CHAPTER 4

REVIEW OF WORKS ON DEFORMED METALS AND ALLOYS:
F.C.C., H.C.P. AND B.C.C. STRUCTURES.
4.1 Introduction

Since the development of the theoretical basis of the X-ray scattering by deformed or imperfect crystal lattices, the studies on lattice imperfections in metals, alloys and other crystalline solids by X-ray diffraction, transmission electron microscopy and also by several other methods have received widespread attention in recent years. In this chapter we present a brief and comprehensive review of the works made on deformed metals and alloys by X-ray diffraction and also by transmission electron microscopy with a special mention to those having specific importances. In the past two decades or so a considerable amount of literature has already been accumulated in this particular field of study and it will be difficult to summarise the whole at this stage. However, an extensive review has earlier been made by Greenough (1952) and Warren (1959) and, recently by Wagner (1965). Some specific mentions have also been made in the texts by Klug and Alexander (1964), Taylor (1961) and Barrett and Massalski (1966).

4.2 Studies on face centred cubic metals and alloys

4.2.1 X-ray line profile observations

This f.c.c. system is perhaps the most extensively attended one, at least so far as the X-ray line profile analysis is concerned. The work on this system was initiated more than two decades ago by Barrett (1950), who first investigated the effect
of silicon as solute on the stacking fault concentrations in copper-silicon solid solutions. Since then, noble metals and solid solutions of these were studied extensively. Warren and Warekois (1955) studied the effects on Cu-brass and found that the stacking faults tend to increase with increasing zinc content. Schoening and Niickerk (1955) failed to demonstrate the presence of stacking faults in electrolytic silver of high purity. Williamson and Smallman (1956) gave a derivation of dislocation density from the domain size and strain values, and showed that each dislocation was attached to a stacking fault for Cu-Zn alloy systems and for some pure metals like Al, W, Mo and Re. Wagner (1957a) investigated pure copper and Cu-Zn alloys at liquid nitrogen temperature by X-ray diffraction and associated the asymmetry in the observed line profiles with the presence of twin faults in the deformed structure. Wagner (1957b) extended the study of imperfections introduced by cold-work at low temperature to silver and aluminium systems. While the former (silver) was observed to be more prone to stacking faults, the latter (aluminium) showed a near isotropy in domain sizes and strains with a total absence of stacking fault concentrations and associated with its high stacking fault energy arising possibly from Fermi surface-Brillouin zone interaction of conduction electrons and cross slip phenomenon. Similar observations on Ni was also found by Michell and Haig (1957). Smallman and Westmacott (1957), Christian and Spreadborough (1957), Cahn and Davies (1960) and Davies and Cahn (1962) made several detailed and significant
observations on a number of silver and copper-based alloy systems in α (f.c.c.) phase, namely Ag-Zn, Ag-Cd, Ag-In, Ag-Sn and Cu-Ni, Cu-Zn, Cu-Al, Cu-Sn and Cu-Ge alloys for different solute concentrations and tried to correlate the increase in stacking fault concentrations with solutes from several aspects namely free energy considerations of f.c.c. and faulted h.c.p. structures, solvent solute size and period difference etc. Davies and Cahn (1962) observed a roughly parabolic variation of stacking fault probability with solute concentration. Vassamillet (1961) while making observations with some Au, Cu and Ag based alloy systems namely Cu-Zn, Ag-Zn and Au-Zn in different compositions, obtained some discontinuity in the assumed linear relation between stacking fault densities and solute concentrations. Vassamillet (1961) also obtained the relative magnitudes of stacking fault (S.F.) energy from X-ray analysis following the method given by Smallman and Westmacott (1957). Vassamillet and Massalski (1963a, 1963b) further studied some silver and copper based and some inter-noble metal alloys. They compared in their previous work (1963a) the results with electron microscopical investigation by Howie and Swann (1961) and reported the S.F. energies of pure copper and silver to be of the order of $67 \pm 17$ ergs/cm$^2$ and $14 \pm 3.5$ ergs/cm$^2$ respectively. In the later work (1963b) Vassamillet and Massalski interpreted the discrepancy between the extent of change in stacking fault probability with the addition of 1% solute in Cu, Au and Ag by Fermi-surface topology. Adler and Wagner (1962) investigated some silver base binary alloys (Ag-Cd, Ag-In and Ag-Sn) and
observed linear dependence of stacking fault probability with solute concentration. Adler and Wagner (1962) applied peak shift and lattice parameter change for the determination of deformation fault probability \( p \), and peak asymmetry for the evaluation of twin fault \( \beta \). Klein et al. (1962) observed the decrease in stacking fault probability \( \xi \) and hence increase in S.F. energy in Ag and in some of its dilute alloys with Mg, Cu and O.

