CHAPTER I

GENERAL INTRODUCTION

INTRODUCTION

In crystalline solids, the atoms are stacked together in a regular manner forming a three dimensional configuration which is obtained by a three dimensional repetition of a certain pattern unit. When the periodicity of the pattern extends throughout a certain piece of material, the material is spoken of as a single crystal. A perfect crystal should be infinite in size since finiteness of size means break of regularity of atomic arrangement at the boundaries. Atoms in a perfect crystal must necessarily be stationary at lattice points.

These conditions of an ideal crystal are not realizable in practice. All real crystals are finite in size and even a so-called single crystal consists, in reality, of small crystallites called domains, tilted among themselves by small but finite angles. At all temperatures, even at absolute zero, the atoms in a crystallite should execute small oscillations about their equilibrium positions. Apart from this, there may be displacements of the mean positions of atoms from the lattice site, caused by strain, dislocations, stacking and twining faults and also by the introduction of foreign atoms. There may be vacancies and interstitials and sometimes cracks and voids. A different type of defect is the lattice disorder where different constituent atoms randomly occupy the lattice sites. The periodicity of the lattice is thus broken due to the presence of these defects.

The very fact that a real crystal invariably contains defects is convincing enough that the study of lattice defects and disorders and their effects on the behaviour of solids, is a very much important field of solid state physics. Although different processes like cold working, hot working, annealing, quenching etc for changing these lattice imperfections have been in use for ages, studies on their effect on the latter started only during this century, when the crystalline concept of solids was proved to be correct and study of atomic arrangements in solid was made possible by X-ray diffraction. In fact, a considerable amount of recent research activity is concentrated along this line and gradually it is being felt that many of the peculiar behaviours of solids have to be attributed to the presence of these lattice defects. It is known that even a small number of defects contributes to striking macroscopic effects. Impurities change the relaxation times by several orders of magnitude in magnetic materials[1]. Electrical and heat conductions are controlled by scattering of electrons and phonons by defects[2,3]. Localized electronic levels, which lie in the energy gap between the valence and the conduction bands and which arise because of impurities, are responsible for electrical properties of semiconductors[4]. Strength properties of metals and alloys are known to be dependent on the size[5] and angular misorientation of mosaic blocks[6], lattice distortion, dislocation density and stacking fault probability[7]. Localized normal modes of vibrations around defects may cause normally

forbidden transitions to occur[8]. Lattice disorder causes an increase in the strength properties but at the same time reduces the thermal and electrical conductivities. Hence an understanding of the true nature of lattice defects and disorders is extremely important in order to understand the behaviour of real crystals.

As has been pointed out, lattice vibrations can be considered to be a dynamic lattice defect in contrast with the other static lattice defects. All thermodynamic properties, the electrical and heat conductions and many of the electronic processes are dependent on the frequency distribution of the normal modes of vibrations of the solid. The Debye characteristic temperature is an important parameter of lattice vibrations and the X-ray Debye temperature at high temperatures is a measure of the negative second moment of the frequency spectrum. That it is related to many physical properties like hardness, elastic properties, specific heat, thermal expansion, electrical resistivity etc is well known. In recent years many emperical relations have been obtained connecting the Debye temperature of materials with the formation energies of vacancies in alkali halides[9], activation energy of self diffusion in solids[10], formation and migration energies of point defects in metals[11], surface energy of brittle fracture[12], electrical super conductivity in transition metal binary alloys[13] etc. Hence experimental evaluation of this parameter is of extreme importance.

The static lattice defects interact with the lattice vibrations causing change in the frequency distribution function of the lattice. Following the pioneering work of Lifshitz[14] on the effect of lattice defects and disorders on the dynamical properties of crystals, the theoretical work in this branch of solid state physics has made considerable amount of progress. Any change in the frequency spectrum due to presence of disorder, therefore, is expected to be reflected in the measured Debye temperature which unlike the frequency spectrum can be experimentally evaluated accurately without much difficulty. Hence an experimental study of the influence of the lattice defects on the Debye characteristic temperature would be highly useful.

In the present work, an attempt has been made to study lattice defects and disorder and their effect on lattice vibrations in several alloys. For studying lattice defects one obvious scheme would be to make the atoms observable by using radiations whose wavelengths are of the same order as the atomic separations. X-ray, electron and neutron waves satisfy this criterion. We can either use microscopy if possible or employ the diffraction techniques. Construction of neutron and X-ray microscopes is a very difficult task. Although X-ray microscopy has made some progress, it has not been used so far for the present purpose. Electron microscope has not been able to resolve atoms because of aberrations involved, but it has been successful in giving

useful informations regarding lattice defects. Electron microscopy has the drawback that because of the poor penetrability of the electron beam, either the crude replica technique is to be used or the sample has to be cut into a very thin section. The process of making such thin sections may itself introduce new defects. Therefore, electron microscopy may not yield representative information regarding defects in the bulk of the sample. We have thus at our disposal the diffraction techniques. Because of the poor penetrability of the electron beam, electron diffraction techniques can not be used for studying bulk samples. Neutron diffraction requires a large sample, and the sample can be damaged and extra defects may be produced during experimentation. A reactor, which very few laboratories can provide, is needed for this purpose. On the other hand, X-ray diffraction method is free from the above difficulties and that is why it is much more common and of general use for studying lattice defects.

Since X-ray diffraction pattern is the Fourier transform of the electron distribution in matter, all the different types of defects should, in principle, be detected by X-ray diffraction studies. Practically, however, sensitivity of X-ray detection is the limiting factor. While the maximum sensitivity attainable by modern counter methods is of the order of one in a thousand, actual detection of the distortion in electron distribution due to defects would demand a sensitivity of the order of one in a million. There are also

theoretical difficulties like lack of precise knowledge of atomic scattering factor for the atoms in imperfect solids. Hence direct observation of the defects on an electron density map is not possible at the present stage of instrumentation and theoretical development. There are, however, certain effects of defects like size of coherently diffracting domains, strain distribution, cooperative displacement of atoms like stacking faults etc. which influence different parameters of X-ray diffraction. Careful study of the different X-ray diffraction parameters result in information regarding such effects on the basis of which a consistant model of defects may be attempted to be built up.

It is known that the effect of thermal motion on lattice vibrations is to decrease the intensity of Bragg reflection with an increase in the temperature. This reduction in intensity is more pronounced at higher Bragg angles. In addition to this effect a general background appears because of thermal diffuse scattering. These two effects may be made to yield informations regarding lattice vibrations in crystals. The reduction of intensity gives the value of the mean square displacement of atoms and the Debye temperature. The negative second moment of the frequency distribution function can also be evaluated from this. The temperature diffuse scattering, however, yields much more useful information. The intensity of temperature diffuse scattering gives the dispersion curve along symmetry directions which, when compared with the theo-