4.1. Crystal Structures:

In this thesis we have dealt with three different host crystals $\text{Cs}_2\text{CdCl}_4$, $\text{Rb}_2\text{CdCl}_4$ and $\text{CdCl}_2$ doped with different divalent first-row transition-metal ions and one concentrated crystal $\text{Rb}_2\text{MnCl}_4$, structures of which have been reported respectively by Siegel and Gerbert \cite{1}, Seifert and Koknat \cite{2}, Pirsker and Tatarinova \cite{3} and Goodyear et al \cite{4}. All the compounds $\text{Cs}_2\text{CdCl}_4$, $\text{Rb}_2\text{CdCl}_4$ and $\text{Rb}_2\text{MnCl}_4$ are isostructural with $\text{K}_2\text{NiF}_4$ so that they may be discussed under the general name $A_2B\text{Cl}_4$ (where $A = \text{Cs}$ or $\text{Rb}$ and $B = \text{Cd}$ or $\text{Mn}$).

All the $A_2B\text{Cl}_4$ compounds under our investigation are tetragonal belonging to the space group $I4/mmm$. Each unit cell contains two molecules which are equivalent in all respects. The $B^{2+}$ ions are octahedrally coordinated by six $\text{Cl}^{-}$ ions. The $\text{Cl}^{-}$ ions at the equatorial vertices are shared with neighbouring octahedra so that each octahedron is linked to four other octahedra to form layers perpendicular to (001) plane, the $c$ dimension accommodating two such layers. The two $\text{Cl}^{-}$ ions at the unshared vertices are closer to the $B^{2+}$ ions in all the compounds, so that the octahedra are axially compressed along
the four-fold axis. The crystallographic c-axis and the four-fold rotation axis also coincides for all the compounds. Thus the site symmetry of the $B^{2+}$ ions is (axially compressed) tetragonally distorted octahedral, i.e. $D_{4h}$.

In $Cs_2 CdCl_4$, the crystallographic parameters are $a = 5.26$, $c = 16.88$, $Cl(1)-Cl(1) = 3.72$, $Cl(1)-Cl(2) = 3.64$, $Cd-Cl(1) = 2.64$ and $Cd-Cl(2) = 2.51$ and those for $Rb_2 MnCl_4$ are $a = 5.05$, $c = 16.14$, $Cl(1)-Cl(1) = 3.57$, $Cl(1)-Cl(2) = 3.55$, $Mn-Cl(1) = 2.53$ and $Mn-Cl(2) = 2.50$ all in units of $\AA$. These parameters for $Rb_2 CdCl_4$ are not available in the literature but the structure is strictly isomorphous [2] with that of $K_2 NiF_4$. On the other hand, $CdCl_2$ has $D_{3d}$ site symmetry at the $Cd^{2+}$ sites [3] with hexagonal unit cell (consisting of three rhombohedral cells) having the parameters $a = 3.85$, $c = 17.46$, $Cd-Cl = 2.74$, and $Cl-Cl = 3.68$ $\AA$.

