1.1 Introductory remarks:

Different properties of materials depend to a great extent on the type of constituent atoms and the nature of their arrangement in the solid. Solid state materials can be divided into two groups - amorphous and crystalline with various shades of crystallinity lying in between. The ideal amorphous material is one in which atoms are distributed at random. It can be easily seen that such perfect amorphous materials are very difficult to obtain specially when the finite size of the atoms produces a regularity of local arrangements. Similarly a perfect crystal is defined to be consisting of atoms stacked in a regular manner, forming a three dimensional array, which may be obtained by a three dimensional repetition of a certain pattern unit. It should also be infinite in size since finiteness of size means break in the regularity of the atomic arrangement. The atoms in a perfect crystal should necessarily be stationary at the lattice points. These conditions of a perfect crystal are very difficult to realise in practice. All real crystals are finite in size and even the single crystals consist, in reality, of small crystallites called domains tilted amongst themselves by small but finite amounts. The atoms in a crystalline solid execute small oscillations about the ideal lattice positions at all temperatures including absolute zero. Again the perfect crystallinity can break down because of the difference in the sizes of the constituent atoms. Moreover the atoms may be displaced from the ideal lattice sites as a result of the occurance of strain, dislocations, stacking faults, vacancies, interstitials etc. Thus it is obvious that the local arrangement of the atoms is a very important factor in determining the physical properties of materials.

Because of the fact that a real crystal invariably contains defects, the study of lattice defects and disorders and their effect on the behaviour of solids has developed into a very important branch of solid state physics. In fact, a considerable amount of recent research activity is concentrated in this line and many of the peculiar behaviour of the solids have been attributed to the presence of these lattice defects. It is well known that even a small concentration of defects change the macroscopic properties substantially. Impurities change the relaxation times of magnetic materials by several orders of magnitude. Electrical and thermal conductivities are controlled by the scattering of electrons and phonons by the lattice defects. Localised electronic levels which arise because of the impurities are responsible for the electrical properties of the semiconductors and the optical properties of the luminescent materials. Strength properties of the materials are influenced by the size and the misorientation of the mosaic blocks, lattice distortion, dislocation density and stacking fault probability. Lattice defects cause an increase in the strength properties but at the same time, reduce the thermal and electrical conductivities. Hence an understanding of the nature of the lattice defects 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 function of the normal modes of vibration 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 empirical relations have been obtained connecting the Debye temperature of materials with the formation energies of vacancies in alkali halides[1], activation energy of self diffusion in solids[2], formation and migration energies of point defects in metals[3], surface energy of brittle fracture[4], electrical super conductivity in transition metal binary alloys[5] etc. Hence experimental evaluation of the same is of extreme importance.

Anharmonicity in lattice vibration of materials is another important parameter and it accounts for many physical properties like thermal expansion which the harmonic approximation fails to explain. As has been discussed by Willis[6], the contributions to the Debye Waller factor because of the anharmonic vibrations is significant. Hence a knowledge of the extent of anharmonicity of lattice vibration in materials is essential for accurate determination of the structure factors. From a knowledge of the temperature variation of the Debye characteristic temperature the parameters characterising the atomic interaction potential can be obtained and most of the physical properties can be evaluated from the same.

The static lattice defects interact with the lattice vibrations causing a change in the frequency distribution function of the lattice. Following the pioneering work of Lifshitz[7] on the theory of lattice defects and disorder 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 the 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.

1.2 Defects in crystals:

It has been already indicated in the previous section that the arrangement of atoms in a real crystal cannot be ideally regular because of at least two compelling regions, viz., the finite size of the crystal causing a break in the regularity of the atomic arrangements at the boundary faces and the oscillations of atoms about their mean positions due to thermal effects. Considerations of extinction again show that a single crystal really consists of a number of mosaic blocks misoriented with respect to each other and each subject to limitations in regularity of atomic arrangements indicated above. There has been a systematic search for and study of similar limitations which are known as crystal defects or structure defects. Some of the important structure defects, other than those mentioned above are listed below:

Vacancies: Vacancies are caused by atoms being omitted from positions allotted to them according to the given scheme of regular arrangements. Vacancies can migrate inside a crystal and can sometimes form clusters.

