3.1. Introduction:

Since the emergence of the ligand field theory extensive studies have been made on the optical properties of the first-row transition metal ions in various ligand environments. It is, therefore, not feasible to give a comprehensive reference of all such studies. So we have confined our review mainly to the works on some selected halide compounds with special attention to the doped crystals. In spite of our best effort some relevant references may have escaped our attention due to non-availability of some journals and late arrival of a few other journals and periodicals. Some review articles on the subject are already available in the literature [1-7] which provide an overall idea of the absorption and emission profiles of the $3d^n$ ions.

3.2. Review of the Absorption Studies:

Many of the transition metal ions of the first series form stable compounds in different oxidation states. It therefore, appears to be inconvenient to deal with their spectra only by the names of the metals and, consequently, we discuss them
systematically under the electronic configuration to which they belong.

3.2.1. Configuration 3d$^1$:

Divalent scandium, Sc$^{2+}$, having the 3d$^1$ electronic configuration is not known to have any compound in this oxidation state. But Ti$^{3+}$, which has also 3d$^1$ structure, forms two octahedral halide compounds, α-TiCl$_3$ and α-TiBr$_3$. Dijkgraaf and Rousseau [9] measured the polarized absorption spectra of these two crystals at room-temperature (RT) and found that the bands are isotropically polarized in the (001) plane of the crystals. Two charge-transfer (CT) bands were also detected in the higher energy region.

3.2.2. Configuration 3d$^2$:

Both Ti$^{2+}$ and V$^{3+}$ belong to the 3d$^2$ configuration. No single crystal absorption spectra of Ti$^{2+}$ is found in the literature, but only the diffuse reflectance spectra of TiCl$_2$ and TiBr$_2$ are available [9,10].

The RT absorption spectrum of tetrahedral CsAlCl$_4$:V$^{3+}$ shows four bands at 8250, 9400, 10250 and 15000 cm$^{-1}$ out of which the first and the last were assigned to the $^3T_1(P)$ and $^3T_1(P)$ bands respectively and the other two remained unassigned [11]. Clark [9] studied VCl$_3$ and obtained three bands at 12500, 18300 and 19600 cm$^{-1}$. The first and the third were assi-
gned to the $^{3}T_{2g}(F)$ and $^{3}T_{1g}(P)$ bands respectively while the second to a CT transition.

3.2.3. Configuration $3d^3$:

$V^{2+}$ and $Cr^{3+}$ belonging to this configuration. Single crystal absorption spectra of $VCl_2$, $VBr_2$ and $VI_2$ have been reported at temperatures down to 5K by different workers $^{12-15}$. All the three spin-allowed and a number of spin-forbidden transitions have been definitely established in these compounds $^{13,15}$. However, there exists some difference between the assignments of vanErk and Haas $^{15}$ and Smith $^{13}$ on some of the bands. On the other hand, some of the spin-forbidden transitions above 20000 cm$^{-1}$ in all these compounds show an anomalous temperature dependence and high intensity which are still not well-explained. Two possible explanations have been provided: (i) cooperative intensity mechanism of Lohr and McClure $^{16}$ and (ii) the intensity borrowing mechanism of Kim et al $^{14}$.

Smith $^{12}$ reported the results of another set of experiments on $KVCl_3$ and $V^{2+}$ doped in $CdCl_2$, $K CdCl_3$ and NaCl single crystals. He succeeded in interpreting all the observed bands on the basis of a four-parameter (B, C, Dq, $\lambda$) crystal field theory of Eisenstein $^{17}$ which includes spin-orbit (S-O) interactions. $K CdCl_3;V^{2+}$ showed low symmetry splitting under $D_{2h}$ field whereas the other trigonally distorted crystals did not show any such evidence. However, Smith $^{12}$ could not analyze the fine-structures in the $^{4}T_{2g}(F)$ band of $KVCl_3$. 
Wood et al. [18] studied Cr$^{3+}$ in three different halide environments and fitted the observed spectra to a four-parameter crystal field theory. All the octahedral compounds $\text{K}_2\text{NaCrF}_3$, $\text{CrCl}_3$ and $\text{CrBr}_3$ showed the normal features expected from a d$^3$ ion, though all the spin-allowed bands were not observed. The spin-forbidden transitions were shown to gain intensity through mixing with the spin-allowed transitions and the percentage characters were calculated. Simo and Holt [19] reported the 5K absorption spectrum of CdF$_2$:Cr$^{3+}$ and the Cr$^{3+}$ ions appeared to reside in trigonally distorted sites.

