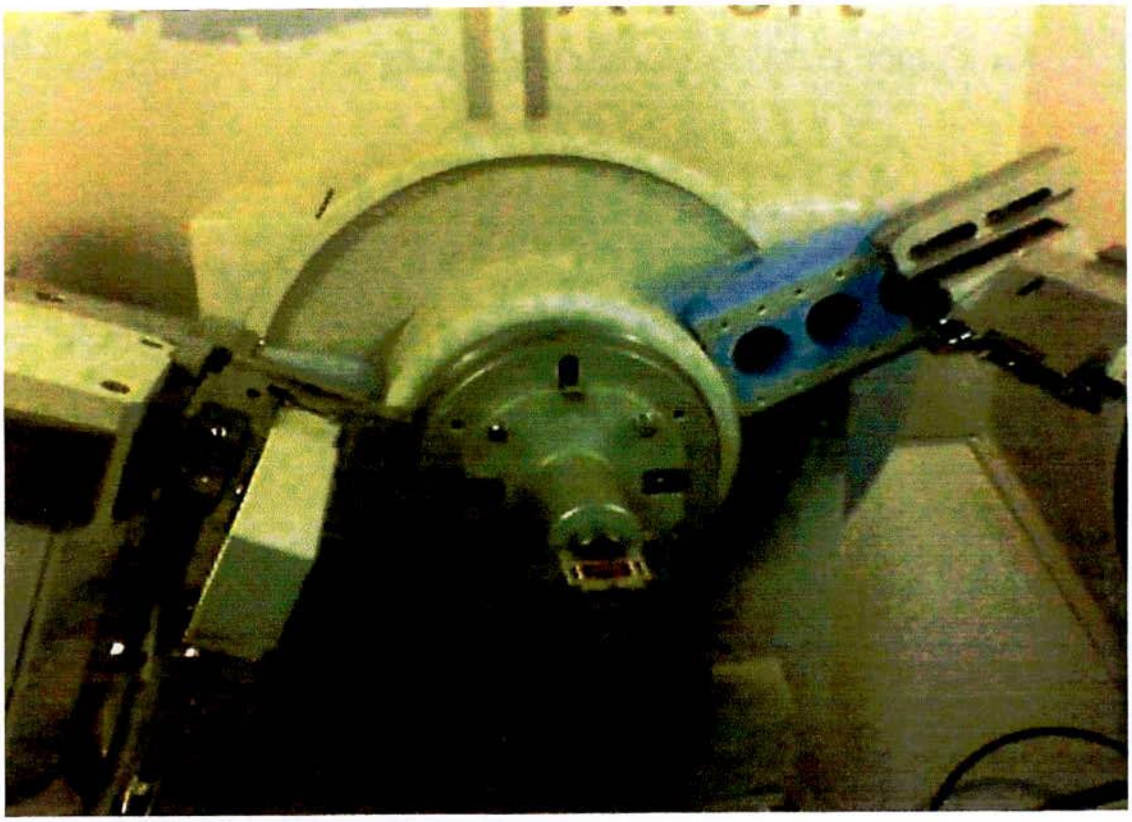


Fig: 3.2. Inside view of the x'Part PRO XRD System

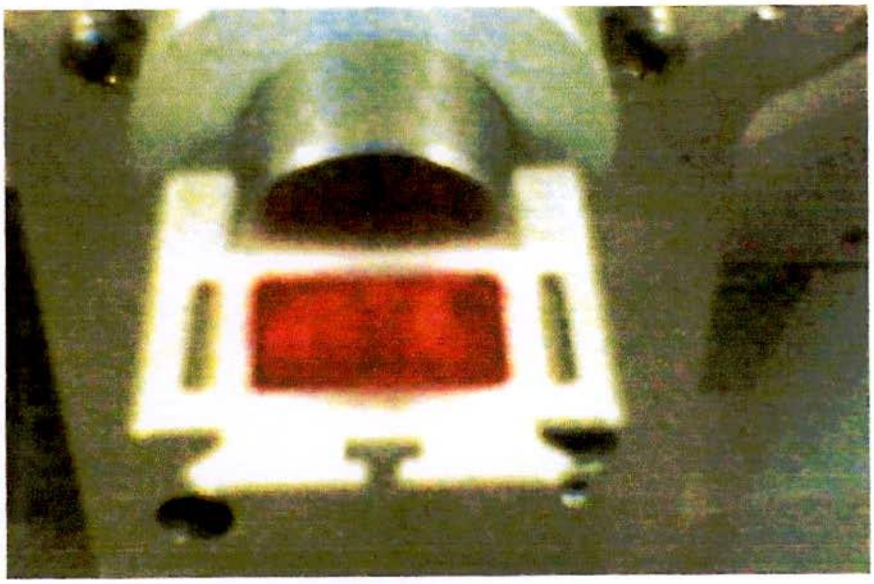


Fig: 3.3. Sample on the sample holder

3.2.2. Different Part of the X' Pert PRO XRD System

The X' Pert PRO XRD system contains the following parts:

(i) "Cu-Tube" with maximum input power of 60 kv and 55mA.

(ii) "Ni-Filter" to remove Cu K_α component.

(iii) "Soller Slit" to pass parallel beams only.

(iv) "Programmable Divergent Slit" (PDS) to reduce divergence of beam and control irradiated beam area.

(v) "Mask" to get desired beam area.

(vi) "Sample holder" for powder sample.

(vii) "Anti Scatter Slit" (ASS) to reduce air scattering background.

(viii) "Programmable Receiving Slit" (PRS) to control the diffracted beam intensity.

(ix) "Soller Slit" to stop scattered beam and pass parallel diffracted beam only.

3.2.3. Measurement System of the X' Pert PRO XRD

The block diagram of the X'Pert PRO XRD System is shown in fig-3.4. The powder diffraction technique was used with a primary beam power of 40kV and 30 mA for Cu-radiation. A nickel filter was used to reduce Cu-k_β radiation and finally Cu-k_α radiation was only used as the primary beam.

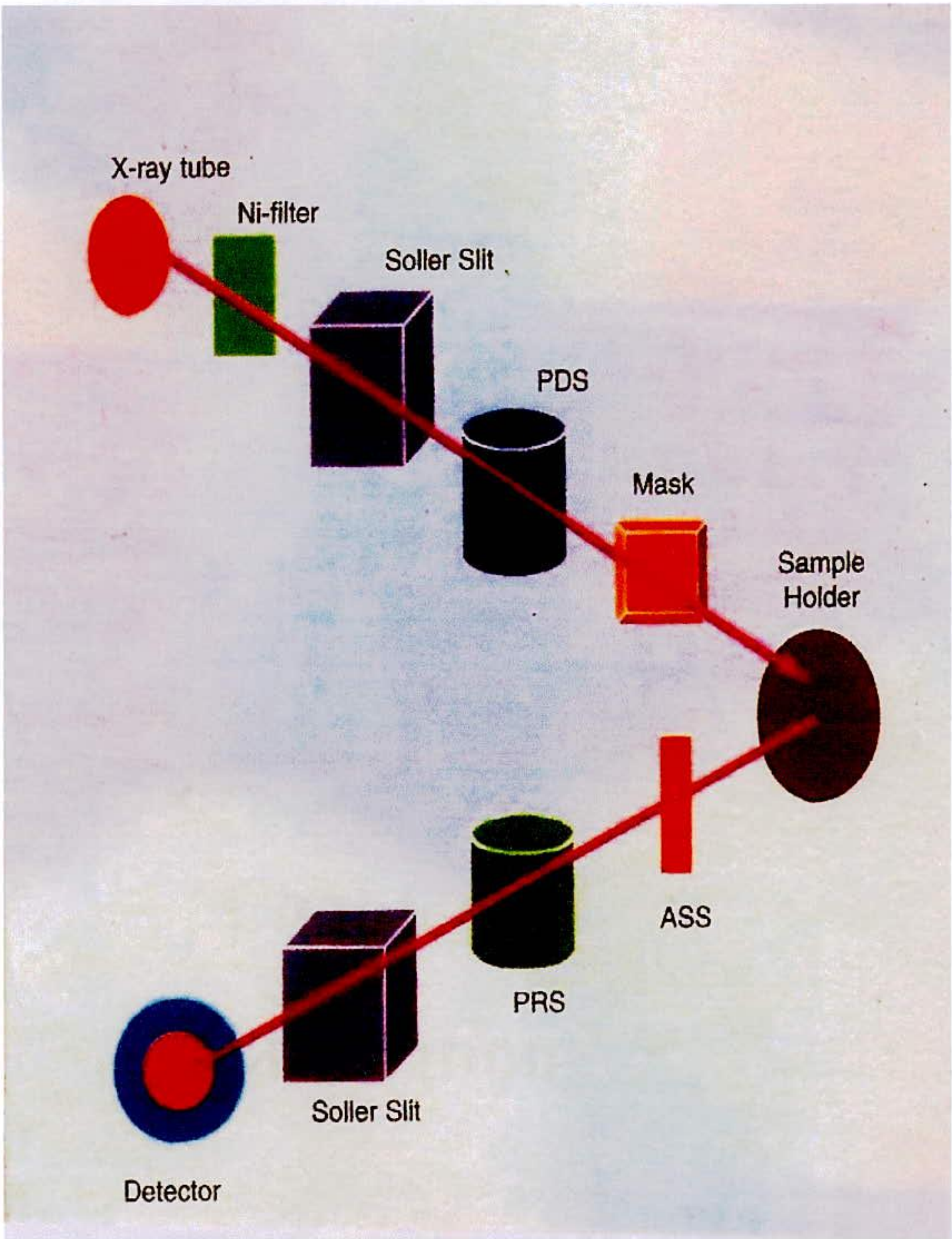


Fig: 3.4: Block diagram of the X'Pert PRO XRD System

The experiment has been performed at room temperature. A 2θ scan was taken from 20^0 to 120^0 to get all possible fundamental peaks of the sample with the sampling pitch of 0.02^0 and time for each step data collection was 1.0 sec. Both the programmable divergence and receiving slits were used to control the irradiated beam area and output intensity from the sample, respectively. An anti scatter slit was used just after the sample holder to reduce air scattering. Two solar slits were used just after the tube and in front of the detector to get parallel beam only. All the data of the samples were stored in the computer memory and later on analyzed them using computer "software "X' PERT HIGHSCORE". For XRD experiment each sample was set on a glass slide and fixed the sample by putting adhesive type at the two ends of the sample.

3.2.4. Interpretation of the XRD Data

The XRD data consisting of θ_{hkl} and d_{hkl} values corresponding to the different crystallographic planes are used to determine the structural information of the samples like lattice parameter and constituent phase. Lattice parameters of Ni-Pt alloys samples were determined. Normally, lattice parameter of an alloy composition is determined by the Debye-Scherrer method after extrapolation of the curve. In the present case, at least 14 reflection planes are prominent in all XRD patterns and we would like to understand how the value of lattice spacing (inter planer distance), d using these reflections from the equation:

$$2d\sin\theta = \lambda$$

$$\text{i.e. } d = \frac{\lambda}{2\sin\theta} \qquad 3.1$$

The lattice parameter for each peak of each sample was calculated by using formula:

$$a = d_{hkl} \times \sqrt{h^2 + k^2 + l^2} \qquad 3.2$$

where h, k and l are the indices of the crystal planes. The get d_{hkl} values from the computer using software "X PERT HIGHSCORE". So we got fourteen 'a' values for 14 reflection planes such as a_1, a_2, a_3, a_4 ------------- - etc.

To determine the exact lattice parameter for each sample, Nelson-Rally method was used. The Nelson-Rally function F(θ), can be written as

$$F(\theta)=\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right) \qquad 3.3$$

Now drawing the graph of 'a' vs F (θ) and using linear fitting of those points will gives as the lattice parameter a_0. This is the values of 'a' at F(θ) = 0. These 'a_0's are calculated within an error estimated to be ± 0.0004.