Interstitials: These are caused by the inclusion of extra atoms in the space between the atoms in a regular lattice. Both interstitials and vacancies interact with neighbouring atoms in the regular lattice causing them to be displaced from their usual positions at lattice points - thus giving rise to strain fields. Interstitials and vacancies may also interact with each other causing a collapse of the vacancies.

Foreign atoms: Sometimes a lattice site or an interstitial position can be occupied by an atom of an electronic configuration which is different from the one stipulated in the lattice scheme. This gives rise to a change in the inter-atomic forces resulting in a strain field.

Dislocations: A crystal deforms by a portion of it being displaced with respect to the rest along an atomic plane. This displacement is called "slip" and the plane along which the slip occurs the "slip plane". The slip is not uniform over a slip plane in most real crystals. Slip may occur over only a part of a slip plane, the rest of the planes remaining unslipped. Read[8] has defined a dislocation to be a line imperfection forming the boundary within the crystal of a slipped area. It is not implied however, that every dislocation originates in a slip although it is a good pictorial representation. When the slip vector is at right angles to the slip planes the dislocation is said to be an edge dislocation. When the slip vector is parallel to the dislocation line the dislocation is called a screw dislocation. Within the dislocated region the general scheme of atomic arrangements is different from that of the undistorted crystal.

Burgers[9] showed that a dislocation can be characterised by what is known as the Burgers vector. It is defined as the vector which gives the magnitude and direction of the slip.

Dislocations may be distributed at random or may be arranged along arrays. Under certain circumstances the dislocations may be mobile and while moving may give rise to vacancies as well as interstitials. The out of step lengths due to dislocations when suitably combined partition a crystal into domains misoriented with respect to one another. The unequal bond-forces acting on either side of the out of step atom will cause displacement of neighbouring atoms which will be transmitted to some distance thus giving rise to a strain field. Under certain circumstances dislocations give rise to "stacking" and "twinning" faults - faults in the sequence between layer arrangements.

All the defects enumerated above are defects on an atomic scale. Besides these there may be defects on the electronic scale like colour centres, trapped electrons, holes etc.

1.3 X-ray studies on lattice defects:

Kinematical theory of X-ray diffraction tells us that for a perfect crystal intensities are concentrated at the reciprocal lattice point. Any kind of lattice defect spreads the intensity over domains of varying extent around the lattice point. Since spread in the intensity distribution curve is caused by lattice defects the nature and extent of the intensity spread is an obvious measure of the extent of crystal imperfection in the sample under study. This is true provided the intensity distribution curve can be interpreted in terms of the nature and the extent of lattice imperfection. A large volume of work has been concentrated around this effect and extremely illuminating results have been obtained.

Since different types of defects may be coexistent in different proportions, the problem is the separation of the observed effect into those for the different types of defects and then to identify and also make a quantitative estimation of the extent and distribution of each type of defect. If the defects are assumed to be unrelated to each other, the observed profile is a convolution of the diffraction profiles due to the individual defects and their separation is basically a problem of deconvolution. In the absence of precise information regarding the nature of diffraction profiles for different defects, deconvolution becomes a difficult task. The problem becomes comparatively easy if some parameter of the intensity spread is considered.

A diffraction pattern has the following characteristics - (a) positions of the diffraction maxima and (b) distribution of intensity about the diffraction maxima. It is easily seen that (a) is not independent of (b) since the position of the diffraction maxima is the peak of the intensity distribution.

The positions of the diffraction maxima in combination with the Bragg Law give the inter-planar spacings and the unit cell dimensions. The unit cell dimensions yield informations regarding the concentration of vacancies and interstitials[10] and dislocations[11]. Shift of the peaks also gives informations about the stacking fault probability[13].

Table 1.1

Parameters for the measurement of the spread of the intensity distribution around reciprocal lattice points.