Welch and Otte (1962) in their work on a ternary system i.e., Cu-6.6 Sn-1.2 Mn, found that the acts of filing and wire drawing were more capable in introducing stacking faults in this system than the uniaxial tension. Foley, Cahn and Raynor (1963) determined stacking fault probabilities and its variation with electron-atom ratio for several copper based alloy systems like Cu-Ge, Cu-Si and a ternary Cu-Ge-Si.

Sundahl and Silvertsen (1963) measured stacking fault probability \( \xi \) in a series of Ag-Li alloys and explained the observed change in \( \xi \) with solute concentration by the existence of large difference in electro-chemical behaviour of the constituents as the electron-atom ratio remained constant with alloying. Koda et al. (1963) examined the segregation of solute atoms into stacking faults (known as Suzuki effect), and determined stacking fault energy both by X-ray and electron-microscopy in Cu-Ge systems. Vassamillet and Massalaki (1964) and Nakajima and Namakura (1965) studied a series of Cu based (Cu-Ge, Cu-Ni and Cu-Mn) alloys. In the latter observation the effect of transitional solutes on pure Cu has been found to be comparatively less than that due to non-transitional solutes.
Wagner and Helion (1965) tried to determine the existence of extrinsic faults along with the intrinsic and twin faults in Cu-Zn and Cu-Sn systems. This work is of much importance as it considers for the first time the existences of extrinsic or double deformation faults along with internal stresses from X-ray measurements.

Several f.c.c. copper and silver-base alloys containing both transitional and non-transitional solutes namely, Cd, In, Sn, Sb, Zn, Mn and Ni have been studied in detail by Goswami, Sen Gupta and Quader (1966a, b, c; 1967a, b; 1965) and De (1969). These measurements reveal in general, that for fixed valence electron-atom ratio, the stacking fault probability increases with the increasing solute valency and also that the variation of fault probability with solute concentration is linear for Ag-base alloy systems and parabolic in Cu-base alloys. All the existing methods namely peak shift, peak asymmetries and peak broadening analyses were applied in their studies, and microstructural parameters and fault probabilities were also critically examined. In agreement with the previous observations by Nakajima and Numakura (1965), it has been observed that the additions of transitional solutes Mn and Ni in the noble metals inhibit the formation of stacking faults in appreciable concentration. This marked influence of transitional solutes was attributed to the interaction of unfilled electronic levels of the atom.
Sastry, Bao and Anantharaman (1966) and Lele (1966) studied the various types of faults arising due to cold-work in Ag-Sb alloys. The works of Ahlers and Vassamillet (1967) on Cu-Ge indicating the uncertainty which might arise in twinning fault estimation from centroid measurements and of Krishnan (1967) on Ag-Zn, Ni-Al and Ni-Co alloy systems indicating existence of extrinsic faults are also worth mentioning. Recently detailed studies have been made by De and Sen Gupta (1970) on Cu-Sb alloys, Rao and Rao (1967, 1968), De (1969) on palladium and Ag-Pd alloys and Vasudevan et al. (1968, 1971, 1972) on Cu-Ga alloy systems. Sen Gupta and De (1970) have also made an interesting observation as regards the presence of extrinsic faults in a number of silver and copper-base alloys.

Delehouze and Deruyttere (1967) from detailed experimental observations on a fairly large number of Cu, Ag, Ni, Al and Pb base alloys, proposed an exponential variation of α with solute concentration $X$ of the form $\alpha = \alpha_0 e^{nX}$. The parameter $n$ is related with the solute-solvent valency difference. This study has been closely examined later on by Liu and Gallagher (1971) who made a theoretical evaluation of the relationship between solute concentrations, normalised by the solubility limit in some noble metal base (Ag and Cu) binary alloy systems and different parameters like deformation fault probability, dislocation density and S.F. energy. With the semi empirical relation of the form

$$\alpha = \alpha_0 \exp \left[ \frac{K_{\alpha} C}{(1+C)} \right]$$

proposed by Liu and Gallagher (1971) satisfactory agreements have been found with experimental data.
This work is thus an improvement over the similar attempt made by the previous workers namely, Delehouzee and Deruyttere (1967).

Another interesting feature i.e., the effect of the size of solute and solvent atoms in alloy systems (Size factor $S_P$), on the stacking fault concentrations in silver and copper base alloys has been critically analysed (King 1966, 1971; Chatterjee et al 1973; De and Sen Gupta, 1974). Recent analysis by De and Sen Gupta (1974) on a fairly large number of f.c.c. alloys of Cu and Ag has clearly shown that the size factor $S_P$ is also an important parameter in creating fault concentrations in alloys and that this parameter increases linearly with the increase in fault probability $\phi$ in the alloy systems studied.