3.2.4. Configuration 3d$^4$:

Cr$^{2+}$ and Mn$^{3+}$ are the best-known examples of this configuration. Both of them give rise to only one spin-allowed and a number of spin-forbidden transitions. Most of the earlier works were concentrated on the spin-allowed transition only which is often found to split under a Jahn-Teller (J-T) distortion. However, complete analyses including both spin-allowed and spin-forbidden transitions as well as lower field effect have been reported recently [20-26].

Tetragonal splitting of the orbital doublets and triplets were observed in the low temperature polarized single crystal absorption spectra of CrF$_2$ and CrCl$_2$ [20,26]. Both Lim and Stout [20] and Rosseinsky and Dorrity [26] fitted the spin-allowed transitions incorporating the effect of tetragonal field in their calculations but the latter workers omitted this effect in interpreting the spin-forbidden transitions.
Apart from chromium dihalides, \( \text{Cr}^{2+} \) has been studied in \( \text{CsCrCl}_3 \), \( \text{CsCrBr}_3 \), \( \text{RbCrCl}_3 \) and \( \text{CsMgCl}_3;\text{Cr}^{2+} \) \[23-25\]. McPherson et al \[23\] observed strong concentration dependence of the intensities of the spin-forbidden transitions in \( \text{CsCrCl}_3 \) and \( \text{CsMgCl}_3;\text{Cr}^{2+} \). They attempted to assign the observed spectra on the basis of both strong-field and weak-field models, excluding the S-O coupling and the lower field effect, but none of the models alone could satisfactorily fit the observed spectra. Alcock et al \[24\] reported the spectra of \( \text{CsCrCl}_3 \) and \( \text{RbCrCl}_3 \) down to 4K and obtained appreciable polarization effect. The 4K spectra were much complicated compared to that of 77K and for better agreement with theory both S-O coupling and \( C_3^v \) site symmetry require to be considered. Spectrum of \( \text{CsCrBr}_3 \) was similar to that of \( \text{CsCrCl}_3 \) excepting some minor differences \[25\]. However, the static J-T effect observed in \( \text{CsCrCl}_3 \) \[23\] seemed to be absent in \( \text{CsCrBr}_3 \). The somewhat greater breadth and intensity of the 22000 cm\(^{-1}\) band in \( \text{CsCrBr}_3 \) indicates a stronger exchange coupling than in \( \text{CsCrCl}_3 \). This suggests that, in this one-dimensional complex, the coupling mechanism is via a superexchange process through the halogen bridges.

3.2.5. Configuration 3d\(^5\):

Examples of this configuration are \( \text{Mn}^{2+} \) and \( \text{Fe}^{3+} \). In the weak-field approximation, the ground state is \( ^6A_1(S) \) whereas the excited states are quartets and doublets.
Single crystal absorption spectra of the manganese dihalides have been measured down to cryogenic temperatures by many workers [29-39]. It is seen from the literature that there exist disagreements and inconsistencies in the assignments of the higher energy absorption bands and also in the techniques adopted in parameter fitting. The RT 39100 cm\(^{-1}\) band of MnF\(_2\) [29,31] was reassigned by Ferguson [39] to a double-exciton transition \(^6A_{1g}(S) \rightarrow ^4T_{1g}(G) + ^4T_{1g}(G)\) on the basis of a rigorous temperature dependence experiment. Fujiwara et al [41] also confirmed the assignment. Moreover, Ferguson [39] reassigned the 41340 and 43200 cm\(^{-1}\) bands to the \(^4A_{2g}(F)\) and \(^4T_{1g}(G) + ^4T_{2g}(G)\) bands respectively, contrary to the previous assignments [31].