Sl. No.	Parameter	Symbol and definition
1.	Half intensity width	$\beta_{1/2}$
2.	Integral width	$\beta = \frac{\int I(2\theta)\, d(2\theta)}{I_{max.}}$
3.	Fourier coefficient	F_n
4.	Variance.	$W = \frac{\int [2\theta - \langle 2\theta \rangle]^2 I(2\theta)\, d(2\theta)}{\int I(2\theta)\, d(2\theta)}$
5.	Fourth moment about mean	$\mu = \frac{\int [2\theta - \langle 2\theta \rangle]^4 I(2\theta)\, d(2\theta)}{\int I(2\theta)\, d(2\theta)}$

The curve representing the intensity distribution can be characterised by different parameters. The different parameters which are used in the study of lattice defects have been given in Table 1.1. With the help of these parameters detailed informations regarding crystallite size, crystallite size distribution, strain, strain gradient, dislocation density, faulting probabilities, variation in the interplanar spacings, mistakes, paracrystalline distortion etc. can be obtained. Excellent reviews on the development of the different techniques, their application and sensitivity towards errors are available in Wilson[14,15], Warren[16] and Klug and Alexander[17]. Hence, in the present case the details of those methods which were used in the present investigations have been given in the relevant chapters.

Because of the strain field around the various defects, there is displacement of atoms from their normal positions in the lattice. Huang[18] had shown that such displacements of the atoms would give rise to diffuse scattering of the X-rays. With further development of the theories and improved experimental techniques it has now become possible to study the strain field around the defects from diffuse scattering measurements. Dederichs[19] has reviewed the developments in the field.

1.4 Scattering of X-rays by Lattice vibrations:

At all temperatures - even at absolute zero - the atoms in a crystalline solid execute small oscillations about their equilibrium positions. The relation between the macroscopic elastic properties of the solids with the atomic force constants which together with the atomic masses determine the scale of lattice vibrations has been the subject of considerable study starting with the works of Debye[20] and Born and Von Karman[21].

The development of the theory of lattice dynamics by Debye[20], and Born and von Karman[21] was almost at the same time as the discovery that crystal lattice can diffract X-rays. Immediately afterwards these two branches of physics were connected by the development of the theory of the effect of thermal vibration on the diffraction of X-rays in crystals - the name of workers associated with this development being Debye[22], Schrodinger[23], Waller[24], Faxen[25] and Laval[26]. The whole subject has been brought together by James[27] in his book. Calculation by these workers showed that the effect of temperature vibration is, apart from a diffuse background - a reduction in the intensities of the crystalline reflections by the well known Debye-Waller factor, $e^{-2B\sin^2\theta/\lambda^2}$ where $B = 8\pi^2\langle u_s^2\rangle$. In this expression $\langle u_s^2\rangle$ is the mean square displacement of a lattice point in a direction perpendicular to the reflecting plane, θ is the Bragg angle and λ the wave length of the incident X-rays. For a cubic crystal the quantity B will be independent of the choice of the direction S, otherwise it has the property of a second order tensor. The above is true for a crystal containing only one kind of atom. For the general crystal containing more than one kind of atom the effect would be to replace the atomic scattering factor of each atom in the structure factor by $f_n e^{-B_n \sin^2\theta/\lambda^2}$. Here B will be different for different types of atoms.

In addition to the reduction in the intensities of the crystalline reflections, appearance of diffuse scattering is observed because of the thermal motion of the atoms in the lattice. Faxen[25] had shown that there would be a maxima in the diffuse background and gave a formula for their positions.

Experimental discovery of the extra laue spots in 1938 by Laval[26] Raman[28] and Preston[29] stimulated new interest in the field and lead to the determination of the elastic constants and frequency spectrum of lattice vibrations of many materials (Wooster[38]).

The intensity of scattered X-rays from a monatomic cubic crystal can be written as a series of terms given by,

$$\begin{aligned} I_{eu} = & f^2 e^{-2M} \sum_m \sum_n e^{(2\pi i/\lambda)\vec{S}\cdot(\vec{r}_m-\vec{r}_n)} \\ & + f^2 e^{-2M} \sum_m \sum_n e^{(2\pi i/\lambda)\vec{S}\cdot(\vec{r}_m-\vec{r}_n)} \sum_{kj} G_{kj} \cos 2\pi \vec{k}\cdot(\vec{r}_m-\vec{r}_n) \\ & + f^2 e^{-2M} \sum_m \sum_n e^{(2\pi i/\lambda)\vec{S}\cdot(\vec{r}_m-\vec{r}_n)} \Big[\sum_{kj} G_{kj} \cos 2\pi \vec{k}\cdot(\vec{r}_m-\vec{r}_n)\Big]^2 \Big/ 2 \\ & + \cdots \end{aligned} \qquad \ldots \quad 1.1$$