In addition to the observations on binary alloys, X-ray diffraction studies have also been extended to a few ternary alloy systems by Patterson (1969), Salonen et al (1969) and very recently by Nagendra Naidu and Houška (1970) on Pd-Ag-An alloys. In these studies the solute effects on various micro-structural parameters have been investigated.

Apart from alloy systems a number of pure metals have also been studied. These include Ag and Al (Wagner, 1967), Wolfram (Williamson and Hall, 1953) thorium and $\alpha$-uranium (Krishnan 1966a,b), thorium and cerium (Ne Hargue, 1961; Arunachalam and Tangri, 1963), platinum (Toranto and Brotzen, 1961), lead (Bolling et al, 1961), silver (Agnihotri, 1963), iridium (Fortes, 1971) and palladium and iridium (Singh and Anantharaman, 1967, 1972).
4.2.2 Transmission electron microscopic observations

As a supplementary to the X-ray diffraction studies of stacking faults and stacking fault energy in f.c.c. metals and alloys, recently quite a large number of works have been made by transmission electron microscopy also, which revealed in certain cases interesting comparisons with the X-ray diffraction observations.

Imura et al (1963) and Art, Gevers and Amelinckx (1964) studied the effect of solute atoms on stacking fault energies in Cu-Mn, Cu-Zn, CuSi and Cu and Ag base Sn, Cd, Ge and Ga alloys respectively by the extended mode techniques of transmission electron microscopy. It has also been observed that while the additions of Zn and Si in the solvent Cu decrease the stacking fault energy of the respective systems the addition of Mn has least effect. This is quite in agreement with the X-ray observations of the effects of transitional solutes. The addition of non transitional solutes Sn, Cd, Ge and Ga in noble metals produce a non linear decrease in S.F. energy which is also in agreement with the increase in stacking fault probability with solute concentration as observed in X-ray analysis considering an inverse relationship between fault probability $\phi$. Similar observations have been made by Howie and Swann (1961). Gallagher (1966a,b) and Gallagher and Washburn (1966) from a node technique of T.E.M. in Ag-In system have made an important observation that the stacking fault energies of intrinsic and extrinsic faults are nearly equal.
so that there exists a possibility of the creation of extrinsic faults simultaneously with the intrinsic ones. However, comparatively less density of extrinsic faults as observed in X-ray and other studies was explained as due to the impedance to the occurrence of this fault arising from the co-operative glide which is necessary for its formation. In addition to these, many other interesting features including the presence of solute impedance force at room temperature which causes an irreversible increase of S.F. energy in high solute content alloys following a high temperature annealing treatment. Gallagher (1968a,b) also summarised the relative magnitudes of extrinsic and intrinsic stacking fault energies for a number of Ag and Cu-base alloys which requires confirmation from other experimental measurements.

Otte (1967) have made a good comparative study of X-rays and transmission electron microscopy on this, and concluded that X-ray measurements can yield absolute values for stacking fault energies if the values of certain parameters are known more accurately than they are at present.

Quader and Dodd (1968) from measurements of extended node radii of T.E.M. on Ag-Mn and Cu-Mn alloys concluded that Mn in copper base alloys behave as a multivalent element in reducing the stacking fault energy and confirmed the earlier X-ray observations by Goswami et al (1966).
Tistone, Sundahl and Chin (1970) have proposed a model for the stacking fault energy calculation in noble metals and alloys based on both d-band and free electron contribution to the cohesion. This theoretical model is able to explain at least qualitatively some of the experimental observations. A decrease in S.F. energy by the addition of a solute with an empty d-band and with (electron atom ratio Z = 1) (i.e. lithium in silver) was also predicted by this medel and verified in AgLi systems by the extended node technique. In a subsequent work, Tistone and Sundahl (1970) gave an explanation of the shape of the curve of stacking fault energy vs. the electron atom ratio observed in noble metal base alloys in terms of the singularity in screening of a free electron gas. Pande (1970) has made some estimation of stacking fault energies on Cu-Al alloy systems. Recently, Beissner (1973) and Chen and Falicov (1974) respectively made some theoretical calculations of stacking fault energy in pure metals like Al, Mg, Be, Cu, As and Au from model potential and in Si from the pseudo potential with a less satisfactory agreement with experimental data.