Pappalardo [33,34] first reported the 77K single crystal absorption spectra of MnCl\(_2\) and MnBr\(_2\) which were later reinvestigated by many workers [35,36,38]. Contrary to Pappalardo's assignment, Mehra [35] assigned a band at 30500 cm\(^{-1}\) to the \(^4T_{1g}(P)\) band which was not observed by the former in MnCl\(_2\). The 36500 cm\(^{-1}\) band, originally assigned to the \(^4T_{1g}(P)\) band by Pappalardo, was reassigned to a doublet level by Low and Rosengarten [40] from a theoretical calculation. Similar reassignments were also made by vanErk and Haas [38] for MnBr\(_2\). The only known report on MnI\(_2\) has not yet raised any controversy and the spectral features [38] are very similar to those of MnCl\(_2\) and MnBr\(_2\).
Mehra and his co-workers [42, 43], Ferguson and his co-workers [39, 45-48] and Stevenson [49, 50] investigated the single crystal absorption spectra of RbMnF$_3$, NaMnF$_3$, KMnF$_3$ and CsMnF$_3$. In all the cases, interpretation of all the transitions below 35000 cm$^{-1}$ did not pose any problem. But most of the transitions beyond 35000 cm$^{-1}$ could not be accounted for by any single excitation. Pair-exciton or double-exciton transitions were found to be operative in this region.

Ferguson et al [47] established that the electronic absorption spectra of Mn$^{2+}$ ions in these perovskite fluorides are strongly modified by the magnetic exchange interactions in them as is evident from the fine-structures on the two sharp bands $^{4}A_{1g}$, $^{4}E_g$(G) and $^{4}E_g$(D).

Qualitatively the absorption spectra of Mn$^{2+}$ ions doped in different chloride single crystals do not differ remarkably from those of concentrated systems, except that some of the fine-structures are lost. All these systems show at least a two-fold structure at about 23900 cm$^{-1}$ which are usually assigned to the accidentally degenerate states $^{4}A_{1g}$(G) and $^{4}E_g$(G). Lifting of this degeneracy is normally ascribed to the covalency effects. The $^{4}T_{2g}$(D) band is seen to exhibit a wealth of fine-structures in all the cases. Though earlier workers [51-53] attributed these splittings to lower field effects and S-O coupling, recently Popov and Kotlyarskii [55] have shown them to be due to excitation-magnon and phonon sidebands in Rb$_2$MnCl$_4$. 
Vala et al. [56] and Lawson [57] studied chloride and bromide crystals of Mn$^{2+}$ in tetrahedral geometry. A large number of fine-structures were observed, most of them being vibrational in nature. The other fine-structures were accounted for by S-O interactions. The effects of tetragonal distortion were considered and shown to be small.

Fe$^{3+}$, which has isoelectronic structure with Mn$^{2+}$, has been studied by Vala et al. [58] and by Lakshman and his co-workers [59-61]. Goode [62] studied a number of hydrated salts of Mn$^{2+}$ and claimed to reproduce reasonably the fine-structures on the $^4T_2g$ (D) band by considering both lower field and S-O coupling effects. Some other interesting studies on Mn$^{+2}$ and Fe$^{3+}$ may be found in references [63-81] where the ligands are other than the halides.

3.2.6. Configuration 3d$^6$:

The most common examples of this configuration are Fe$^{2+}$ and Co$^{3+}$. Among the dihalides of Fe$^{2+}$, reports are available only on the absorption spectra of FeF$_2$ [82-85] and FeCl$_2$ [83,86-88]. The observed spectral features of FeF$_2$ reveal a tetragonal symmetry around the Fe$^{2+}$ ion, though the actual site symmetry is D$_{2h}$ [82,84]. On the other hand, octahedral FeCl$_2$ shows the only spin-allowed $^5T_2g$ $\rightarrow$ $^5E_g$ transition as a broad band having two components at 6500 and 7470 cm$^{-1}$. The splitting was found to decrease with decreasing temperature [83,87,88], which is the characteristic of
a dynamic J-T effect. Schlatterly and Fontana [56] observed some spin-forbidden transitions in FeCl₂, but could not assign them because their observed positions did not agree at all with the calculated spectrum. Fe²⁺ has also been studied in different octahedral or near octahedral host single crystals of CdCl₂, CdBr₂, MgCl₂, MnCl₂ and CsCdCl₃ [52,83,87]. In all the cases, the spin-allowed band was found to split into two components under the action of a dynamic J-T effect.