CHAPTER- IV

Results and Discussion

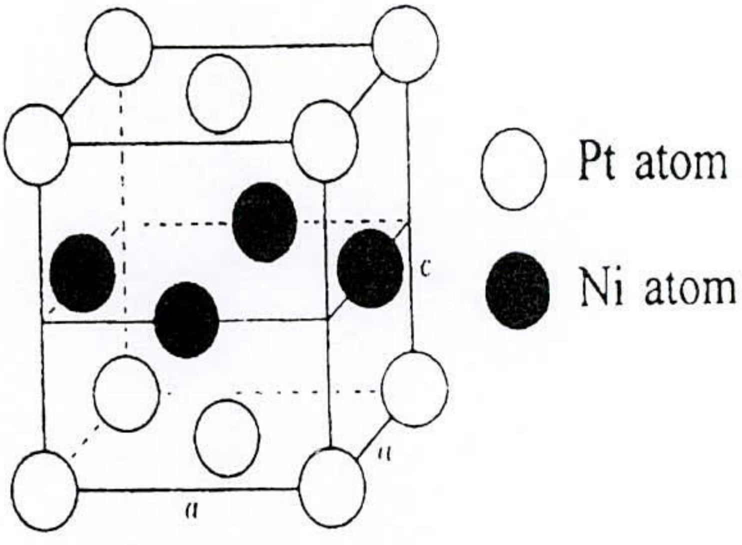
4.1. X-ray Diffraction (XRD)

X-ray diffraction technique has been an important tool in both the structural characterization and identification of order-disorder phase transition. A direct way of investigating the ordering is by X-ray, neutron or electron diffraction (4.1 – 4.3). In these methods, long-range ordering manifests itself by the appearance of extra (super lattices) lines or ring on the X-ray, neutron or electron diffraction pattern in addition to the fundamental lines or rings. According to the theory of X-ray diffraction by crystals, the wave scattered by the A atoms in an ordered alloy will all be exactly in phase with each other and exactly out of phase with those scattered by the B atoms. If the scattering factors of the two kinds of atoms are different, the scattered waves will not cancel and hence a super-lattice line will appear on the X-ray pattern. On the other hand, if the atoms are distributed at random over the rise to scattered wave whose amplitude is the average for A and B atoms according to their atomic concentrations. Then the waves scattered by the successive net planes cancel each other completely owing to equal amplitude and no X-ray line is observed in the diffraction pattern.

4.1.1. Order-disorder phase Identification of Ni-Pt Alloy

The presence of super-lattice lines on an X-ray or neutron diffraction pattern is the decisive proof of the existence of the ordered arrangement of atoms in the alloy. X-ray investigations have been done on $Ni_{0.5}Pt_{0.5}$ to determine lattice parameters, crystal structures and also to confirm ordered lattice. X-ray measurements were performed on alloy powder taken from the ordered and disordered sample by filing. Calibrated with Si powder (a= 5.431065Å) was used for recording the powder pattern of all Ni-Pt alloys at room temperature. In wide range of 2θ values (10° <2θ <140°) using a step scanning mode with step size 0.02° and time for each step data collection was 1.0 sec. All the data of the sample were stored in the computer memory and later analyzed them using computer software "X'PERT HIGHSCORE".

X-ray measurements show that all the disordered Ni-Pt alloy have face centered cubic (fcc) all, structures and the lattice parameters increase with increasing platinum concentration. The ordered alloy in the simple cubic, LI_2 (isomorphous with Cu_3Au) structure and the lattice parameters are almost same in the ordered and disordered states. There are average four atoms per unit cell distributed at random at [000], $\left[\frac{1}{2}\frac{1}{2}0\right]$, $\left[\frac{1}{2}0\frac{1}{2}\right]$ and $\left[0\frac{1}{2}\frac{1}{2}\right]$. The $Ni_{0.5}$ $Pt_{0.5}$ alloys in the ordered states crystallize in the face centered tetragonal (fct), LI_0 structure (prototype CuAu). Each unit cell for equiatomic Ni-Pt contains two Pt atoms, at [000], $\left[\frac{1}{2}\frac{1}{2}0\right]$, and two Ni atoms, at $\left[\frac{1}{2}0\frac{1}{2}\right]$, $\left[0\frac{1}{2}\frac{1}{2}\right]$. The structure is built up of [001] planes alternately containing only Ni or only Pt atom. Each atom has eight nearest neighbors of the opposite kind in the adjacent [001] planes and four of the same kind in its own [001] plane at a slightly greater distance, since the axial ratio $\frac{c}{a}$, is usually less than one. Fig-4.1 shows the atomic positions of a unit cell of LI_0 ordered phase of Ni-Pt alloy and fig-4.2 shows the atomic position of a unit cell of LI_2 ordered phase of Ni_3Pt alloys. The alloys are found to be single phase.



4.1. Atomic positions of a unit cell of ordered NiPt alloy

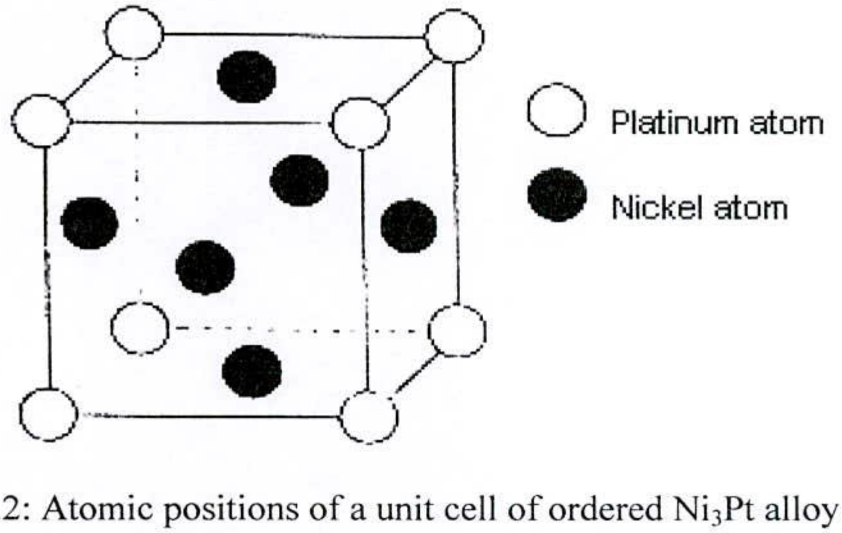


Fig. 4.2: Atomic positions of a unit cell of ordered Ni_3Pt alloy

Fig- 4.3, shows the XRD pattern of disordered $Ni_{0.5}Pt_{0.5}$ alloy at room temperature. In the diffraction pattern of disordered $Ni_{0.5}Pt_{0.5}$ shows in fig- 4.3, it is observed that no reflections of mixed indices are present. The diffraction lines (111), (200), (220), (113), (222) etc corresponds to any face centered cubic lattice. All the reflections correspond to fcc structure in the disordered state of the alloy. No super-lattice reflections are present in the XRD pattern.

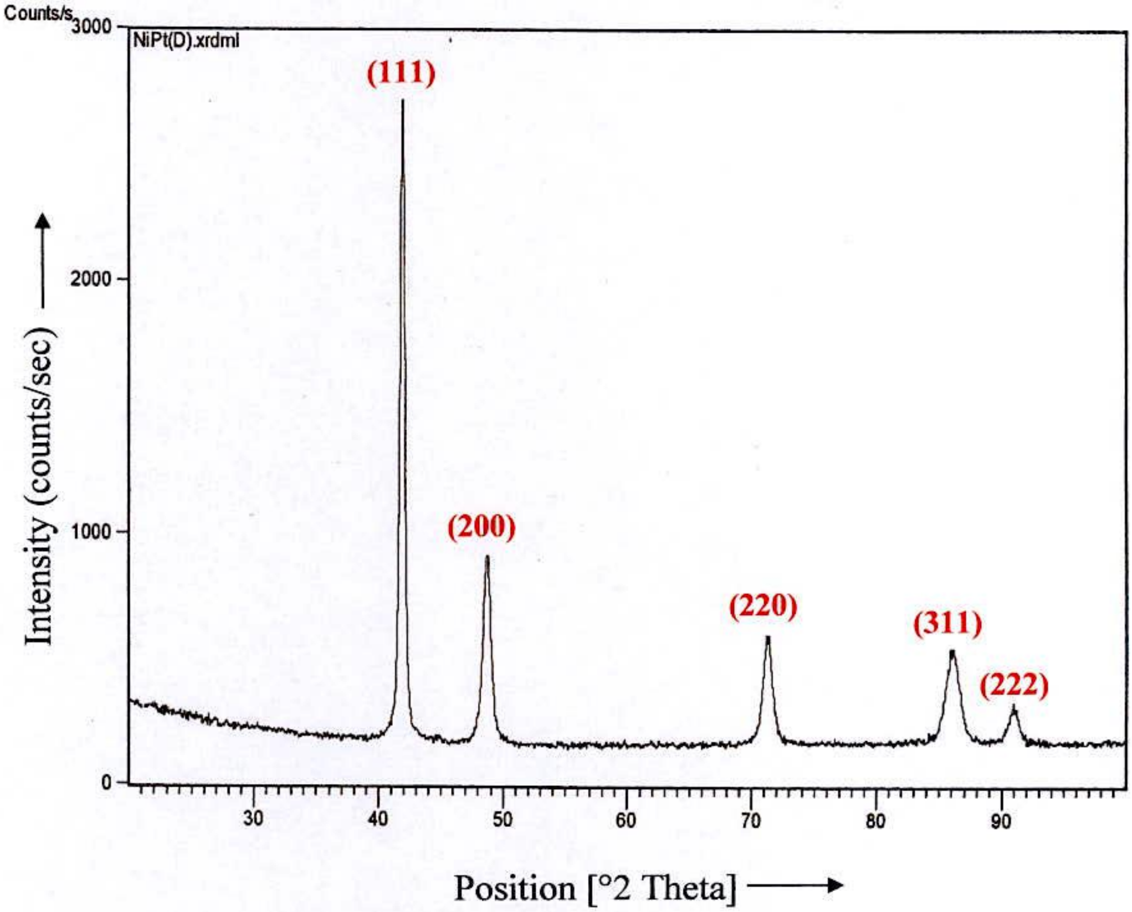


Fig-4.3: XRD pattern of disordered $Ni_{0.5}Pt_{0.5}$ alloy, where the indices of the reflecting planes are shown in the parenthesis

We obtained well-resolved diffraction lines on the X-ray photographic film. Then measuring the angle of the diffracted lines by using a comparison with the corresponding full width at half maximum (FWHM), d-spacing and integrated intensity of all fundamental reflection indices from disordered XRD pattern of $Ni_{0.5}Pt_{0.5}$ alloys were calculated were shown in table- 4.1.

Table- 4.1 Experimental disordered XRD pattern data of $Ni_{0.5}Pt_{0.5}$ alloys.

Reflection indices (hkl)	Position (°2 Theta)	Height [cts]	FWHM (°2 Theta)	d-spacing [Å]	Relative intensity [%]
(111)	41.8540	1751.36	0.3840	2.15663	100.00
(200)	48.6334	489.21	0.6720	1.87066	27.93
(220)	71.2206	288.83	0.8640	1.32293	16.49
(311)	86.0724	243.92	0.4800	1.12871	13.93
(222)	90.8973	99.82	0.7680	1.08094	5.70

Fig- 4.4 shows the XRD pattern of the same ordered alloy with composition $Ni_{0.5}Pt_{0.5}$. In the figure, the indices of the reflecting planes are shown in the parenthesis. All the reflections indicate the ordered state of the alloy with the appearance of super-lattice reflections together with the fundamental ones in the XRD pattern are peak list shown in table- 4.2.