4.3. Studies on hexagonal metals and alloys

Relatively few studies have been made in hexagonal close packed structures though the X-ray diffraction study was initiated much earlier in this system.
Among pure hexagonal metals it is cobalt which perhaps received the earliest and also major attention. Edwards and Lipson (1942) made this early observation on cobalt and found that some of the X-ray lines are broadened. Wilson's (1942) interpretations of these results were only partially successful as he considered the existence of growth fault only. Detailed X-ray diffraction theory of deformed hexagonal system having been established, new measurements on the same cobalt by X-ray line breadth and line shape were made by Anantharaman and Christian (1956) and Houska and Averbach (1958). They established the ample evidence of the existence of both deformation and growth faults. Rama Rao and Anantharaman have recently made a series of studies (1962, 1963, 1965) on this hexagonal cobalt mainly by integral breadth and half-peak breadth methods. They have also studied the impact of thermal or mechanical treatments on the concentration of stacking faults in this metal. In addition to these, Mitra and Halder (1964) have made a detailed study on Co and adopting both line shape and line breadth measurements have determined the deformation and growth fault probabilities in the material annealed at different temperatures.

Besides cobalt, X-ray line broadening measurements have been made on hexagonal zirconium by Mogard and Averbach (1958). They used three sets of reflections and failed to get any concentration of stacking faults. Similar observation was also made by Spreadborough and Christian (1959) on hexagonal titanium. Recently, Lele and Anantharaman (1967) and Krishnan (1967) have
made comparatively detailed studies on hexagonal zirconium, titanium and hafnium. In the former study both the fourier analysis of line shape and the integral breadth method have been applied on these three hexagonal metals, while in the latter the deformation and growth fault probabilities of these three metals have been estimated depending only on half-width measurements. In all these measurements, zirconium showed negligible presence of deformation fault and titanium showed very small concentration \( (d \approx 0.008) \). Growth fault was considered to be absent in these hexagonal metals. Recently Gupta et al (1972) made a detailed integral breadth analysis on titanium and titanium-aluminium alloys in the hexagonal phase. The deformation fault density was found to increase gradually with the increase of aluminium content.

Akhtar and Teghtsoonian (1971) have utilised recently transmission electron microscopy on zirconium single crystal, and calculated the stacking fault energy on prismatic plane to be 66 ergs/cm\(^2\). They concluded that the plastic yielding of Zr crystal takes place by prismatic slip if the angle between tensile axis and basal plane is less than a certain critical value, and dynamic recovery occurs due to cross slip from prisms to the basal planes. In a later work on Zr Akhtar (1973) concluded that of the two most commonly observed slip planes viz. basal \( \{0002\} \) and first order prism \( \{10\overline{1}0\} \), prismatic slip continues to be easiest slip mode at all temperatures below 860°K and with increasing temperature the relative ease of basal slip increases.
These investigations pointed out that the stacking fault energy is the only decisive factor rather than c/a ratio of close packing as was pointed out by Tyson (1967) in finding out the easiest slip mode in hexagonal systems. Recently Carpenter and Watters (1973) using transmission electron microscopy have studied the vacancy precipitation and resulting dislocation loops in quenched and aged Zr-Al alloys and zircaloy-2. They observed the presence of large vacancies in α-zirconium alloys at temperatures approaching α→β transformation. Ferguson et al (1973) studying hydrides in Hydrogen-zirconium alloys cooled from α-zirconium phase field by X-ray powder diffraction method, found that f.c.t. and β phase hydrides were formed when hydrogen-zirconium alloys were cooled from α-phase field, and quenching favoured the formation of the β phase. Recently Shechtman and Brandon (1973) studying on cold-rolled polycrystalline titanium sheet by T.E.M. observed that the active primary slip system is prismatic type slip \( \{11\overline{2}0\} \langle11\overline{2}0\rangle \) while the secondary slip system was found to be either prismatic or pyramidal type \( \{10\overline{1}1\} \). Basal slip could only in certain orientation of load directions be the primary slip systems. Wanhill (1973) in his work on the consideration of cleavage in alpha-titanium concluded from electron microscopical observations that cleavage fracture in α-Ti occurs only in alloys and on planes with high indices.