In addition to the ⁵T₂₉ → ⁵E₉ transition, a number of spin-forbidden transitions have been detected and assigned by different workers in the AFeX₃ and ABX₃·Fe²⁺-type compounds [44,83,89,90]. The intensity of the spin-forbidden transitions was shown to result from a cooperative mechanism which relaxes the spin selection rule without energetically perturbing the electronic states involved [89,90]. The higher energy bands in the 20000 - 25000 cm⁻¹ region showed a wealth of fine-structures supposedly arising from the S-O interactions and, possibly, from the actual D₃d site symmetry of the metal ions.

3.2.7. Configuration 3d⁷:

Co²⁺ is the commonest example of this configuration and has been the subject of study of a large number of investigations both in octahedral and tetrahedral coordinations.

The single crystal absorption spectra of cobalt dihalides, except CoI₂, have been reported at different tem-
peratures [91-95]. In addition to the three spin-allowed bands, a few weak spin-forbidden bands were also observed in CoF$_2$ [93,94]. Ferguson et al [95] measured the spectra of CoCl$_2$ and CoBr$_2$ down to 20K and observed many fine-structures which were ascribed to S-0 coupling.

The isostructural compounds CsCoCl$_3$ and RbCoCl$_3$ have been investigated thoroughly [96,97] and a surprising number of magnon sidebands were observed at low temperatures. From the study of Putnik and Holt [96] it appears that the transition from the paramagnetic phase to the antiferromagnetic phase proceeds through a phase of extended one-dimensional spin correlation which exists over a remarkably broad span of temperature. Studies on the octahedral or nearly octahedral CdCl$_2$, AgCl and CsCdCl$_3$ doped with Co$^{2+}$ have revealed the same spectral features [52,98,99] as in CsCoCl$_3$ and RbCoCl$_3$. The number of bands due to the d-d transitions detectable in the doped crystals are remarkably less than in the pure crystals, particularly in the higher energy region. It is probable that the low concentration of the metal ions in the doped crystals reduce the intensity of the already weak d-d bands so much that they are completely obscured by the strong CT transitions dominating in higher energy region.

Tetrahedral or nearly tetrahedral Co$^{2+}$ compounds received much attention [100-109] possibly due to the many difficulties in assignments presented by the polarized single crystal spectra. The compounds Cs$_2$CoCl$_4$, Cs$_3$CoCl$_5$ and
Cs$_2$ZnCl$_4$:Co$^{2+}$ all contain near-tetrahedral Co$^{2+}$ ions, though they have different crystal structures. Cs$_2$CoCl$_4$ has been studied in different spectral regions by different workers /103,104,106/ and the lowest two-spin-allowed bands were found at 3100 and 5460 cm$^{-1}$, respectively. In Cs$_2$ZnCl$_4$:Co$^{2+}$, the structures obtained on the $^4T_1(F)$ band at 20K have been assigned to six electronic origins, associated with each a progression of the same vibrational mode /106/. More than 140 lines were observed in the 4.2K spectrum of Cs$_3$CoCl$_5$ in the 15390 - 32870 cm$^{-1}$ region which could not be interpreted satisfactorily /100,103-105,108,109/ due to the lack of proper knowledge of the Co$^{2+}$ environment at that temperature.

Recently Ferguson and his collaborators /110-112/ reported the results of a set of experiments in which they have established the tetragonal and pseudo-tetragonal nature of the crystal field around the Co$^{2+}$ ions exactly as predicted by their respective crystal structures. The A$_2$CoF$_4$ and A$_2$BF$_4$:Co$^{2+}$ type crystals having K$_2$NiF$_4$ type structure showed large splittings ($\sim$1000 cm$^{-1}$) of the $^4T_{1g}(F)$ band and high dichroic ratios (up to 7:1). Polarization selection rules indicated predominantly $E_g$ character of the ground states. The spin-forbidden bands in the 21000 cm$^{-1}$ region were found to steal intensity through S-O coupling between the doublet and quartet states. The signs of the tetragonal splitting parameters $D_s$ and $D_t$ were established without any a priori assumptions.
Before concluding our review of the main features of absorption studies on 3d ions, we would like to mention that references [113-127] contain some information of general interest about these ions.