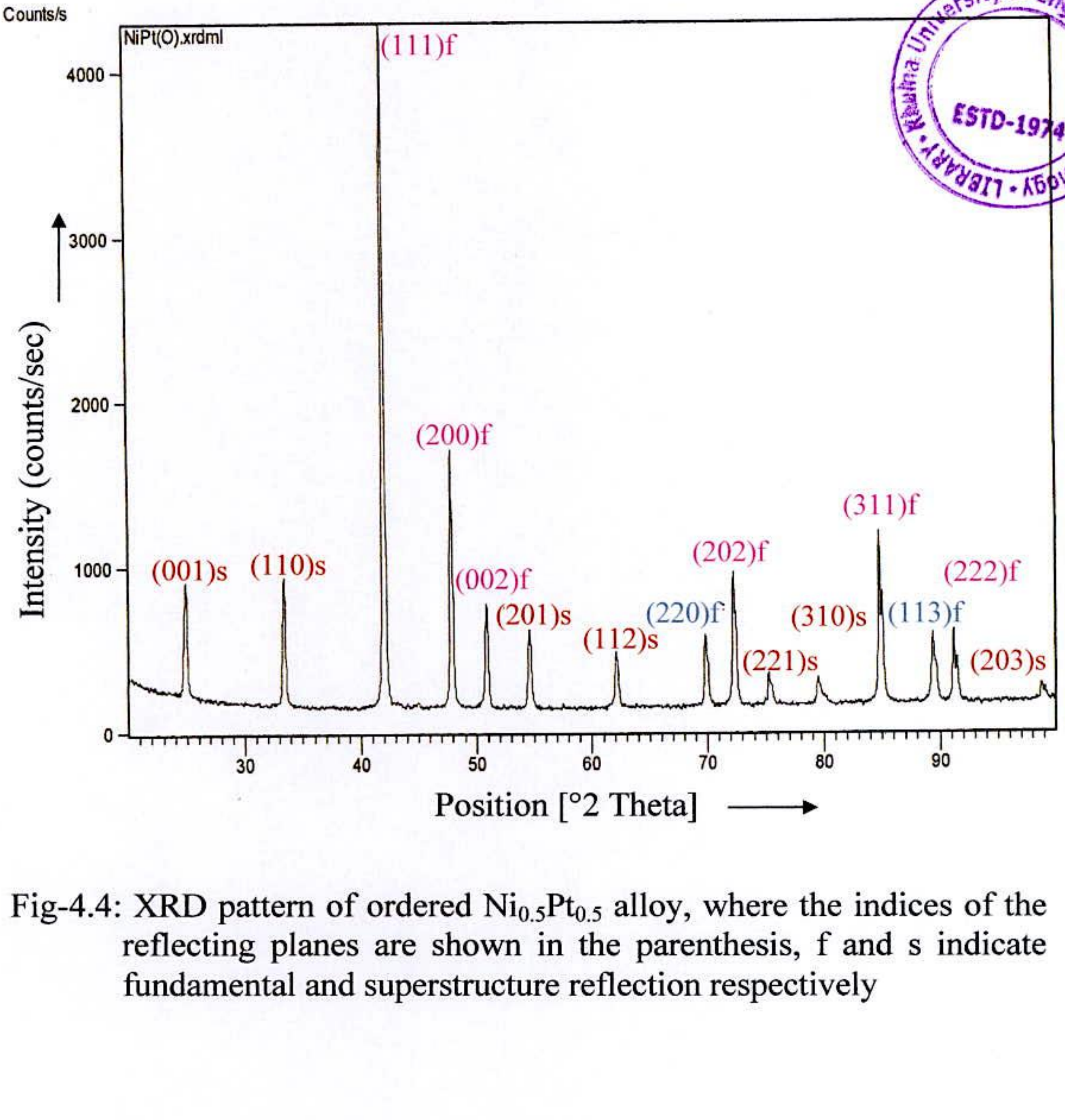


Fig-4.4: XRD pattern of ordered $Ni_{0.5}Pt_{0.5}$ alloy, where the indices of the reflecting planes are shown in the parenthesis, f and s indicate fundamental and superstructure reflection respectively

Table- 4.2 Peak list of XRD pattern of ordered $Ni_{0.5}Pt_{0.5}$ alloy

No.	h	k	l	d-spacing (Å)	Relative Intensity (%)
1	1	0	0	3.82300	0.1
2	0	0	1	3.58900	30.0
3	1	1	0	2.70327	26.9
4	1	0	1	2.61662	0.1
5	1	1	1	2.15928	100.00
6	2	0	0	1.91150	31.5
7	0	0	2	1.79450	13.1
8	2	1	0	1.70970	0.1
9	2	0	1	1.68713	12.1
10	1	0	2	1.62444	0.1
11	2	1	1	1.54351	0.1
12	1	1	2	1.49507	8.0
13	2	2	0	1.35163	8.4
14	2	0	2	1.30831	14.9
15	3	0	0	1.27433	0.1
16	2	2	1	1.26491	4.2
17	2	1	2	1.23783	0.1
18	3	1	0	1.20894	3.7
19	0	0	3	1.19633	0.9
20	3	1	1	1.14569	17.3
21	1	0	3	1.14174	8.6
22	1	1	3	1.09399	7.2
23	2	2	2	1.07964	6.9
24	3	2	0	1.06031	0.1
25	3	0	2	1.03900	0.1
26	2	0	3	1.01410	2.3
27	3	1	2	1.00264	4.1
28	2	1	3	0.98020	0.1
29	4	0	0	0.95575	2.3
30	4	0	1	0.92356	1.7
31	3	2	2	0.91287	0.1
32	3	3	0	0.90104	0.8
33	4	1	1	0.89725	1.0
34	2	2	3	0.89583	1.7
35	3	3	1	0.87397	4.0
36	3	0	3	0.87221	2.0
37	4	2	0	0.85485	3.9
38	1	1	4	0.85157	1.6
39	3	1	3	0.85036	7.7
40	4	0	2	0.84357	3.8
41	4	2	1	0.83158	3.2
42	4	1	2	0.82375	0.1
43	2	0	4	0.81222	3.7
44	3	3	2	0.80527	1.6

The diffraction patterns obtained from the specimen quenched from 610°C show the fcc structure. The diffraction pattern of ordered $Ni_{0.5}Pt_{0.5}$ is shown in fig- 4.4, where the mixed index lines (001), (110), (201), (112), (221), (310), (203) etc correspond to super-lattice reflections are obtained. The structure of the ordered alloys has lower symmetry than those of the corresponding disordered fcc alloy and their diffraction pattern have, therefore extra Bragg reflections. The presence of super-lattice lines mixed (hkl) and their sharpness and no diffuse intensity between the fundamental lines (200) and (002) and around the (001) line together with the knowledge of the kinetics of ordering of this alloy system has convinced that maximum degree of order has been attained. Similar extra lines have also been observed on the X-ray powder photograph, for the ordered powder. Integrated intensity of all fundamental and superstructure reflection from ordered XRD pattern of $Ni_{0.5}Pt_{0.5}$ alloys were calculated separately are shown in table- 4.3. The full-width at half maximum (FWHM) of all the diffraction peaks (fitted by using Gaüssian fitting method) become almost equal in this phase of the specimen. These facts characterize the existence of ordering in this alloy. Then measuring the angle of the diffracted lines by using a comparator the corresponding FWHM, d-spacing and relative intensity percent were shown in table 4.3.

Table- 4.3 Experimental ordered XRD pattern data of $Ni_{0.5}Pt_{0.5}$ alloy

Reflection indices (hkl)	Position (°2 Theta)	Hight [cts]	FWHM (°2 Theta)	d-spacing [Å]	Relative intensity (%)
(001) s	24.9081	463.85	0.3840	3.57188	15.12
(110) s	33.3872	550.29	0.1680	2.68160	17.94
(111) f	41.9906	3068.02	0.2880	2.14992	100.0
(200) f	47.8119	1263.02	0.2400	1.90086	41.17
(002) f	50.8485	504.30	0.2400	1.79424	16.44
(201) s	54.5505	405.72	0.2400	1.68090	13.22
(212) s	62.0954	302.33	0.1920	1.49355	9.85
(220) f	69.8026	395.53	0.1920	1.34629	12.89
(202) f	72.2276	755.62	0.1920	1.30694	24.63
(221) s	75.2897	187.35	0.1920	1.26120	6.11
(310) s	79.4978	151.83	0.2400	1.20468	4.95
(311) f	84.7729	1009.24	0.1920	1.14266	32.90
(113) f	89.3847	396.48	0.1920	1.09526	12.92
(222) f	91.1666	432.60	0.1680	1.07844	14.10
(203) s	98.7567	96.45	0.2880	1.01485	3.14

4.1.2. Order-Disorder Phase Identification of Ni-Fe-Pt Alloy

X-ray diffraction has been done on $Ni_{0.5-x}Fe_xPt_{0.5}$ with x=0.05 by both diffractometer and powder diffraction photographic techniques using Cr-K_α radiation (λ= 2.89976 Å). Fig-4.5 (a) and Fig- 4.5 (b) shows the diffraction pattern recorded for ordered and disordered $Ni_{0.5-x}Fe_xPt_{0.5}$ powder alloy. A detail X-ray analysis shows (table 4.4) that the disordered alloy is face centered cubic (Ni-Pt phase)

Table- 4.4 Experimental disordered XRD pattern data of $Ni_{0.5-x}Fe_xPt_{0.5}$ with x=0.05 alloy

Reflection indices (hkl)	Position (°2 Theta)	Height [cts]	FWHM (°2 Theta)	d-spacing [Å]	Relative intensity (%)
(111)	41.7015	1689.43	0.3739	2.16595	100.00
(200)	48.4904	520.38	0.2558	1.87739	30.80
(220)	71.1015	291.90	0.7085	1.32595	17.28
(311)	85.9560	253.84	0.7872	1.13087	15.03
(222)	90.7716	105.34	0.8640	1.08211	6.23

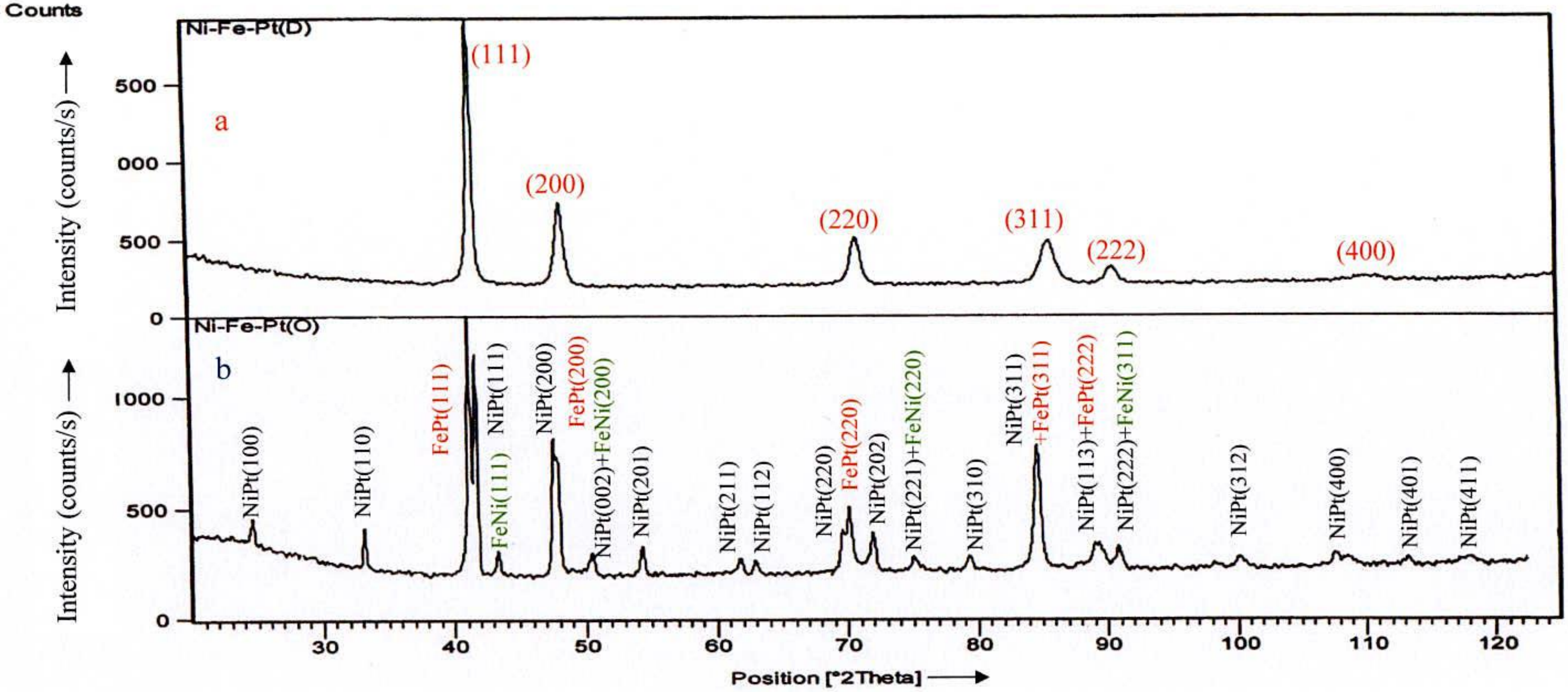


Fig.-4.5 : X-ray diffraction pattern for $Ni_{0.5-x}Fe_xPt_{0.5}$ with x=0.05 of (a) disordered and (b) ordered alloy

