SYNOPSIS

The thesis is divided into two parts. Part one deals with the magnetic study of a reversible phase transition in paramagnetic crystals and part two describes the magnetic property of uranium complexes.

Part one of the thesis opens with a general discussion on the origin and nature of paramagnetism in the crystals. In the next section the various interactions within and external to a paramagnetic ion which profoundly affect the magnetic behaviours of the paramagnetic ions have been discussed. The general development of the crystalline electric field has been given in the next section. Then the problem of calculation of energy levels in crystals of iron group of salts and their susceptibilities according to the method of Van Vleck, Penney and Schlapp and others, taking mainly the lowest level in the Stark pattern as contributing to the magnetic susceptibility by which the major features of the magnetic behaviours of the salts could be explained fairly satisfactorily are given. The perturbation technique of Abragam and Pryce is then discussed in the case where the ground level is degenerate or non-degenerate under cubic field (Co^{+2} and Ni^{+2}) and the susceptibility equations are derived by replacing ordinary Hamiltonian with spin Hamiltonian. The relation between the ionic and the crystalline susceptibility is then deduced where more than one non-equivalent ions are present in the unit cell. Th magnetic data of $CoSiF_6$, $6H_2O$ (Mazumdar and Datta) where due to the phase transition at 246 ± 2°K magnetic symmetry of the crystal changes from uniaxial to orthorhombic symmetry has been explained with the help of a model derived from the low temperature x-ray data of Watanabe and the magnetization data of Ohtsubo. Comparison of the structural data of $Co(NH_4SO_4)_2$, $6H_2O$ with that of the low temperature structural data of $CoSiF_6$, $6H_2O$ indicate a close similarity. Though the room temperature structure of $CoSiF_6$, $6H_2O$ is uniaxial become monoclinic below the transition temperature. Similarity has been further elucidated from the development of weak ferromagnetism along the monoclinic axis. The origin of weak ferromagnetism in these two crystals is of Dzialoshinski - Moriya (D-M) type. Uryu's calculation for the interpretation of weak ferromagnetism in $Co(NH_4SO_4)_2$, $6H_2O$ has been carefully analysed and found that D-M interaction responsible for weak ferromagnetism in $CoSiF_6$, $6H_2O$ originates from the orientation of the ionic axes. This model explains both (a) the appearance of anisotropy in the symmetry plane (b) the presence of weak ferromagnetism.

Chapter 2 describes the various aspects of the design, construction and working of the different apparatus and the apparatus utilized for the present measurement. In the next section the preparation and analysis of the single crystals (both concentrated and dilute) studied in the present work have been given. Lastly the formula used for the calculation of gramme molecular susceptibility and anisotropy for Co^{+2} ion from the result of dilute crystal have been presented.

The magnetic anisotropy and the principal susceptibility results of $CoF_2 5HF$, $6H_2O$, $CoZrF_6$, $6H_2O$, $NiF_2 5HF$, $6H_2O$, four dilute crystals of $CoSiF_6$, $6H_2O$ and seven dilute crystals of CoF_25HF, $6H_2O$ are presented in chapter 3.

In chapter 4 the results of chapter 3 have been analysed and compared with the results of $CoSiF_6$, $6H_2O$. The analysis of the magnetic anisotropy and susceptibility results of CoF_25HF, $6H_2O$ and $CoZrF_6$, $6H_2O$ indicates that these two crystals undergo phase transition similar in nature to that of $CoSiF_6$, $6H_2O$. Further similarities are derived from the room temperature x-ray and optical absorption studies. The results of $CoSiF_6$, $6H_2O$ are discussed on the light of the model developed in chapter 1. Ionic susceptibilities obtained from the model are fitted with the theory by varying the trigonal separation $\triangle$ at different temperatures. $\triangle$ values obtained are different for different temperatures. The same type of $\triangle$ variation has been observed by Bose et al in $Co(NH_4SO_4)_2$, $6H_2O$. Similar interpretation as in $CoSiF_6$, $6H_2O$ has been made for hydrofluoride and fluozirconate crystals. Results of the dilute crystals ($Co_{1-x}Zn_xF_25HF$ $6H_2O$ and $Co_{1-x}Zn_xSiF_6$, $6H_2O$) indicate that the phase transition temperature shifts towards the low temperature side as the concentration of the zinc salt increases and finally when the concentration x is above a critical concentration x_c the phase transition disappears. The apparent discrepancy between the e.s.r. study of $CoSiF_6$, $6H_2O$ by Bleaney et al (ionic axis is along the crystal symmetry axis) and the low temperature x-ray observation of Watanabe (ionic axes are oriented with respect to the room temperature hexagonal axis) is resolved from the results of dilute crystals. The e.s.r. data has been taken on dilute crystal where phase transition is absent whereas the x-ray observation is for the concentrated salt. Finally a comparison has been made between the phase transition observed in cobalt hydrofluoride, fluosilicate and fluozirconate crystals to that of the other second order transition classified by Landau.

In the second part of the thesis the magnetic susceptibility of nine u^{+4} compounds have been examined over a temperature range 90 - 300°K. Appreciable variation of $\chi_1 T - T$ for u^{+4} ion from salt to salt and also with temperature has been observed for all the compounds. A theory of magnetic susceptibility based on point charge model has been worked out for u^{+4} ion in crystalline state including exchange term. The calculation yields a nonmagnetic singlet as the ground state and a magnetic doublet close to it; in oxycompounds exchange term is finite, whereas exchange is negligible in nonoxycompounds.

The scope of the present work and the general layout of the thesis is shown in the list of contents which immediately follow the synopsis.