where,

$$2M = \frac{2B \sin^2\theta}{\lambda^2} = \sum G_{kj} \qquad \ldots \quad 1.2$$

$$G_{kj} = \frac{1}{2}\Big[\frac{2\pi\vec{S}}{\lambda}\cdot\vec{e}_{kj}\Big] \langle a_{kj}^2 \rangle \qquad \ldots \quad 1.3$$

$$\langle a_{kj}^2 \rangle = \frac{2\langle E_{kj}\rangle}{N m \omega_{kj}^2} \qquad \ldots \quad 1.4$$

$$\langle E_{kj} \rangle = \frac{\hbar\omega_{kj}}{e^{\hbar\omega_{kj}/kT}-1} + \frac{1}{2}\hbar\omega_{kj}$$

$$\vec{S} = \vec{s} - \vec{s}_0 \qquad \ldots \quad 1.5$$

In the above equations I_{eu} is the intensity in electron units, f the atomic scattering factor, λ the wavelength of X-rays, $\vec{r}_m$, $\vec{r}_n$ the position vectors of the m^{th} and n^{th} atoms, $\langle\vec{e}_{kj}\rangle$ the unit vector in the vibration direction, a_{kj} the amplitudes, $\langle E_{kj}\rangle$ the average energy per wave and ω_{kj} the frequency of the elastic wave with wave vector $\vec{K}$ and with j^{th} polarisation ($j = 1, 2, 3$), N the total number of atoms and $\vec{s}, \vec{s}_0$ are the unit vectors along the directions of the incident and diffracted waves.

The zeroeth term in equation 1.1 is the ordinary sharp crystalline reflection reduced by the temperature factor e^{-2M}. The next term is called the first order temperature diffuse scattering and gives the diffuse scattering in which one phenon is involved. The next term is second order temperature diffuse scattering in which two phonons are involved and so on. Generally terms involving third or higher order interaction are negligible compared to the first order one. Equation 1.2 can be written in case of monatomic ~~cubic~~ cubic crystals as,

$$2M = \frac{4}{3}\,\frac{\sin^2\theta}{\lambda^2}\,\frac{1}{Nm}\sum_{\nu}\nu^{-2}E\left(\frac{h\nu}{kT}\right) \qquad \ldots \quad 1.6$$

where N is the total number of particles in the crystal, m the atomic mass and ν the frequency of vibration and

$$E\left(\frac{h\nu}{kT}\right) = \frac{1}{2}h\nu + \frac{h\nu}{e^{h\nu/kT} - 1} \qquad \ldots \quad 1.7$$

In terms of the frequency distribution $N(\nu)$ defined as the number of frequencies between the frequency range ν and $\nu + d\nu$ in the limit $d\nu \to 0$, equation 1.6 can be written as

$$2M = \frac{\sin^2\theta}{\lambda^2}\,\frac{4}{m}\,\frac{\int E\left(\frac{h\nu}{kT}\right)\nu^{-2}N(\nu)\,d\nu}{\int N(\nu)\,d\nu} \qquad \ldots \quad 1.8$$

Since $2M$ involves a sum over all of the elastic waves it is possible to make certain approximations which amount to averaging before summation. We make the assumption as given in James[27], that all waves can be considered as purely longitudinal or purely transverse. By taking average longitudinal and transverse velocities, we have,

$$2M = \frac{4h^2 T}{mk}\left(\frac{\sin^2\theta}{\lambda^2}\right)\left\{\frac{1}{\Theta_l^2}\left[\phi(x_l) + \frac{x_l}{4}\right] + \frac{2}{\Theta_t^2}\left[\phi(x_t) + \frac{x_t}{4}\right]\right\} \qquad \ldots \quad 1.9$$

where $\Theta_l = \frac{h\nu_{ml}}{k}$; $\Theta_t = \frac{h\nu_{mt}}{k}$; $x_l = \frac{\Theta_l}{T}$; $x_t = \frac{\Theta_t}{T}$

and $$\phi(x) = \frac{1}{x}\int \frac{\xi\, d\xi}{e^{\xi} - 1} \qquad \ldots \quad 1.10$$