FWHM, d-spacing, integrated intensity of all fundamental and superstructure reflections from ordered XRD pattern of $Ni_{0.5-x}Fe_xPt_{0.5}$ with x=0.05 alloy were measurement data separately are shown on table- 4.5

Table-4.5 : Experimental ordered XRD pattern of $Ni_{0.5-x}Fe_xPt_{0.5}$ with x=0.05 alloy

Reflection indices (hkl)	Phase Structure	Position (°2 Theta)	Hight [cts]	FWHM (°2 Theta)	d-spacing [Å]	Relative intensity (%)
(001)	Ni-Pt	24.6940	118.44	0.1968	3.60534	10.13
(110)	Ni-Pt	33.2253	180.99	0.2165	2.69653	15.48
(111)	Fe-pt	41.2803	1169.24	0.2362	2.18707	100.00
(111)	Ni-Pt	41.8059	977.31	0.2362	2.16078	83.58
(111)	Fe-Pt	43.4505	99.24	0.2362	2.08273	8.49
(200)	Ni-Pt	47.6825	612.60	0.2165	1.90730	52.39
(200)	Fe-Pt	48.0283	503.69	0.2165	1.89437	43.08
(002)+(200)	Ni-Pt + Fe-Pt	50.5876	101.41	0.2755	1.80437	8.67
(201)	Ni-Pt	54.4307	121.79	0.2558	1.68571	10.42
(211)	Ni-Pt	61.9286	61.67	0.3149	1.49841	5.27
(112)	Ni-Pt	63.0180	53.07	0.3149	1.47510	4.54
(220)	Ni-Pt	69.5853	168.82	0.1968	1.35108	14.44
(220)	Fe-Pt	70.1491	292.79	0.2362	1.34160	25.04
(202)	Ni-Pt	71.9302	170.94	0.2558	1.31270	14.62
(221)+(220)	Ni-Pt + Fe-Ni	75.1503	56.25	0.4723	1.26424	4.81
(310)	Ni-Pt	79.3784	61.52	0.3936	1.20719	5.26
(311)+(311)	Ni-Pt+ Fe-Pt	84.5875	525.00	0.2362	1.14564	44.90
(113)+(222)	Ni-Pt+ Fe-Pt	89.2170	100.63	0.7872	1.09780	8.61
(222)+(311)	Ni-Pt+ Fe-Ni	90.8827	97.89	0.3149	1.08197	8.37
(312)	Ni-Pt	100.2162	46.42	0.4723	1.00480	3.97
(400)	Ni-Pt	107.5917	45.54	0.4723	0.95541	3.89
(401)	Ni-Pt	113.1601	27.74	1.1520	0.92289	2.37

Fig-4.5 (b) shows the ordered alloy is face centered tetragonal with a certain amount of disordered phase present. Moreover two reflection peaks on either side of (111) line could not be indexed either by (fcc) or (fct). This might belong to a very small amount of complex phase. It is observed that the reflections are not so sharp as that of (fct) Ni-Pt alloy. So the alloy is not perfectly ordered and single phase.

4.1.3. Order-disorder Phase Identification of Ni-Co-Pt Alloy

The $Ni_{0.5-x}Co_xPt_{0.5}$ alloy X-ray measurements have been performed on alloys with x=0.05 with PHILPS PW3040 X'Pert PRO PW3040 X-ray diffractometer at room temperature the ordered and disordered states. For comparison a single composition with x=0.05, X-ray diffraction pattern recorded on diffractometer are shown in fig-4.6 (a) and fig-4.6 (b) for an alloy with x=0.05. A detail X-ray analysis shows table-4.6 that all the disordered alloys are single phased with (fcc) structures.

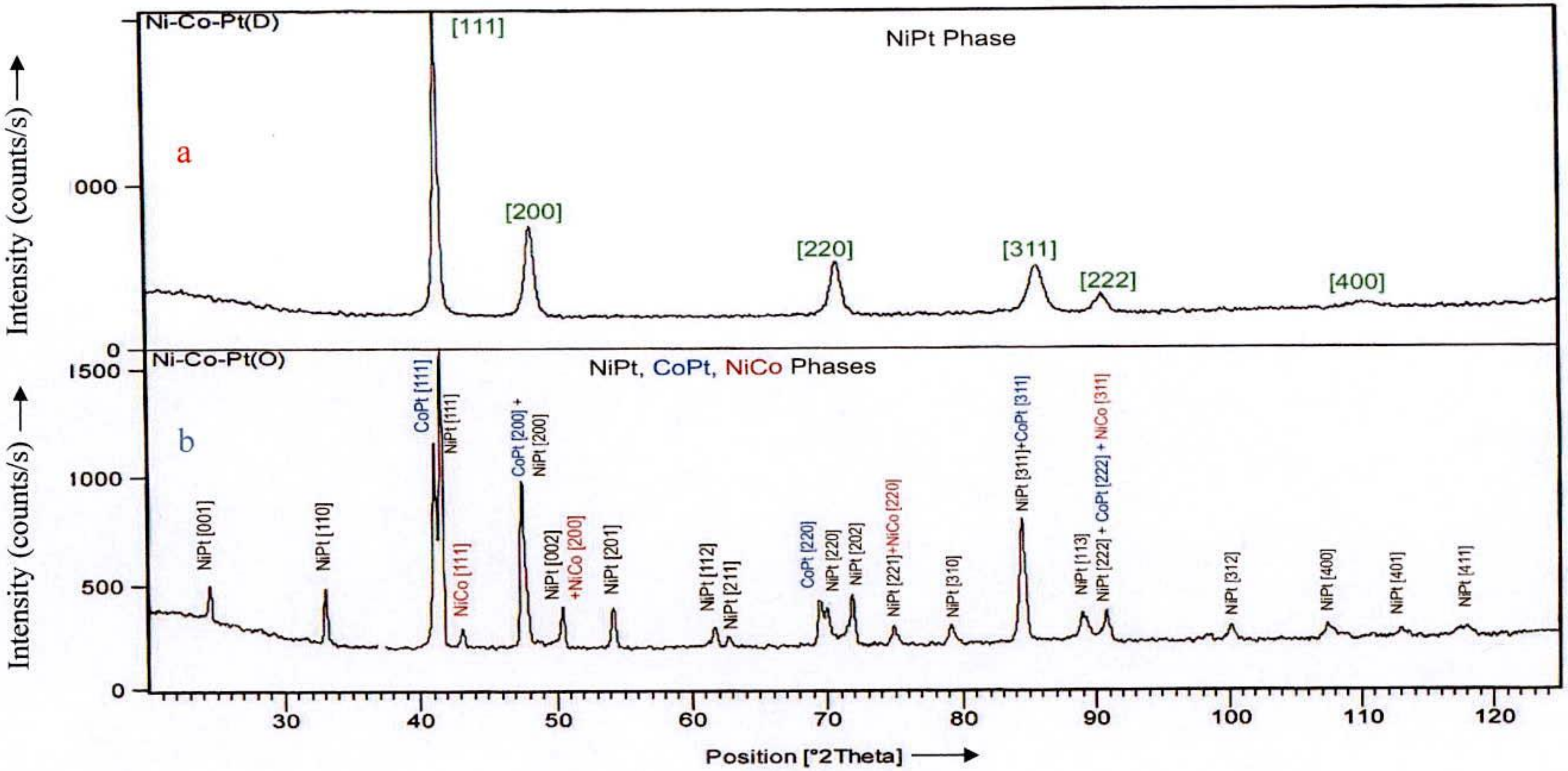


Fig. 4.6 X-ray diffraction for $Ni_{0.5-x}Co_xPt_{0.5}$ with x=0.05 of (a) disordered and (b) ordered alloys

Table- 4.6 Experimental disordered XRD pattern data of $Ni_{0.5-x}Co_xPt_{0.5}$ with x=0.05 alloy

Reflection Indices (hkl)	Position (°2 Theta)	Height (cts)	FWHM (°2 Theta)	d-spaing (Å)	Relative intensity (%)
(111)	41.5470	1821.25	0.3542	2.17365	100.00
(200)	48.1881	478.97	0.2880	1.88690	26.30
(220)	71.0515	295.37	0.4723	1.32676	16.22
(311)	85.6751	254.87	0.7872	1.13386	13.99
(222)	90.7006	102.87	0.9600	1.08277	5.65

But the ordered ones are face centered tetragonal with some disordered phases in an ordered matrix. Like $Ni_{0.5-x}Fe_xPt_{0.5}$, the alloys may contain small amount of second phase the composition of which could not be identified. Extra reflections with weak intensity occurs on either side of (111) line. So the ordered alloys are not single phase. Table-4.7 summarizes the results of X-ray investigations of ordered $Ni_{0.45}Fe_{0.05}Pt_{0.5}$ alloy.

Table: 4.7- Experimental ordered XRD pattern data of $Ni_{0.45}Co_{0.05}Pt_{0.5}$ alloy

Reflection indices (hkl)	Phase Structure	Position (°2 Theta)	Hight [cts]	FWHM (°2 Theta)	d-shading [Å]	Relative intensity (%)
(001)	Ni-Pt	24.6024	155.04	0.1968	3.61856	11.75
(110)	Ni-Pt	33.0940	293.90	0.2165	2.70692	22.28
(111)	Co-Pt	41.1506	956.55	0.2362	2.19366	72.52
(111)	Ni-Pt	41.7162	1318.95	0.2558	2.16522	100.00
(111)	Ni-Co	43.1885	88.99	0.2362	2.09476	6.75
(200)+(200)	Co-Pt+ Ni-Pt	47.5291	770.67	0.2362	1.91309	58.43
(002)+(200)	Ni-Pt+ Ni-Co	50.5319	188.29	0.2362	1.80623	14.28
(201)	Ni-Pt	54.2686	192.53	0.2558	1.69036	14.80
(112)	Ni-Pt	61/7088	89.98	0.3542	1.50322	6.82
(221)	Ni-Pt	62.7760	45.97	0.3149	1.48021	3.49
(220)	Co-Pt	69.4275	192.62	0.2558	1.35376	14.60
(220)	Ni-Pt	69.9566	173.25	0.2165	1.34481	13.14
(202)	Ni-Pt	71.8255	222.61	0.2362	1.31435	16.88
(221)+(220)	Ni-Pt+ Ni-Co	74.9671	87.59	0.3149	1.26688	6.64
(310)	Ni-Pt	79.1769	91.26	0.3149	1.20975	6.92
(311)+(311)	Ni-Pt+ Co-Pt	84.4889	574.31	0.2165	1.14672	43.54
(113)	Ni-Pt	88.9934	131.49	0.4723	1.09997	9.97
(222)+(222) + (311)	Ni-Pt+ Co-Pt+ Ni-Co	90.8484	148.60	0.2165	1.08229	11.27
(312)	Ni-Pt	100.2410	71.59	0.3149	1.00462	5.43
(400)	Ni-Pt	107.5788	57.58	0.6298	0.95549	4.37
(401)	Ni-Pt	113.1340	29.64	0.9446	0.92380	2.25
(411)	Ni-Pt	117.8096	36.58	1.1520	0.89956	2.77

4.2. Lattice Parameter Determination of XRD data

From the powder pattern, as for example shown in fig- 4.3 for disorder Ni-Pt alloy, we have got 2θ values for the diffraction of X-ray in particular direction. The angle 2θ between the transmitted ray and the diffracted ray and is called the scattering angle.