3.2.8. Configuration 3d^8:

The commonest example of this configuration is Ni^{2+} which has been the subject of a large number of investigations since the early days. Apart from the usual d-d bands in NiF_2 [128,129], a few bands in the UV region were assigned a fortiori to some double-exciton transitions [3]. Kozielski et al. [130] and Ackerman et al. [131] reported the 5K absorption spectra of NiCl_2, though some of the band positions and assignments differed remarkably. They have also investigated NiBr_2 at 5K and the same type of confusion persists regarding the assignments as for NiCl_2, except that the occurrence of the CT bands at about 23000 cm^{-1} reduces the number of observable bands [130,131]. NiI_2 has been studied by Rosseinsky and Dorrity [132] down to 5K and only four d-d bands and one CT band were observed.

Ferguson and his collaborators [133-137] reported the results of a series of experiments on Ni^{2+} doped in KMgF_3 and KZnF_3 and the pure KNiF_3 single crystals. From the concentration dependence studies, they showed that the excited states are only weakly perturbed by exchange interactions [135].
They interpreted the mechanisms of various electronic transitions and fine-structures and established the magnetic dipole character of the $^3T_{2g}(F)$ band $[136]$ in all the compounds. Transitions due to pair-excitations have also been detected in the high energy region of the spectrum of KNI$_3$ $[133]$. All these fluoride systems were seen to agree well with the calculated energy positions which involves a four-parameter ligand field model $[164]$. Orthorhombic splittings of the $^3T_{2g}(F)$ band were observed in Ni$^{2+}$ doped in MgF$_2$ and ZnF$_2$ $[137]$.

Compared to the fluoride environment, less reports are available on the absorption spectra of Ni$^{2+}$ in chloride and bromide environments. McPherson and Stucky $[138]$ reported the absorption spectra of CsNiCl$_3$, CsNiBr$_3$ and Ni$^{2+}$ doped in CsMgCl$_3$ and CsKBr$_3$. Though the exact site symmetry of the Ni$^{2+}$ ions in all these compounds is $D_{3d}$, its presence was not revealed in the spectra. Enhanced intensities of some triplet $\rightarrow$ singlet transitions in the pure crystals strongly suggested an exchange interaction between the Ni$^{2+}$ ions. Brynestad et al $[139]$ reported the results of an elaborate study on KMGl$_3$:Ni$^{2+}$ in the temperature range 80-763K. The study supported the idea of vibrationally perturbed electric dipole processes for the observed transitions. Investigations have also been carried out on Ni$^{2+}$ doped in CdCl$_2$, AgCl and CsCdCl$_3$ by different workers $[52,99,131]$. 
Ni$^{2+}$ doped in CdBr$_2$ and CsCdBr$_3$ have been reported by Ackerman et al. [13] and McPherson et al. [14], respectively, revealing more or less the same spectral features as the fluoride and chloride crystals. Tetrahedrally coordinated and eight-fold coordinated Ni$^{2+}$, in Cs$_2$ZnCl$_4$:Ni$^{2+}$ [140] and CdF$_2$:Ni$^{2+}$ [197], respectively, has also been studied.

3.2.9. Configuration 3d$^9$:

Cu$^{2+}$ is the best-known example of this configuration which has only one free-ion term $^2D$. In an octahedral field $^2D$ splits into $^2E_g$ and $^2T_{2g}$ in order of increasing energy. But the considerable J-T effect often observed in the Cu$^{2+}$ complexes splits the levels further. All the compounds CuF$_2$, CuCl$_2$ and CuBr$_2$ provide a $D_{4h}$ symmetry at the Cu$^{2+}$ sites and therefore three transitions are expected altogether from the $^2B_{1g}$ ground state. Out of the many studies on CuF$_2$ [142-144], only Oelkrug [142] succeeded in recording all the three expected bands. But the bands of CuCl$_2$ and CuBr$_2$ remained either unassigned or were assigned to the transitions pertaining to octahedral environment only [143,145]. Cu$^{2+}$ doped in CdCl$_2$ and CdBr$_2$ has been studied and all the expected bands were observed in both the compounds [146,147]. Hatfield and Piper [145] measured the spectra of CsCuCl$_3$ and Cs$_2$ZnCl$_4$:Cu$^{2+}$, the former being octahedrally and the latter being tetrahedrally coordinated. Ferguson [148] reported the
spectrum of $\text{Cs}_2\text{CuCl}_4$ where the exact symmetry around the 
$\text{Cu}^{2+}$ ion is $D_{2d}$ obtaining four d-d bands in the near IR 
region and six CT bands in the UV region. The four d-d bands 
were assigned on the basis of a $D_{2d}$ field and the CT bands 
on the basis of MO theory. $\text{Cs}_2\text{CuBr}_4$ and $\text{Cs}_2\text{ZnBr}_4\cdot\text{Cu}^{2+}$ which 
are isostructural with each other also provide $D_{2d}$ field, 
but no such lower symmetry effect were observed in the 
spectra $[149]$.