ν_{ml} and ν_{mt} are the maximum frequencies for longitudinal and transverse waves. For $x < 2$, i.e. $T > \frac{\Theta}{2}$; $\left(\phi(x) + \frac{x}{4}\right)$ is closely the same for longitudinal and transverse waves. We next introduce an average Θ defined by,

$$\frac{3}{\Theta^2} = \frac{1}{\Theta_l^2} + \frac{2}{\Theta_t^2} \qquad \ldots \quad 1.11$$

With this average characteristic temperature Θ and the average ratio $x = \frac{\Theta}{T}$ we have,

$$2M = \frac{12h^2 T}{mk\Theta^2}\left[\phi(x) + \frac{x}{4}\right]\frac{\sin^2\theta}{\lambda^2} \qquad \ldots \quad 1.12$$

The averaging involved in equation 1.11 is a little different from the Debye theory of specific heats so that Θ of equation 1.12 is different from Θ_D obtained from the specific heats. Zener and Billinsky[31] have obtained a relation connecting the X-ray and specific heat Debye temperatures in terms of the Poisson's ratio.

Comparing equations 1.8 and 1.12 we can express the experimentally determined Debye temperature in terms of the frequency distribution. One obtains,

$$\frac{1}{\Theta^2} = \frac{k}{3h^2 T\left[\Phi(x) + \frac{x}{4}\right]} \quad \frac{\int E\left(\frac{h\nu}{kT}\right)\nu^{-2} N(\nu)\, d(\nu)}{\int N(\nu)\, d\nu} \qquad \ldots \quad 1.13$$

The above relation simplifies at high temperatures to

$$\frac{1}{\Theta^2} = \frac{k^2}{3h^2} \quad \frac{\int \nu^{-2} N(\nu)\, d\nu}{\int N(\nu) d\nu} \qquad \ldots \quad 1.14$$

Thus at high temperatures, the experimentally determined X-ray Debye characteristic temperature is related to the negative second moment of the frequency spectrum.

1.5 Contribution of anharmonicity of lattice vibrations to the reduction in diffracted intensities:

There are certain limitations in the conventional procedure for determination of the structure factors because of the use of the harmonic approximation in the evaluation of the Debye Waller factor. Harmonic vibration of the atoms in a crystal does not explain many important physical properties like thermal expansion. Anharmonic effects are observed in crystals even at 0°K and their contribution is quite large at high temperatures. In 1962, Lonsdale[32] had commented that "the Debye Waller theory has never been extended quantitatively .... to temperatures near the melting point, where anharmonic vibrations become increasingly important". Since then, several workers have given expressions for the Debye Waller factor and the Debye characteristic temperature at high temperature by including cubic and quartic anharmonic terms on the expressions for the interaction energies in the crystal. Some of the important works being that of Krivoglaz and Tekhonova[33], Hahn and Ludwig[34], Maradudin and Flin[35], Kashiwase[36] and Willis[37]. As has been pointed out by Willis[37], the most detailed analysis of the effect of anharmonicity on the Debye-Waller factor is that of Maradudin and Flin[35]. Willis[37] has simplified their calculations by assuming that the atoms vibrate in a potential field which is not effected by the motion of the neighbouring ones and have reproduced some of the important results. In spite of these developments very few experimental works on the X-ray diffraction studies of anharmonicity of lattice vibrations in materials have been reported.

1.6 Effect of defects and ordering on lattice vibrations:

Many works on the theory of the effects of defects on the dynamical properties of crystals starting with the pioneering work of Lifshitz[38,39] have been reported. Lifshitz[40] and Maradudin[41,42] have given an excellent review of all the works in this field of solid state physics. These are mainly concerned with the modifications in the frequencies of atomic vibrations due to the introduction of impurity atoms in the crystals. It is found that because of introduction of the impurities localised modes are produced which lie outside the frequency spectrum of the host lattice. For example, when a lighter atom or an atom whose force of interaction with the host atom is larger than that between the host atoms is introduced into the crystal, modes of vibration whose frequencies are larger than the maximum frequency of the unperturbed host lattice occur. In addition to the production of localised vibrations, the introduced impurities also alter the continuous frequency spectrum of a perfect crystal. Lehman and Dewames[43] and Kagan and Iosilevskii[44] have explained the low temperature enhancement of the specific heat of crystals containing heavy impurities to be due to such changes.