The Bragg equation is given by, $2d\sin\theta = \lambda$

$$\therefore d = \frac{\lambda}{2\sin\theta} \qquad 4.1$$

The equation for the inter planer spacing of a (fcc) lattice is

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2}$$

$$\therefore a = d\sqrt{h^2+k^2+l^2} \qquad 4.2$$

Putting the value of θ in the Bragg eq^n (4.1), we get the value of inter planar spacing 'd' for a particular reflection (i.e. for a particular 2θ). Again substituting the value of (hkl) of that reflection and 'd' in eq^n (4.2) we have got the corresponding lattice parameter (a). For the structural analysis of any material or alloy it is essential to know the lattice parameter precisely. The lattice parameters of the quenched specimens in the disordered state were measured with an X-ray Debye-Scherre camera using Cu-K_α radiation. We have calculated the lattice parameters of XRD reflection in fig- 4.3 for disordered $Ni_{0.5}Pt_{0.5}$ alloy as shown Table- 4.8

Table- 4.8

Reflections indices (hkl)	Lattice parameter 'a'
111	3.7354
200	3.7413
220	3.7418
311	3.7435
222	3.7445

4.2.1. Average lattice parameter

The process measuring the lattice parameter is a very indirect one, and is fortunately of such a nature that high precision is fairly easily obtained. The parameter 'a' of a cubic system is directly, proportional to the inter planer spacing 'd' of any particular set of lattice planes, we can see use the Bragg law to determine d and knowing d we can calculate 'a'. But it is sinθ, not θ, which appears in the Bragg law. Precision in d, or a therefore depend on precision in sinθ, a derived quantity, and not on precision in θ, the measured quantity. This fortunate became the value of sinθ changes very slowly with θ in neighborhood of 90°, as inspection of fig- 4.7. For this reason, a very accurate value of sinθ can be obtained from a measurement of θ, which is itself not particularly precise, provided that θ is nearly 90°. For example, an error in θ of 1° leads to an error in sinθ of 1.7 percent at $\theta=45°$ but only 0.15 percent at $\theta=85°$. We can calculated the fractional error of inter planar spacing, $\frac{\Delta d}{d}$, directly by differentiating to Bragg law with respect to θ.

We obtain

$$2d\sin\theta = \lambda$$

$$\text{or, } \Delta d \sin\theta + d\cos\theta\ \Delta\theta = 0$$

$$\text{or, } \frac{\Delta d}{d} = -\frac{\Delta\theta\cos\theta}{\sin\theta} = -\Delta\theta.\cot\theta \qquad 4.3$$

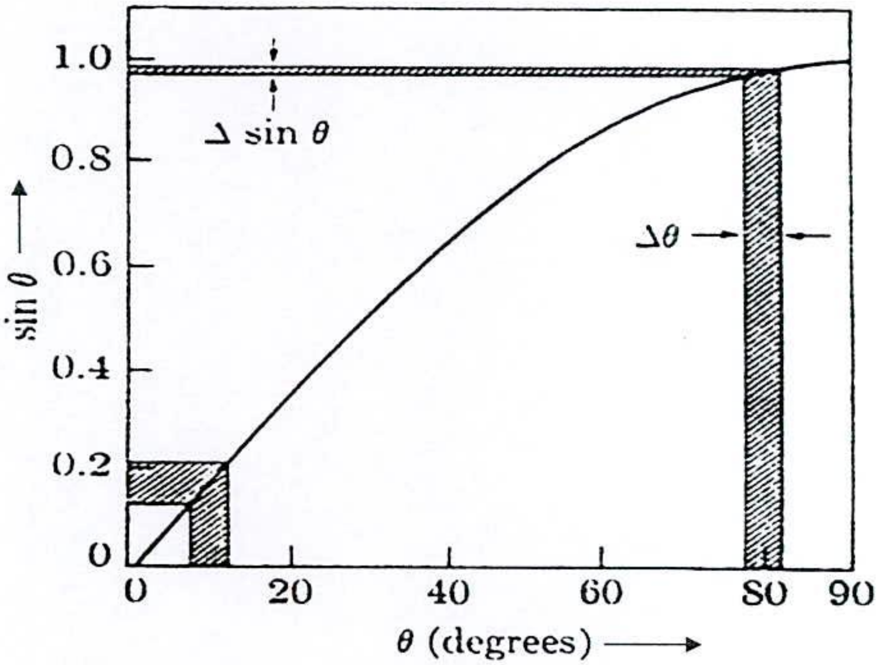


Fig- 4.7. The Variation of sinθ with θ. The error in sinθ caused by a given effort θ decreases as θ increases (Δθ exaggerated)

In the cubic system

$$a = d\sqrt{\left(h^2 + k^2 + l^2\right)}$$

Therefore similarly

$$\frac{\Delta a}{a} = \frac{\Delta d}{d} = -\Delta\theta.\cot\theta \qquad 4.4$$

Since cotθ approaches zero as θ approaches 90°, $\frac{\Delta a}{a}$, the fractional error caused by a given error in θ, also approaches zero as θ approaches 90°, or as 2θ approaches 180°. The key to precession in parameter measurement therefore lies in the backward reflected beams having 2θ values as near to 180° as possible.

Although the parameter disappears as 2θ approaches 180°, we can not observe a reflected beam at this angle. But since the values of a calculated for the various lines on the pattern approach the true value more closely as 2θ increases. We should be able to find the true value of the lattice parameter 'a' simply by plotting the measured values against 2θ and extra plotting to 2θ = 180°. Unfortunately this curve is not linear and the, extrapolation of a nonlinear curve is not accurate. However, it may be shown that if the measured values of the lattice parameter 'a' are plotted against θ or 2θ directly, the resulting curving curve is a straight line, which may be extrapolated with confidence.

Nelson and Rally $^{(4.5)}$ and Tailor and Sinclair $^{(4.6)}$ analyzed the various source of error, particularly absorption more rigorously than we have done and showed that the relation.

$$\frac{\Delta d}{d} = k\left[\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right] \qquad 4.5$$

Where k is a constant, whose value is considered here $\frac{1}{2}$, holds quite accurately down to very low values of θ and not just at high angles. The bracketed terms are sometimes called the Nelson-Rally function.

The Nelson-Rally function (N-R function) is more generally written as

$$\text{N-R function} = \frac{1}{2}\left[\frac{\cos^2\theta}{\sin^2\theta} + \frac{\cos^2\theta}{\theta}\right] \qquad 4.6$$

Now substituting the value of θ in the above expression of N-R function we have determined the N-R function for each scattering angle for the three experimental samples of with composition $Ni_{0.5}$-$Pt_{0.5}$, $Ni_{0.45}Fe_{0.05}Pt_{0.5}$ and $Ni_{0.45}Co_{0.05}Pt_{0.5}$ are shown in table 4.9, table- 4.10 and table- 4.11 respectively.

Table- 4.9 Lattice Parameter to disordered state of $Ni_{0.5}Pt_{0.5}$ alloy

Reflection Planes	Lattice parameter to disordered state 'a' in Å	N-R function	Average lattice parameter a_0 in Å ±0.0005
111	3.7354	1.24	
200	3.7413	1.03	
220	3.7418	0.57	3.7468
311	3.7435	0.39	
222	3.7445	0.30	

Table- 4.10 Lattice parameter of disordered state of $Ni_{0.45}Fe_{0.05}Pt_{0.5}$ alloy

Reflection Planes	Lattice Parameter to disordered state 'a' in Å	N-R function	Average lattice parameter a_o in Å
(111)	3.7514	1.2	3.7483
(200)	3.7548	1.03	
(220)	3.7502	0.57	
(311)	3.7508	0.40	
(222)	3.7485	0.35	

Table- 4.11 Lattice parameter of disordered state of $Ni_{0.45}Co_{0.05}Pt_{0.5}$ alloy

Reflection Planes	Lattice Parameter to disordered state 'a' in Å	N-R function	Average lattice parameter a_o in Å
(111)	3.7648	1.25	3.7488
(200)	3.7677	1.03	
(220)	3.7526	0.57	
(311)	3.7605	0.40	
(222)	3.7508	0.35	

We have plotted the lattice parameter 'a' versus the N-R function for different scattering angles for each sample and from the intercept of y-axis of the graph we have determined the average lattice parameter, 'a_o'. $Ni_{0.5}Pt_{0.5}$ alloy graph of lattice parameter versus N-R function is plotted as shown in fig-4.8. The least square liner fitting given the precise lattice parameter as an intercept on the y-axis.

In the similar way the average lattice parameter calculated for $Ni_{0.45}Fe_{0.05}Pt_{0.5}$ and $Ni_{0.45}Co_{0.05}Pt_{0.5}$ alloys are shown in fig- 4.9 and fig- 4.10 respectively. The average lattice parameter are shown in table 4.9, table-4.10 and table- 4.11.

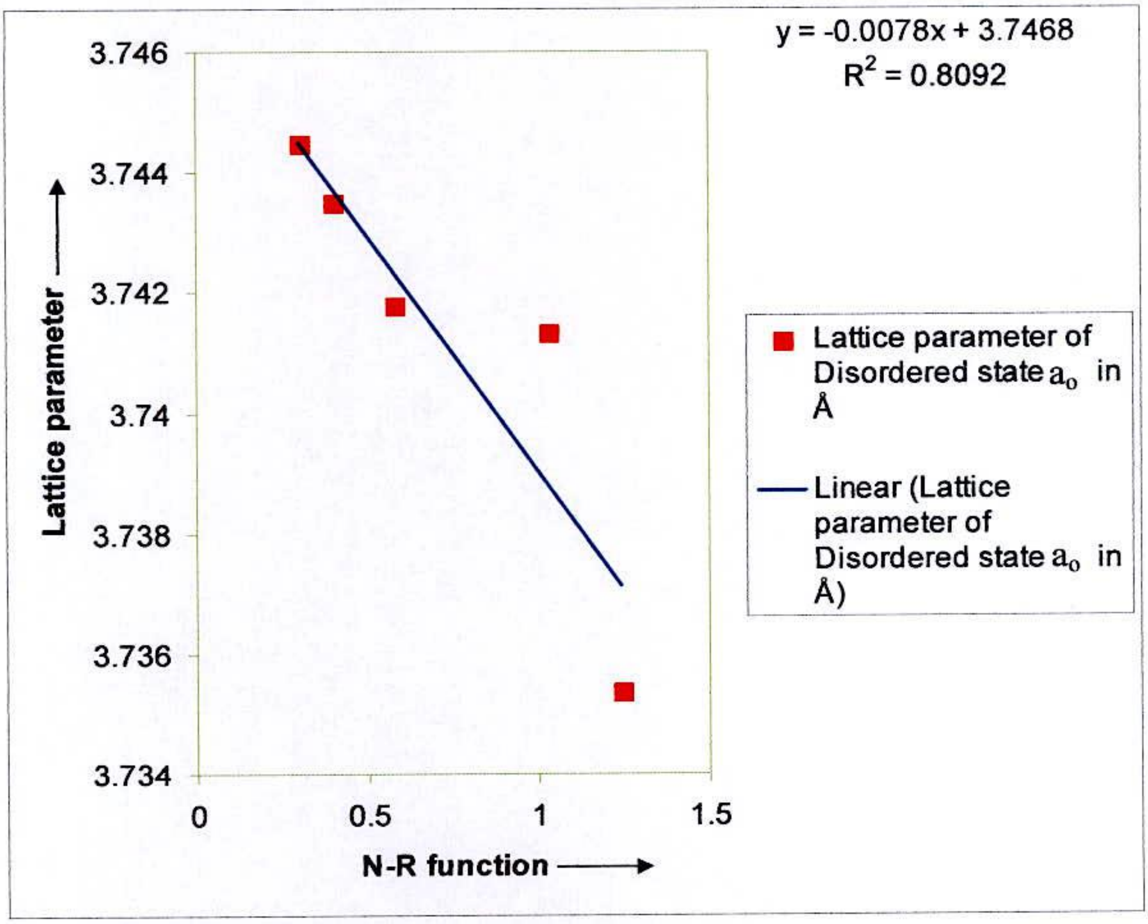


Fig- 4.8: Lattice parameter versus N-R function plots of disordered $Ni_{0.5}Pt_{0.5}$ alloy