3.3. Emission and Excitation profiles of 3d$^n$ ions:

In this section we shall confine our review to only 
three 3d$^n$ ions, viz. $3d^5(\text{Mn}^{2+})$, $3d^8(\text{Ni}^{2+})$ and $3d^9(\text{Cu}^{2+})$ among 
which we could observe luminescence, for the first two.

The $\text{Mn}^{2+}$ compounds are known to exhibit brilliant 
luminescence due to the spin-forbidden character of all the 
excited states. Both in the octahedral and tetrahedral $\text{Mn}^{2+}$ 
compounds, energy migrates through non-radiative process from 
the higher excited states to the lowest excited state, $^4\text{Tl}(G)$; 
the $^4\text{T}_1(G)$ state being subsequently de-excited through radiative 
process to the ground $^6\text{A}_1(S)$ state. $\text{MnF}_2$ and $\text{RbMnF}_3$ have 
been the subject of a large number of investigations due to 
the two-fold structure shown by the emission bands $[150-157]$. 
On the other hand, $\text{KMnF}_3$ showed three emissions $[158]$ which 
could not be interpreted exactly. One of the possible expla-
nations assume the presence of an impurity ion, but it is more
likely a Mn\(^{2+}\) level strongly perturbed by a certain type of impurity (e.g., an interstitial fluorine ion). In addition, the presence of some fine-structures at very low temperatures makes the problem more complicated. Kestigian and Holloway (159) reported the temperature dependence of the emission bands of some chloride crystals of Mn\(^{2+}\). At low temperatures, all the bands were observed to shift to lower energies which were simple consequences of the lowering of energy of the emitting state, \(4T_1(G)\), as was evident from the absorption spectra.

Among the halide compounds of Ni\(^{2+}\), only three fluorides are known to exhibit luminescence. They have been studied in details by Ferguson and Masui (160), Vehse et al. (161), and by Iverson and Sibley (162). The latest work of Iverson and Sibley (162) has established unambiguously the origins of three emissions observed from Ni\(^{2+}\) doped in KZnF\(_3\), KMgF\(_3\), and MgF\(_2\).

Contrary to the earlier belief, they showed that the green emission (\(~20000\) cm\(^{-1}\)) and the red emission (\(~12500\) cm\(^{-1}\)) originate from the same excited state \(^1T_{2g}(D)\) but terminates on the ground state and on the first excited state, \(^3T_{2g}(F)\), respectively. The last infra-red emission (\(~5000\) cm\(^{-1}\)) originates from \(^3T_{2g}(F)\) and terminates on the ground state. Ferguson and Masui (160) studied the decay rates and relative quantum efficiencies for \(^1T_{2g}(D) \rightarrow ^3A_{2g}(F)\) and \(^1T_{2g}(D) \rightarrow ^3T_{2g}(F)\) emissions of KZnF\(_3\):Ni\(^{2+}\) for various Ni\(^{2+}\) concentrations. This study indicated that the \(^1T_{2g}(D) \rightarrow ^3T_{2g}(F)\)
emission is a mixture of a magnetic dipole and a phonon-assisted electric dipole transitions.

Cu$^{2+}$ is not known to exhibit luminescence in the solid state. But Matsumoto et al. [1637] found emissions from CdCl$_2$;Cu$^+$ and CdBr$_2$;Cu$^+$. To interpret this observation, they proposed the existence of 0.47 eV deep electron trap in the Cu$^+ \rightarrow$ Cu$^{2+}$ process in CdBr$_2$. 

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