4.2.1 Preparation of crystals:

All the doped and concentrated crystals used in our study were grown by vertical Bridgman technique. The starting chemicals ($CsCl$, $RbCl$, $CdCl_2\cdot2.5H_2O$, $MnCl_2\cdot4H_2O$, $FeCl_2\cdot4H_2O$, $CoCl_2\cdot6H_2O$, $NiCl_2\cdot6H_2O$, and $CuCl_2\cdot2H_2O$) were of G.R. quality from either BDH or E.Merek. The starting materials $Cs_2 CdCl_4$ and $Rb_2 CdCl_4$ were prepared by taking stoichiometric amounts of $CsCl$ (or $RbCl$) and $CdCl_2\cdot2.5H_2O$, dissolved in HCl solution, evaporated till precipitated, then dried in a dessicator and
finally dried in an oven at 120°C for hours long enough to drive out any water content. The dopant materials $A_2MCl_4$ (where $M = Mn, Fe, Co, Ni, and Cu$) were also prepared in the same manner. Small amounts (2-5% by weight) of $A_2MCl_4$ was then intimately mixed with $A_2CdCl_4$ and filled in a long tapered specially made pyrex capsule (central diameter $\approx 8$ mm). The capsule was then evacuated and sealed and slowly lowered by means of a variable speed synchromotor through a vertical cylindrical furnace having a constant central temperature zone and a negative temperature gradient towards the lower end. The short central region of the furnace melts the mixture, while the crystal grows and becomes annealed in the lower region. The temperature of the central zone was maintained at 10°C above the melting points of the individual host crystals (melting points for $Cs_2CdCl_4$, $Rb_2CdCl_4$, and $CdCl_2$ are 473°C, 437°C, and 568°C, respectively). The optimum rate of lowering of the capsule through the furnace was found to be 1 mm per hour. The process was repeated several times for obtaining good quality large single crystals. $Rb_2MnCl_4$ and $CdCl_2:M^{2+}$ crystals were also grown similarly.

4.2.2. Chemical analyses of the crystals:

Since the crystals we studied are of the types $A_2Cd_{1-x}M_xCl_4$ and $Cd_{1-x}M_xCl_2$, (where $A = Cs$ or $Rb$ and $M = Mn$, $Fe$, $Co$, $Ni$, and $Cu$) the value of $x$, i.e. the molar proportion
of the paramagnetic ion, is to be known. The following analytical methods were used to find \(x\) for the different compounds. For estimation of elements, known weights of the respective substances were dissolved in water and their aqueous solutions were treated as follows:

**Mn\(^{2+}\):** The aqueous solution was first fumed with sulphuric acid twice or thrice for expulsion of hydrogen chloride and the residue was dissolved in water, the solution was oxidised with sodium bismuthate, filtered through a sintered glass crucible. To the filtrate was added a known volume of excess of Mohr’s salt solution and excess of Mohr’s solution was titrated back with \(\text{KMnO}_4\).

**Fe\(^{2+}\):** The solution was estimated after reduction (if any \(\text{Fe}^{3+}\) is formed due to aerial oxidation) with stannous chloride followed by addition of mercuric chloride, phosphoric acid as usual and titration of the resulting solution with standard potassium dichromate using barium diphenylamine sulphonate indicator.

**Ni\(^{2+}\):** Nickel was determined gravimetrically by precipitation from the aqueous solution with dimethylglyoxime in presence of slight \(\text{NH}_4\text{OH}\). The precipitate was digested on water-bath for about an hour, cooled, filtered, dried and weighed.

**Co\(^{2+}\):** As in the usual analytical method \(\text{Cd}^{2+}\) interferes with \(\text{Co}^{2+}\), we estimated \(\text{Co}^{2+}\) by the spectroscopic method. In this method, 2 ml of conc. \(\text{HNO}_3\) is added to the solution and the
mixture is evaporated to dryness. It was then dissolved in 10 ml of water containing 0.5 ml of (6N)HCl and boiled. 2 ml of 0.1% aqueous nitroso-R-salt followed by 2 gm of sodium acetate was added. Using Bromocresol green indicator pH is brought to 5.5 in cold. Boiled for 1 minute and then cooled and the absorption spectrum of the solution was taken at 550 nm at which the reagent absorbs very little.

Cu$^{2+}$: Copper was estimated volumetrically by iodometric method. The sample was digested with 5 ml conc. HNO$_3$ and 0.5 ml conc. H$_2$SO$_4$ till fuming. The digested mass was dissolved in water and the solution was made ammoniacal. The ammoniacal solution was boiled to remove excess ammonia. To the cooled solution 2 ml acetic acid and 1-2 gm potassium iodide was added and kept in dark. After 5 minutes the liberated iodine was titrated with standard N/100 thiosulphate solution using starch as indicator. For sharp end point ammonia thiocyanate was used.