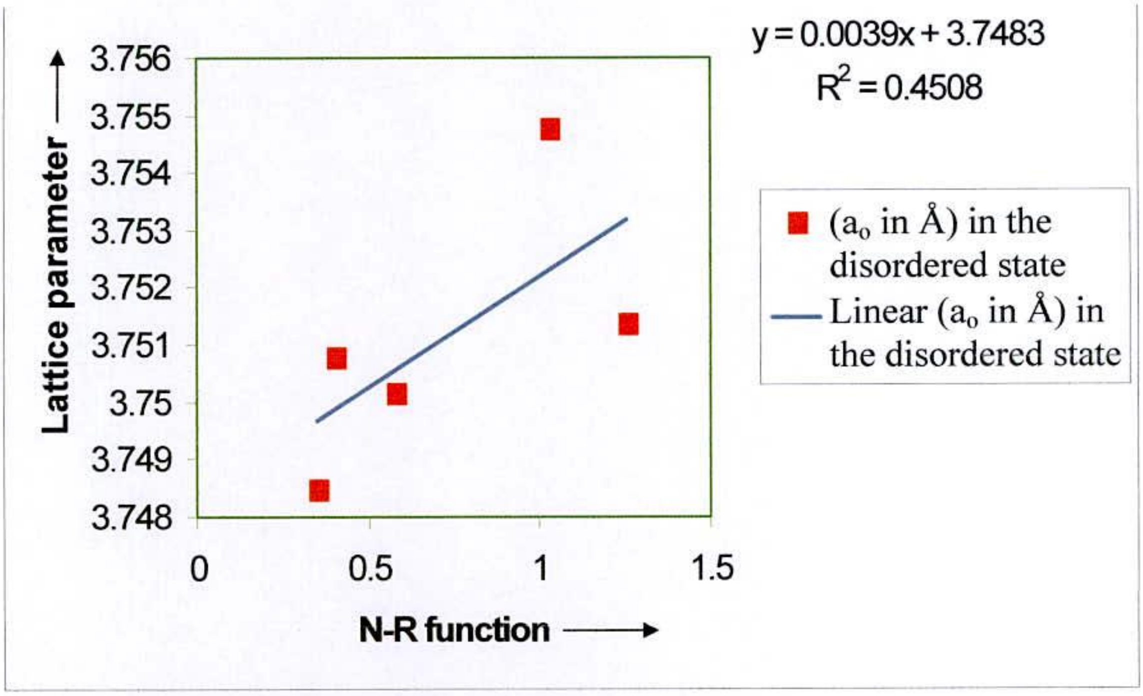


Fig- 4.9 Lattice parameter versus N-R function of $Ni_{0.45}Fe_{0.05}Pt_{0.5}$ alloy in the disordered state

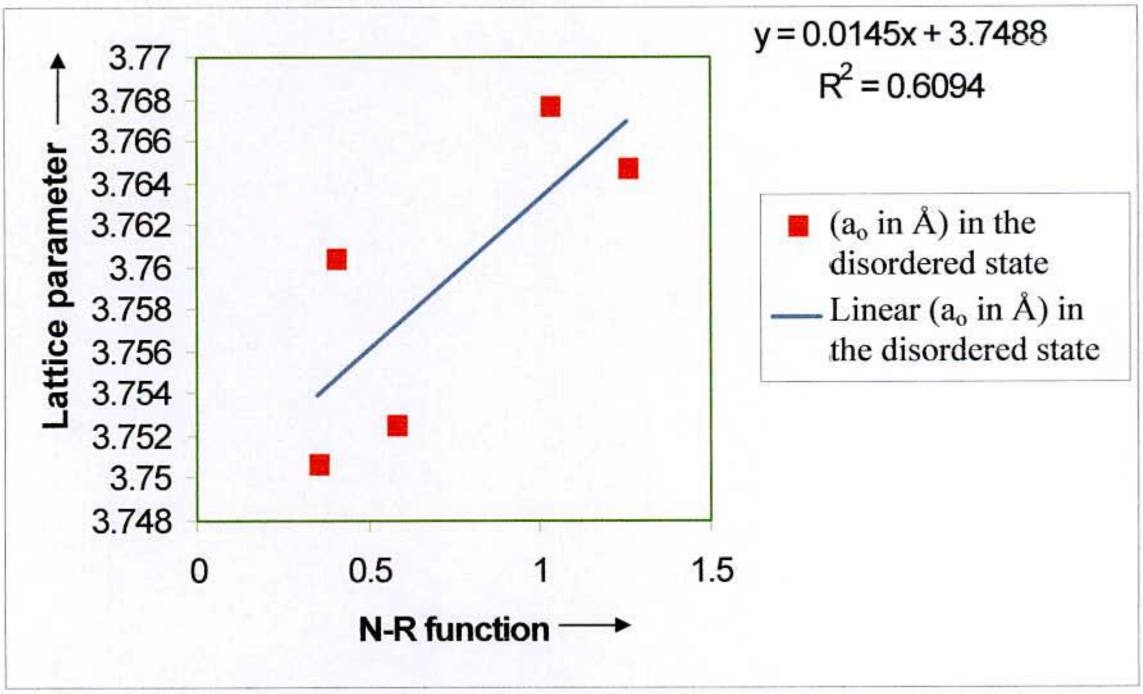


Fig- 4.10 Lattice parameter versus N-R function of $Ni_{0.45}Co_{0.05}Pt_{0.5}$ alloy in the disordered state

In the measurement of a lattice parameter, as in many other physical observations, two kinds of error are involved, systematic and random. A systematic error is one, which varies in a regular manner with some particular parameter. Thus the fractional error in 'a_o' due to the various effect considered above film shrinkage, in correct radius, off-center, specimen, absorption are all systematic errors because they vary in regular way with θ, decreasing as θ increases. Further the systematic error is always of the same sign; for example the effect of absorption in a Debye-Scherrer camera is always to make the computed value of 'a' less than the true value. Random errors, on the other hand, are the ordinary chance errors involved in any direct observation. For example, the errors involved in measuring the position of the various lines on a film are random errors; they may be positive regular manner with the position or negative and not value in any of the lines on the film. In the present study, a special technique was used in the Debye-Scherrer method where fraction error is negligible.

The systematic error in 'a' approaches zero as θ approaches 90° and may be eliminated by the use of the proper extrapolation function. The random errors involved in measuring line position shows up as random errors in 'a', and are responsible for the deviation of the various points from the extrapolation line. The lattice parameter of all the samples have been precisely determined considering all the reflections together with the Cu-$K_{\alpha 1}$ components using the extrapolated Nelson-Rally function $F(\theta)=0$ (4.7).

Lattice parameter of the disordered $Ni_{0.5}Pt_{0.5}$ alloy was determined by X-ray Debye-Scherrer camera method with an error estimated to be ±0.0004Å. The same parameter for the ordered state was determined with composition $Ni_{0.5}Pt_{0.5}$ with an error estimated to be ±0.0004Å.

All the result of the lattice parameter ordered states with N-R function are shown in table-4.12 table-4.13 and table- 4.14.

Table- 4.12 lattice parameter of ordered states $Ni_{0.5}Pt_{0.5}$ alloy

Reflection Planes	Ordered state a in Å	Ordered State c in Å	N-R function
(001)		3.5719	2.25
(110)	3.8024		1.62
(111)	3.8024	3.5971	1.23
(200)	3.8017		1.04
(002)		3.5885	0.96
(201)	3.8051	3.5885	0.87
(112)	3.8024	3.5969	0.72
(220)	3.8100		0.59
(202)	3.8154	3.5964	0.56
(221)	3.8023	3.5966	0.52
(310)	3.8188		0.46
(311)	3.8157	3.5968	0.41
(113)	3.8187	3.5968	0.36
(222)	3.8190	3.5968	0.34
(203)	3.8112	3.5994	0.28

Table- 4.13 Lattice parameter of both the disordered and ordered states of $Ni_{0.45}Fe_{0.05}Pt_{0.5}$ alloy

Reflection planes	Theta	N-R function	Ni-Fe-Pt disordered state a in Å	Ni-Fe ordered state a in Å	Fe-Pt ordered state a in Å	Ni-Pt ordered state a in Å	Ni-Pt ordered state c in Å
(111)	20.75	2.44	3.7514	3.6073	3.6073	3.8135	3.6053
(200)	24.25	1.99	3.7548	3.6092	3.6092	3.8114	3.6086
(220)	35.60	1.09	3.7502	3.5757	3.5757	0	0
(311)	42.85	0.75	3.7508	3.5883	3.5883	0	0
(222)	45.40	0.65	3.7485	3.5741	3.5741	0	0

Table- 4.14 Lattice parameter of both the disordered and ordered states of $Ni_{0.45}Co_{0.05}Pt_{0.5}$ alloy

Reflection planes	Theta	N-R function	Ni-Co-Pt disordered state a in Å	Ni-Co ordered state a in Å	Co-Pt ordered state a in Å	Ni-Pt ordered state a in Å	Ni-Pt ordered state c in Å
(111)	20.75	2.44	3.7648	3.6282	3.7995	3.8043	3.6185
(200)	24.25	1.99	3.7677	3.6142	3.8261	3.8219	3.6140
(220)	35.60	1.09	3.7526	3.5831	3.8290	3.8260	0
(311)	42.85	0.75	3.7605	3.5765	3.8032	0	0
(222)	45.40	0.65	3.7508	3.5716	3.8104	0	0

All the experimental samples graph of lattice parameters are shown in fig-4.11, fig-4.12, fig- 4.13 and fig-4.14.

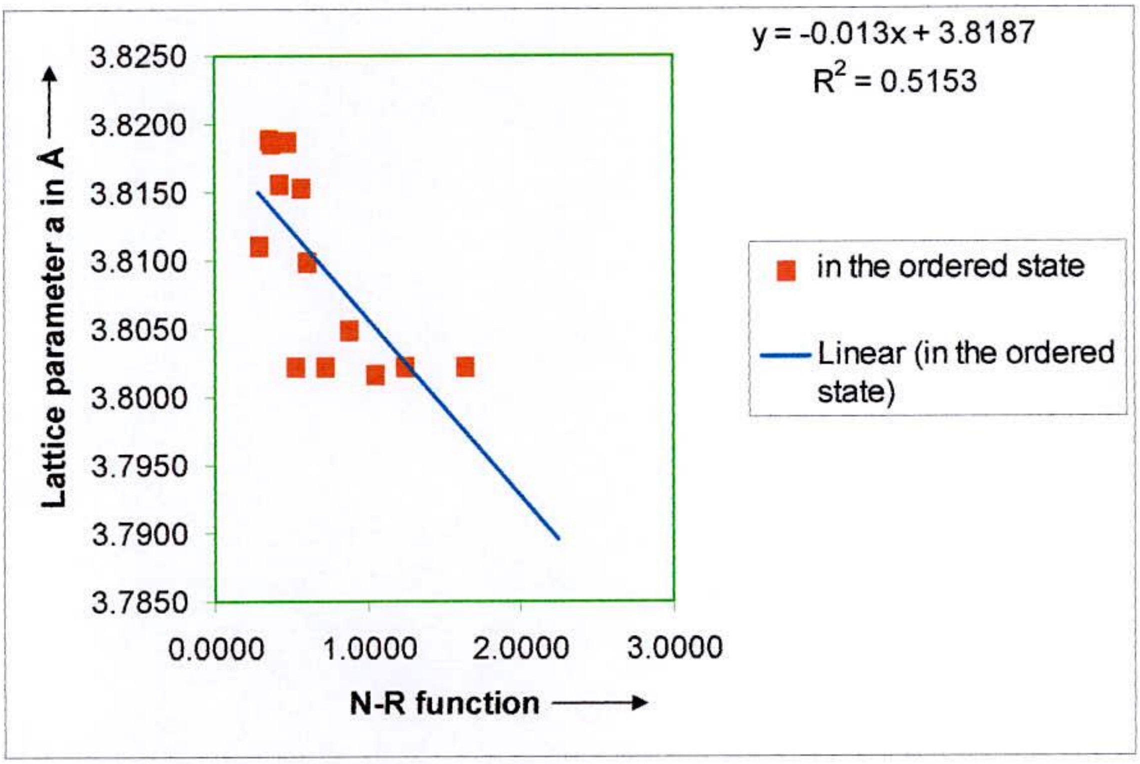


Fig-4.11 Lattice parameter (a axis) versus N-R function of $Ni_{0.5}Pt_{0.5}$ alloy in ordered state