As a consequence of the changes in the frequency specturm, the Debye characteristic temperature and the Debye Waller factor are also expected to change. This view that the Debye characteristic temperature is influenced by the imperfections present has been verified in case of different substances by various techniques like Mossbauer effect, resistivity and specific heat measurements. From resistivity measurements, Bowen and Rodeback[45] have observed a change of 45°K in the Debye temperature of cold worked and annealed copper wires. Giaque and Archibald[46] have reported that the heat capacity of small crystallites of MgO is greater than that of large crystals. Inelastic neutron scattering studies by Reider and Horl[47] on MgO crystallites show that the Debye temperature changes with particle size. Mossbauer effect measurement of the Debye characteristic temperature of small particles of tin (250Å) by Suzdalev et al[48] and gold by Marshall and Wilenzich[49] show similar variations with crystallite size.

Since both the Debye characteristic temperature and the various defect parameters can be obtained accurately from the same intensity data, X-ray diffraction method is most suitable for the study of the influence of the lattice defects on the Debye temperature. Though many works on the X-ray studies of changes in the Debye characteristic temperature due to deformation have been reported, the results are controversial. Again there is no cohsensus of opinion regarding whether the change in integrated intensity is at all associated with changes in the Debye characteristic temperature or is entirely due to other effects. Results of different workers on the Debye characteristic temperature of deformed materials and how correction of the intensities for different effects would improve their results has been discussed in chapter VIII.

Many workers[50-57] have attempted to obtain expressions for the Debye characteristic temperature of binary disordered alloys. Mitra and Chattopadhyay[57] have compared the values predicted by the theoretical expressions obtained by different workers with experimental data for Cu-Ni alloys and have observed that their expressions gives the best fit. Very few works on the additivity of Debye characteristic temperature in ordered alloys have been reported. Mitra and Chaudhuri[58] have extended the expressions of Mitra and Chattopadhyay[57] for the case of binary ordered alloys. Both the above works[57,58] are valid for the case when the alloy and the constituents all have the same structure. Mitra and Chaudhuri[58] have shown that these additivity relations can be used as an alternative method for determining short range ordering at least in those cases where the conventional methods fail because of the constituent atoms having the same scattering factor.

1.7 Aim, objective and scope of the present work:

It is evident from the above sections that lattice defects play an important role in determining the various properties of real crystals including the lattice vibrations. Debye characteristic temperature is an important parameter of lattice vibration and is connected with many physical properties. Hence a study of the lattice defects and Debye temperature of materials, and the effect of lattice defects on the Debye temperature is of great importance. To test the validity of assumptions and approximations of the theories on the effect of lattice defects on the parameters characterising lattice vibrations, it would be necessary to compare the theoretical values with the experimentally determined ones. This comparison may serve as a guide for a better theoretical approach. With this end in view, studies on the variation of the Debye characteristic temperature with defects and ordering was undertaken. Since X-ray diffraction method provides a good means to study both the defects and the Debye temperature of the sample simultaneously without causing any damage to it, this method was chosen for the present investigation. Samples representing different types of materials viz. KCl and KCl doped with TlCl belonging to non metallic ionic crystals; Cu, Al and Cu-Al alloys belonging to the metallic f.c.c. system; W, a highly isotropic b.c.c. metal and Co, an h.c.p. metal having layered structure with strong intra-layer and weak inter-layer bonding were chosen.

In order that the Debye characteristic temperature obtained from the X-ray diffraction method be accurate and reliable, one should correct the intensity data for thermal diffuse scattering, extinction, non-linear background etc. Most of the previous workers have failed to correct for one or more of these factors. In the present investigation the intensities were corrected for all these effects. In some cases where it was felt that the existing methods of correction were inadequate, some improvements were made by developing and modifying them. The expressions available for correcting diffraction profiles for temperature diffuse scattering in h.c.p. metals are that of Mitra and Misra[59] where they have assumed the Brillouin zone to be spherical. This is not true for materials having widely different "a" and "c" values. Hence the expressions were extended for the case of elliptical Brillouin zone. Most of the previous workers have failed to correct their intensities for both primary and secondary extinction. For correcting the intensities diffracted by single crystals of KCl and KCl:TlCl, the polarisation ratios i.e. the ratios of the electric vectors representing the diffracted wave normal and parallel to the plane of reflection were measured and the extinction factors were obtained by using Zachariasen's[60] theory of X-ray diffraction from real crystals. "m", a parameter characterising the degree of perfection, the size and misorientation of the mosaic which are of great importance for characterising single crystals were also obtained from the polarization ratios. Intensities diffracted from polycrystalline samples were also corrected for combined extinction following the newly developed method described by Mitra and Chattopadhyay[61]. Expressions were also obtained in the present case for correcting the intensities for truncation of the line profile at finite intervals which is significant specially in the higher order reflections of cold worked materials.