4.3. Crystal cutting and orientation:

Repeated zone-refinements yielded brilliantly coloured (Mn$^{2+}$: pale rose; Fe$^{2+}$: greenish-yellow; Co$^{2+}$: blue; Ni$^{2+}$: pinc; and Cu$^{2+}$: golden-yellow) doped single crystals of cylindrical shape (diameter $\approx$ 6 mm) and as long as 20 mm. Portions of the crystals with good optical quality were selected and cut from the boule. Since none of the crystals showed any cleavage plane, the optic axis (c-axis) and the axes
perpendicular to the optic axis were determined by means of a polarizing microscope. Then the piece was cut into size with a razor blade and polished on a fine sand-paper. Finally the piece was polished with fine emery paper and chamois leather. Crystals of different dimensions were selected for facilitating the measurements of different polarized spectra. Crystals of different path-lengths were also used depending upon the intensity of the d-d bands under investigation. Crystals were mounted on the brass crystal holders by means of some conducting materials, e.g. silver dag. The proper orientation of the crystals were checked under polarizing microscope after mounting in the cold-finger dewar.

4.4. Instruments for optical measurements:

The absorption spectra were recorded on a Cary model 17-D spectrophotometer and the emission and emission excitation spectra were recorded on a Perkin-Elmer MPF-44A fluorescence spectrophotometer. The spectra were recorded both at room-temperature and liquid nitrogen temperature.

A cold-finger-type metal cryostat with two quartz windows was designed and fabricated to facilitate the low temperature measurement of the optical absorption spectra. Liquid nitrogen was allowed to come in close contact with the brass crystal-holder. Beam condensers were used to concentrate the incoming light beam on the crystal and to focus the outgoing light beam
on the detector system. A U-shaped metallic tube was used to blow dry air on the quartz windows to wipe out any water or ice particles deposited on the windows. A calcite crystal polarizer was used to measure the polarized spectra and was placed in between the source and the crystal. The \( \pi \)- and \( \sigma \)-polarized spectra were recorded with the electric vector of the incident light parallel (\( \hat{E} \parallel c \), \( \hat{I} \perp c \)) and perpendicular (\( \hat{E} \perp c \), \( \hat{I} \perp c \)), respectively, to the crystal \( c \)-axis, the \( c \)-axis being contained in the plane of the crystal. The axial spectra (\( \alpha \)) were obtained with the unpolarized light propagating along the \( c \)-axis (\( \hat{I} \parallel c \)), the \( c \)-axis being perpendicular to the plane of the crystal.

For emission measurements, the single crystals were taken in a long thin-walled quartz tube which was immersed in liquid nitrogen contained in a quartz dewar. Suitable filters were used wherever necessary. A 150W xenon lamp was used as the exciting source. Dry air blowing arrangements were also used in this case.

As it is known that the xenon lamp has some strong emission bands in the 450 - 490 nm spectral region, these emission bands due to xenon were carefully subtracted from the observed emission and excitation spectra with the help of the literature supplied with the instrument. Similarly, the Cary spectrophotometer has some base-line oscillations in the near infrared region due to the quartz optics used and to atmospheric water absorption. These oscillations at about 770,
970, 1270, 1400, 1800, and 2200 nm spectral regions cause uncertainties in the actual band positions and band shapes. However, these oscillations have been carefully corrected for by subtracting the base-line spectrum from the observed spectra.

4.5. Computation:

A matrix diagonalization programme which uses the Jacobi algorithm was written in FORTRAN-IV language to diagonalize the ligand field energy matrices for different 3d^n ions. The programme was designed to give the matrix elements, eigenvectors, eigenvalues and the transition energies for any given set of values of the crystal field parameters B, C, D_q and \( \Lambda \). The jobs were executed on a Burroughes-6700 computing system available at the Regional Computer Centre, Calcutta.
References