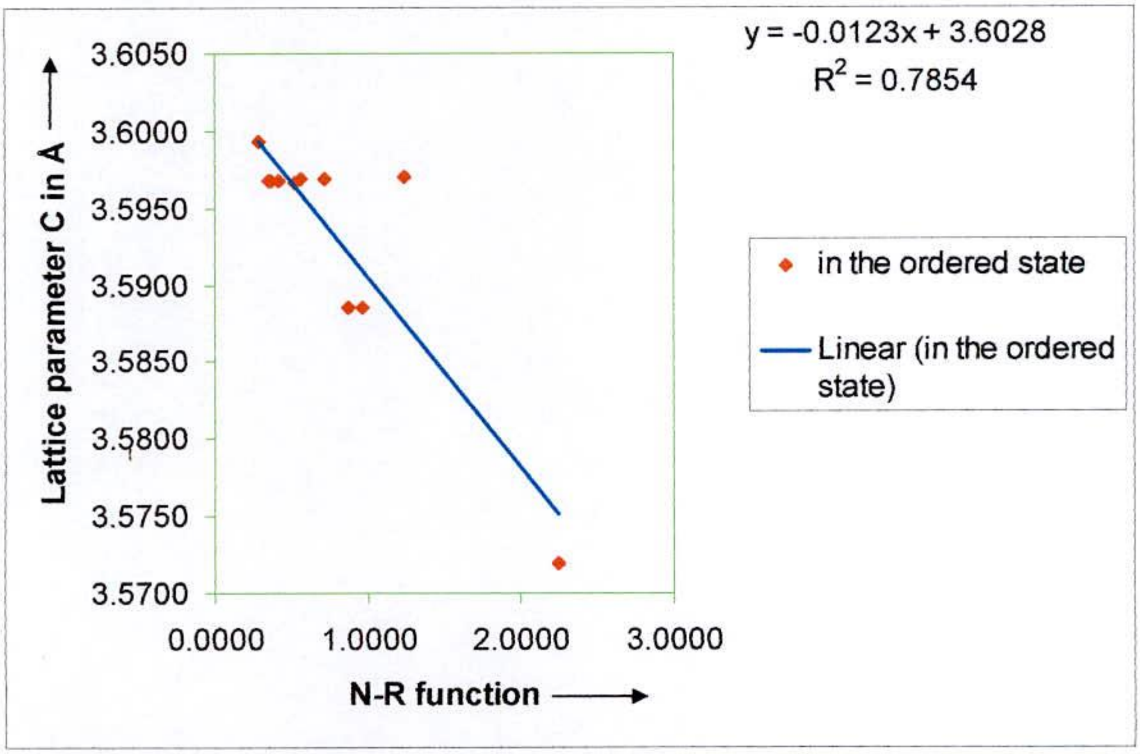


Fig-4.12 Lattice parameter (c axis) versus N-R function of $Ni_{0.5}Pt_{0.5}$ alloy in ordered state

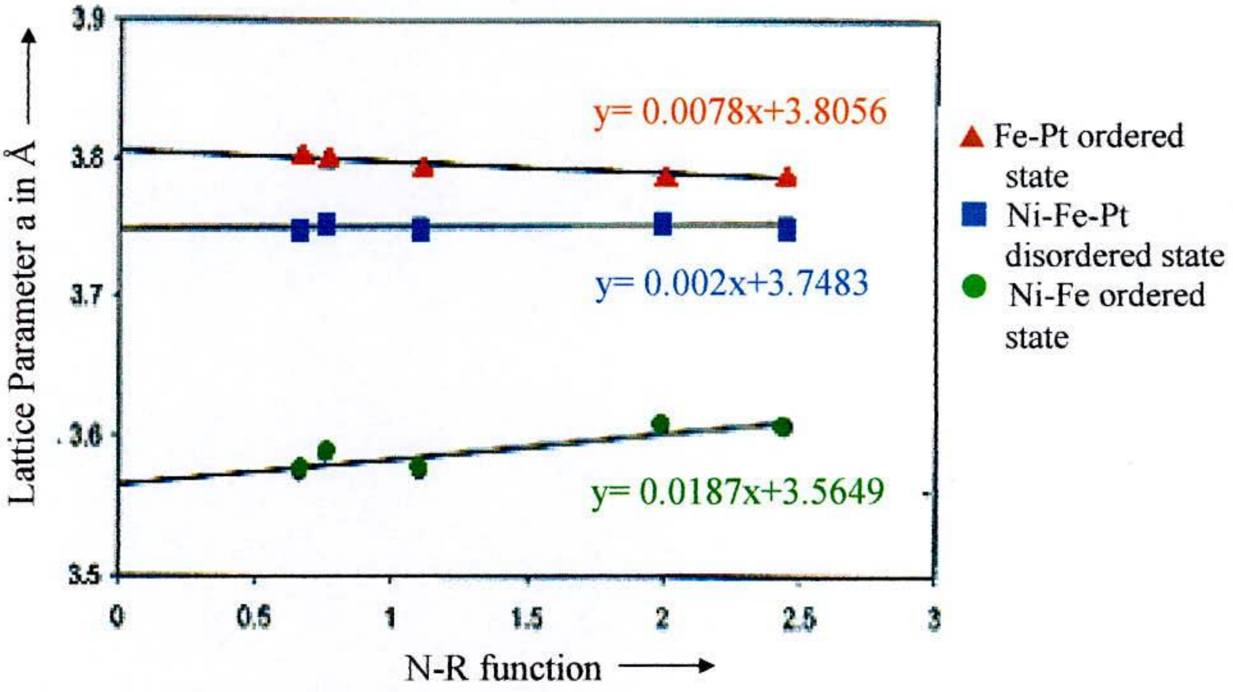


Fig-4.13 Lattice parameter versus N-R function of $Ni_{0.45}Fe_{0.05}Pt_{0.5}$ alloys in both disordered and ordered state

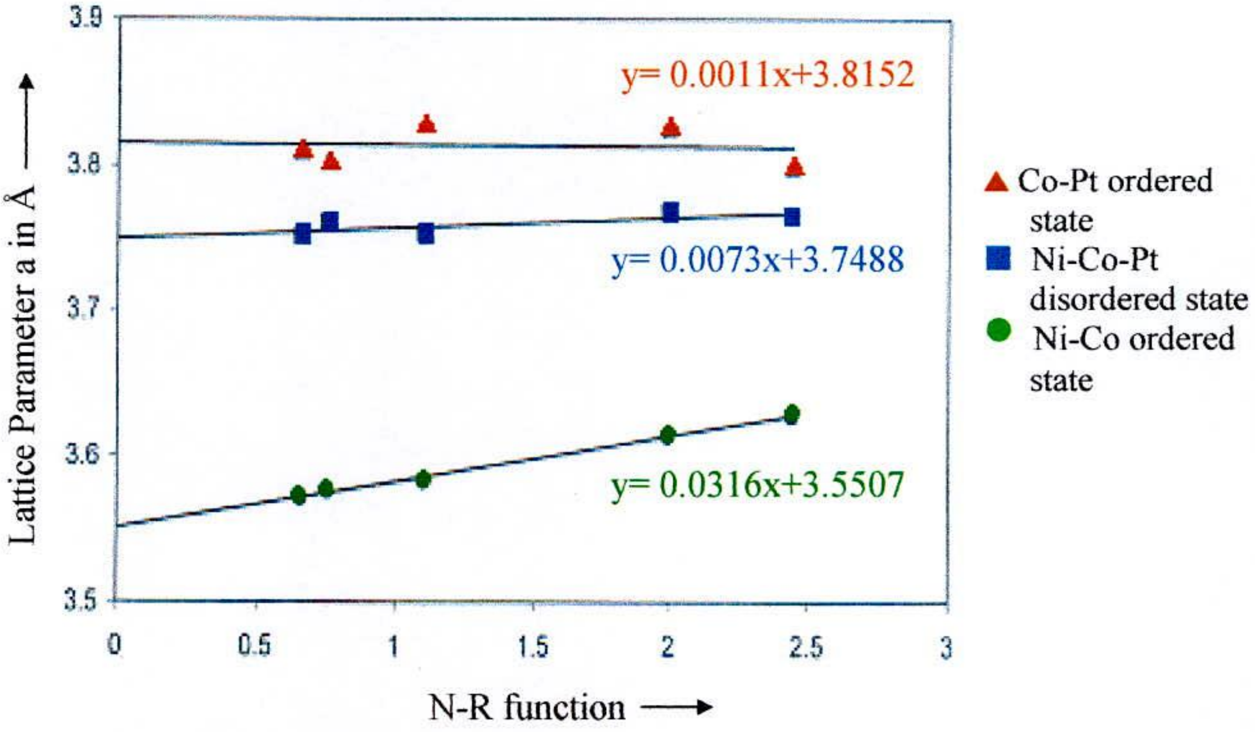


Fig-4.14 Lattice parameter versus N-R function of $Ni_{0.45}Co_{0.05}Pt_{0.5}$ alloys in both disordered and ordered state

All the results of the average lattice parameter for both the disordered and ordered states with $\frac{c}{a}$ ratio will be shown in table- 4.15 and table- 4.16. For the composition $Ni_{0.5}Pt_{0.5}$, the value of c was determined to be 3.6028 ±0.0004Å from the distance.

Table- 4.15 Lattice parameter of both the disordered and ordered states of $Ni_{0.45}Fe_{0.05}Pt_{0.5}$ alloy with compare $Ni_{0.5}Pt_{0.5}$ alloy.

Composition	**Crystal structure in the ordered state**	**Lattice parameter**			$\frac{c}{a}$ **ratio**	**Ref. value of** $\frac{c}{a}$ **ratio**
		(a in Å) in the disordered state (±0.0004Å)	**Ordered state**			
			(a in Å) (±0.0004Å)	**(c in Å) (±0.0004Å)**		
$Ni_{0.5}Pt_{0.5}$	fct	3.7468	3.8187	3.6028	0.943	0.939
$Ni_{0.45}Fe_{0.05}Pt_{0.5}$	fcc	3.7483	-	-	-	
$Ni_{0.5}Fe_{0.5}$	fcc	-	3.5649	-	-	
$Fe_{0.5}Pt_{0.5}$	fcc	-	3.8056	-	-	
$Ni_{0.5}Pt_{0.5}$	fct	-	3.8141	3.6069	0.945	

Table- 4.16 Lattice parameter of both the disordered and ordered states of $Ni_{0.45}Co_{0.05}Pt_{0.5}$ alloy with compare $Ni_{0.5}Pt_{0.5}$ alloy.

Composition	**Crystal structure in the ordered state**	**Lattice parameter**			$\frac{c}{a}$ **ratio**	**Ref. value of** $\frac{c}{a}$ **ratio**
		(a in Å) in the disordered state (±0.0004Å)	**Ordered state**			
			(a in Å) (±0.0004Å)	**(c in Å) (±0.0004Å)**		
$Ni_{0.5}Pt_{0.5}$	fct	3.7468	3.8187	3.6028	0.943	0.939
$Ni_{0.45}Co_{0.05}Pt_{0.5}$	fcc	3.7488	-	-	-	
$Ni_{0.5}Co_{0.5}$	fcc	-	3.5507	-	-	
$Co_{0.5}Pt_{0.5}$	fcc	-	3.8152	-	-	
$Ni_{0.5}Pt_{0.5}$	fct	-	3.8174	3.6154	0.947	

Between the pair (201) and (200) reflections. The $\frac{c}{a}$ ratio of this ordered alloy was found to be 0.943, which is very near to the reference values of $0.940^{(4.8)}$ and $0.941^{(4.9)}$. This difference may be due to experimental uncertainty. Similarly the lattice constants 'a' and 'c' determined by the both the techniques of the ordered (fct) phase of Ni-Pt is comparable. The results of the present X-ray measurements are in reasonable agreement with those reported earlier (4.9-4.11). According to reference Ni-Pt alloy has $\frac{c}{a}$=0.939, where c=3.589Å and a=3.823Å. The corresponding values for the Co-Pt and Cu-Au are $\frac{c}{a}$= 0.981 and $\frac{c}{a}$=0.931 respectively with same crystal structure(4.11, 4.12-4.13). It is calculated that in the ordered (fct) Ni-Pt alloy a Ni atoms has 4 Ni and 8 Pt nearest neighbors and a Pt atom has 4Pt and 8Ni nearest neighbors at a distance of 2.701Å and 2.625Å respectively.