Magnesium was the next hexagonal metal which has also received wide attention by different workers. The earliest work...
on this hexagonal metal is by L'ele and Anantharaman (1964). They considered quite a number of reflections but applied integral breadth method and considered the entire broadening to be either due to particle size or due to strain as a whole, which, however, requires detailed considerations since both the effects act simultaneously in the broadening of diffraction profile. They found that for the strain parameter the mean deviation from mean for all reflections was much smaller than that due to particle size and hence concluded that the entire line broadening was due to strain only. Mitra and Misra (1967) using photographic technique considered four reflections namely 1010, 0002, 1120 and 1013 for Mg, and obtained the particle size and strain parameters from a single reflection method and also from Warren Averbach's (1949) method. These two methods show an appreciable disagreement in the respective parameters. Lele and Anantharaman (1967) in a later work on magnesium adopted both integral breadth and Warren Averbach's Fourier analysis methods for few reflections and observed very negligible concentration of stacking faults in agreement with previous results. Obara et al (1973) recently have observed from studies on single crystals of magnesium after C-axis comparison that \( \{1122\} \langle 1123 \rangle \) slip system operates at all temperatures viz. from room to 500°C, and dislocation has a strong preference to lie along basal plane. Some earlier works by T.E.M. on magnesium and zinc are by Thomas et al (1961) and Berghezan et al (1961) and these studies are also important so
far as the stacking fault energies are concerned for these systems. A detailed review of the works by electron microscopy and also by theoretical considerations have been made by Price, Mader and Swann (1968).

X-ray diffraction study on some hexagonal rare earth metals like Gadolinium, Terbium, Dysprosium, Holmium and Erbium have been done by Gupta and Anantharaman (1971). These studies have shown no evidence for faulting in all these metals except Gadolinium. In addition to the above studies on several hexagonal pure metals, a number of hexagonal alloys were also considered by different workers.

Stratton and Kichingsman (1965, 1966) studied the stacking fault probabilities in Ag-Sn, Ag-In and Au-Sn, Au-In alloys in the hexagonal phase. They found the presence of an appreciable quantity of deformation fault density in all these alloy systems. Sen Gupta and Goswami (1967) have also obtained appreciable quantity of deformation faults in hexagonal (§) phase copper-germanium alloys. Similar investigation and results have also been found by De and Sen (1968) in hexagonal silver-antimony alloys, from Fourier analysis and recently by De and Sen Gupta (1973) from variance method. One of the interesting observations in all these hexagonal alloys is that in contrast to f.c.c. alloy phases the stacking fault density decreases with increasing solute content. This result has qualitatively been explained from the considerations of free energies for the respective phases. The
X-ray observations are in good agreement with the transmission electron microscope investigation on hexagonal Ag-Sn alloy systems made by Ruff and Ives (1962). They observed that the stacking fault energy, a parameter inversely proportional to stacking fault density, increases appreciably and almost linearly with increasing solute content.

4.4 Studies on body centred cubic metals and alloys

X-ray studies on b.c.c. structures are also relatively few. Earlier works in this system are on molybdenum metal by Despujols and Warren (1958) and by Agnihotri (1963). In the later studies from multiple order reflections, no presence of stacking faults could be found in this metal, and this also agrees with the earlier work by Despujols and Warren (1958) on this. Despujols and Warren (1958) from only one pair of reflections have concluded that the particle size isotropy exists in this metal and therefrom they indicated negligible presence of stacking faults. Haider and Mitra (1963) on tungsten and Aqua and Wagner (1964) have extended the work on a number of b.c.c. refractory metals namely, niobium, tantalum, vanadium, chromium and tungsten. They observed that particle size isotropy factor is of the order of unity for most of the cases. Niobium only shows the largest deviation (~1.50) where as for tungsten it is exactly unity.

A brief review of the work on some b.c.c. refractory metals and alloys has been given by Hirschhorn (1963). Wagner and Aqua (1967)
have made a detailed Fourier analysis on a number Fe-Si b.c.c. alloys. They have observed the presence of both deformation and growth faults in these alloy systems due to cold-work. No drastic increase in stacking fault probability has been found with the increase in solute concentration and this has led them to conclude that the stacking fault energy does not change appreciably in this b.c.c. alloys with silicon concentration. Pegel (1968) calculated theoretically the stacking fault energies for different b.c.c. metals from two body central forces between nearest and next nearest neighbours, and concluded that the concept of dislocation splitting on $\{110\}$ planes was reasonable for all metals considered. Rothman and Cohen (1971) have recently studied some b.c.c. Mo-Re alloys, Nb, Fe and $\beta$-brass adopting Cohen's single line method, considering also the possible faulting on the planes other than 211. Sikka and Motoff (1973) studied from electron microscopy the neutron irradiated molybdenum and Suezawa and Kimura (1973) studied recently the quenched-in vacancies and their behaviour in quenched molybdenum. Pu-wen Ling et al (1974) have made recently some investigations on meta-stable beta- Ti-V alloys by optical and also by T.E.M. and have observed some interesting property changes including yield strength, work hardening and deformation texture in these b.c.c. alloys.