The study of lattice defects in materials is necessary in order to correlate the defect parameters with the Debye characteristic temperature. But this study of lattice defects as such is also important. Although the lattice defects in metals and alloys have been studied by a large number of workers, very few investigations on the lattice defects in non-metallic materials like alkali halides have been reported. No work on the annealing behaviour of lattice defects in alkali halides or on the effect of impurities on the same has been reported. Hence a complete study of the lattice defects in KCl and KCl containing different proportions of TlCl, cold worked and then annealed at different temperatures, was undertaken by employing the variance analysis of the line profiles.

Though many workers have measured the Debye characteristic temperature of KCl at different temperatures, some of the results are not accurate because the intensities were not corrected properly for TDS, extinction, background etc. No work on the changes in the Debye temperature due to the addition of impurities or deformation has been reported. Hence a study of the Debye characteristic temperature in pure and doped KCl was undertaken. Measurements were made both in case of single crystals and cold worked and annealed powders. Change in the Debye characteristic temperature as a function of the different defect parameters was studied. Since no reliable X-ray data on the Debye characteristic temperature of the tungsten and cobalt existed and because of the specialities in their structure mentioned earlier, a study of the variation of the Debye characteristic temperature with various defects in them was undertaken. The variation in the Debye characteristic temperature has been explained to be due to changes in the lattice parameter, increasing surface contribution and changes in the force constants at the extended lattice defects. Relative contribution of each of the above causes has been estimated.

Harmonic approximation for lattice vibrations fails to account for many properties of real crystals like the increase in the specific heat beyond the value $3Nk$ with increasing temperature, the existence of thermal resistance, the coefficient of thermal expansion, the occurrence of multiphonon processes in Raman scattering etc. Hence a study of anharmonicity of lattice vibration in materials is of great importance. Thermal expansion of Cu, Al and Cu-Al alloys was studied. Temperature variation of the Debye characteristic temperature is another important parameter and several theoretical works on the determination of the different anharmonicity parameters from the same have been reported. However very few experimental works on their determination have been reported. No work on the effect of lattice defects on the various anharmonicity parameters exists. Hence a study of the anharmonicity of lattice vibrations in deformed and annealed Cu,Al and Cu-Al alloys was undertaken. The parameters characterising the anharmonic potential were obtained and the influence of lattice defects on the same was studied. With the help of these parameters some of the macroscopic properties of the materials were calculated. Change in the force constants and the Debye temperature at the defects was calculated with the help of the potential parameters measured in the present case and a comparison was made with the experimentally observed changes.

Since Debye characteristic temperature is related to many physical properties of materials, an expression connecting the Debye characteristic temperature of alloys with that of the constituents and the degree of ordering would be of great help for material scientists. Though several relations on the Debye temperature of disordered binary alloys[50-57] have been reported, very few works for the ordered alloys[58] exist. Hence relations connecting the force constants, elastic constants and Debye temperature of binary alloys with the corresponding parameters for the constituent metals, concentration of the constituents and the correlation and long range order parameter were derived. Unlike the previous works the present expressions are valid for all cases with the alloy and the constituents having any of the cubic structures without any restriction and for all cubic superlattices. It has been shown that the expressions of Mitra and Chattopadhya[57] and Mitra and Chaudhuri[58] can be obtained as special cases of the present expression. The relations were also extended for the case of ternary alloys and mixed crystals. Validity of the relations were tested by applying to the cases of Ag-Pd, Au-Pd, Au-Pt, Fe-Cr, Cu-Al, Ag-Au-Pd systems and comparing the obtained values with the experimental values taken from literature. The additivity relations successfully explained the concentration variation in the elastic constants of the α-Cu-Al alloys to be due to increase in short range ordering with increase in Al concentration. The obtained S.R.O. parameters agree well with the X-ray diffuse scattering observations by different workers.