Fig- 4.5 shows the diffraction pattern recorded for both ordered and disordered $Ni_{0.45}Fe_{0.05}Pt_{0.5}$ powder. The fct phase has $\frac{c}{a}= 0.945$, where c=3.6069 ±0.0004Å and a=3.8141Å and Fig-4.6 shows the diffraction pattern recorded for both ordered and disordered $Ni_{0.45}Co_{0.05}Pt_{0.5}$ powder, the (fct) phase has $\frac{c}{a}=0.947$ where c=3.6154±0.0004Å and a=3.8174Å values calculated from both the technique are comparable. Table-4.15 shows results of X-ray measurements. The lattice constant increase slightly with substitution of Fe of Ni in either states of order and a slight reduction ($\approx 0.3\%$) in cell volume occurs or ordering. Table- 4.16 shows is little increase in the lattice parameters with addition of cobalt in the both ordered and disordered states. A small reduction ($\approx 0.3\%$) in cell volume occurs on ordering for the (Ni-Co)-Pt alloy as in the case of (Ni-Fe)-Pt alloys.

4.3. Long-range Parameter for the Composition $Ni_{0.5}Pt_{0.5}$ Alloy

The long-range order parameter's' is defined as follows :

$$S = \frac{r_A - F_A}{1 - F_A} \qquad 4.7$$

where r_A is the fraction of A sites occupied by A atoms and F_A is the fraction of A atoms in the alloy. When long-range order is perfect, $r_A=1$, therefore S=1. When the atomic arrangement is completely random then $r_A=F_A$ and S=0. Any departure for perfect long-range order in a super lattice causes the super lattice lines to become weaker.

Fig-4.15 shows a unit cell of ordered Ni-Pt alloys. For complete order, per unit cell atomic positions are [000] and $\left[\frac{1}{2}\frac{1}{2}0\right]$ for Pt atoms and $\left[\frac{1}{2}0\frac{1}{2}\right]$ and $\left[0\frac{1}{2}\frac{1}{2}\right]$ for Ni atoms. The structure factor F would be,

$$F = f_{Pt}[e^{2\pi i(0+0+0)} + e^{\pi i(h+k+0)}] + f_{Ni}[e^{\pi i(h+0+l)} + e^{\pi i(0+k+l)}], \qquad 4.8$$

where f is the atomic scattering factor. For (hkl) unmixed (all even or all odd), then

$$F = 2f_{Pt} + 2f_{Ni}, \qquad 4.9$$

which gives fundamental reflections only. For (hkl) mixed (two even and one odd or one even and two odd), then

$$F = (2f_{Pt} - 2f_{Ni})S, \qquad 4.10$$

Which gives super lattice reflections only and S = 1.

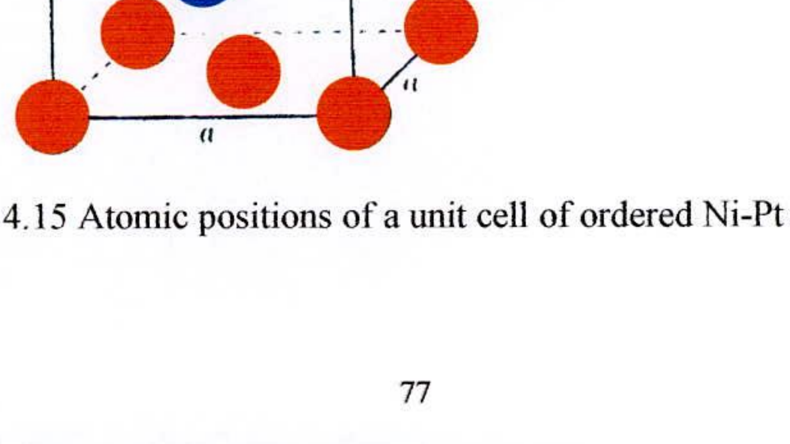


Fig- 4.15 Atomic positions of a unit cell of ordered Ni-Pt alloy

Now, intensity of single reflection I can be calculated by

$$I_{hkl} = F_{hkl}{}^{2}.P_{hkl}\left(.\frac{1+\cos^{2}2\theta}{\sin^{2}\theta.\cos\theta}\right) \qquad 4.11$$

where P_{hkl} is the multiplicity factor and 2θ is the angle of reflection. From eq^n (4.9), eq^n, (4.10) and eq^n (4.11), we get the intensity ratio of super lattice and fundamental lines.

$$\frac{I_S}{I_f} = \frac{(f_{Pt}-f_{Ni})^2}{(f_{Pt}+f_{Ni})^2}.\frac{P_{hkl(S)}}{P_{hkl(f)}}\frac{\left[\dfrac{1+\cos^{2}2\theta}{\sin^{2}\theta.\cos\theta}\right]_S}{\left[\dfrac{1+\cos^{2}2\theta}{\sin^{2}\theta.\cos\theta}\right]_f}.S^2 \qquad 4.12$$

For a like pair of super lattice and fundamental lines, we can calculate theoretical intensity ratio of $\frac{I_s}{I_f}$, when S = 1. Consider "A" is the theoretically calculated intensity ratio, then

$$A = \frac{I_s}{I_f} \qquad 4.13$$

From XRD experiment, the integrated intensity ratio of that particular like pair of superlattice and fundamental lines are obtained. Consider "B" is the experimentally determined intensity ratio, then

$$B = \frac{I_s}{I_f} \qquad 4.14$$

Now from eq^n (4.12), eq^n (4.13) and eq^n (4.14), we get

$$B=A.S^2$$

$$\text{or,}\quad \mathbf{S} = \sqrt{\mathbf{B}/\mathbf{A}} \qquad 4.15$$

So, using equation eq^n (4.12), eq^n(4.13), eq^n (4.14) and eq^n (4.15) long-range order parameter "S" of Ni-Pt alloy can be determined experimentally.

Using eq^n (4.15), the long-range order parameter S was determined from several like pairs of super lattice and fundamental reflections for composition $Ni_{0.5}Pt_{0.5}$ alloy. The results were compared with the available reference data and shown in Table- 4.17

In the calculation, both the multiplicity factor and Lorentz polarization factor were considered. In Table 4.17, the average value of S was found to be 0.951 and that of reference value is 0.98 (4.16). For two pairs of reflections (201) & (200) and (310) & (311), the value of S was found to be 1.00, which indicates the perfect long-range order and the crystal is perfectly ordered. For the pairs of (221) & (220) and (310) & (113) reflections, the value of S was found to be 0.98 and 0.99, respectively, which is very near to unity. For the pairs of (001) & (200) and (110) & (111) reflections, the value of S was found to be 0.84 and 0.90, respectively. Sometimes the factors like surface roughness of particles and extinction affect the line intensity (4.9). On the other hand, preferred orientation increases the line intensity. Probably, due to these effects we have measured slightly lower value of S, 0.84 and 0.90 for two pairs of reflections. The average value of S = 0.951, indicates the crystal is almost perfectly ordered.

Table-4.17 Experimentally determine long-range order parameter "s" for the composition $Ni_{0.5}Pt_{0.5}$ alloy

Nature of reflections	pairs of reflection	Experimental intensity-B	Theoretical intensity-A	Multiplicity factor, P_{hkl}	Long-range order parameter-S	Average value of $S^{(1)}$	Reference value of $S^{(11)}$
Fundamental	200	0.41	0.58	6	0.84	0.951	0.98
superlattice	001			2			
Fundamental	111	0.195	0.243	8	0.90		
superlattice	110			4			
Fundamental	200	0.31	0.31	6	1.00		
superlattice	201			8			
Fundamental	002	0.81	0.90	2	0.95		
superlattice	201			8			
Fundamental	220	0.46	0.47	4	0.98		
superlattice	221			8			
Fundamental	113	0.375	0.38	8	0.99		
superlattice	310			8			
Fundamental	311	0.1	0.14	24	1.00		
superlattice	310			8			

From the experimentally determined long-range order parameter “S”, the actual number of Pt atoms site occupied by Pt atoms in the crystal can easily be calculated. In equational, putting the values of $S = 0.951$ and $F_A = 0.5$, we get the value of $r_A = 0.975$ or $\frac{975}{1000}$ $Ni_{0.5}Pt_{0.5}$. That means, out of 1000 Pt atoms site in the crystal, 975 Pt atoms occupied their places and the rest 25 sites are occupied by Ni atoms in addition to their (Ni) own sites in the crystal. The results have good consistency with lattice parameter values. For this alloy, experimentally determined a_o was found to be 3.7468Å whose literature value is 3.743Å in the disordered state while in the ordered state, values of a, c and $\frac{c}{a}$ ratio were found to be 3.8187Å, 3.6028Å and 0.943, whose literature values are 3.8230Å, 3.509Å and 0.939, respectively. This slightly lower value of lattice parameter is due to Ni atoms in the alloy, because the lattice parameter of pure Ni (3.5240Å) is lower than that of pure Pt (3.9237Å).

CHAPTER- V

Conclusion

5.1. Conclusion

Order-disorder phase transition, order parameter and structural characterization of equiatomic NiPt and Fe and Co doped alloys have been investigated by X-ray diffraction using high temperature attachment.

Therefore NiPt equiatomic alloy offers a good opportunity to investigate in details the order disorder phase transition, lattice parameter in both the ordered and disordered phases. NiPt alloy exhibits order-disorder transition having disordered phase with (fcc) structure at high temperature and undergoes ordering below 630°C in the sequence of simple cubic (LI_2), face centered tetragonal (LI_0), structure around the stoichiometric composition of NiPt. The effect of Fe and Co doped substituted for Ni has been studied in detail.

The sample were prepared by arc melting using high purity ingredient and subjected to thermal treatment in-situ in the diffractometer with high temperature attachment for ordering. The lattice parameter of disordered (fcc) $Ni_{0.5}Pt_{0.5}$ alloy experimentally determined has been found to be $a_0 =$ 3.7468Å where reference value $a_0 = 3.743$Å while in the ordered state value of a, c and $\frac{c}{a}$ ratio were found to be 3.8187Å, 3.6028Å and 0.943. A slight increase in the $\frac{c}{a}$ ratio of the lattice parameter with addition of Fe and Co in the ordered state have been found. The average values of long-range order parameter has been found to be 0.951 compared to that of reference value which is 0.98. It is used to regard the average long-range parameter S as satisfying the inequality $0 \leq S \leq 1$. The determined average value of S indicates the crystal is almost perfectly ordered. Heat treatment temperature is another important factor to form the crystal perfectly ordered. The order-disorder transition temperature of NiPt alloy is 630°C. Ordering has been done in-situ with high temperature attachment. The sample has been heated to 650°C for half an hour, then slowly cool down to 500°C with slep of 10°C with holding time of 30 minute in each step. At 500°C the sample has been kept for 1 hour and then retained at room temperature by slowly quenching to form perfect ordered state. At room temperature the diffraction pattern has been taken for analysis of the ordered state as well long-range order parameter "S". It has been observed that the degree of ordering i.e long-range order parameter has strong (5.1) influence on the magnetic properties. In equi-atomic NiPt alloy, atomic ordering completely destroys the spin orders, i.e disordered alloy is ferromagnetic while ordered one is paramagnetic(5.1. 5.2). The XRD pattern of disordered $Ni_{0.5}Pt_{0.5}$ alloy with composition x=0.50. In the figure, the indices of the reflecting planes are shows in the parenthesis. All the reflections correspond to (fcc) structure in the disordered state of the alloy. No super-lattice reflections are present in the XRD pattern. The same nature of pattern were observed for disordered $Ni_{0.45}Fe_{0.05}Pt_{0.5}$ and $Ni_{0.45}Co_{0.05}Pt_{0.5}$ alloys as well as XRD pattern of same ordered alloy with composition x=0.50. Then the indices of the reflecting planes are shown in the parenthesis. All the reflections correspond to (fct) structure in the ordered state of the alloy with the appearance of super-lattice reflections together with the fundamental ones in the XRD pattern.

But it is very interesting for the ordering diffraction pattern by the effect of Fe and Co doped, with NiPt alloy. The reflecting planes are shown respective figure in parenthesis. All the reflection indicate the ordered $Ni_{0.45}Fe_{0.05}Pt_{0.5}$ and $Ni_{0.45}Co_{0.05}Pt_{0.5}$ alloys with the fundamental and super-lattice reflection not only that it has been seen extra reflecting pahse having FePt, FeNi, NiPt and CoPt, NiCo, NiPt respectively.

(100), (111), (200), (211), (220), (311), (222), (312), (400), (401) and (411) were indicated extra peaks of $Ni_{0.45}Fe_{0.05}Pt_{0.5}$ and $Ni_{0.45}Co_{0.05}Pt_{0.5}$ alloys. This extra peaks have been indicated clearly and successfully.

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