Magnetic and Electric Investigation of Phase Changes in Transition metal Perovskite like Complexes

A Thesis Submitted

by

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Summary

The (Ethanolammonium)$_2$CuX$_6$, X= Cl and Br are examples of one dimensional compounds which will be designated as ECC and ECB respectively. The ac. electric conductivity, permittivity and differential thermal scanning (DSC) are studied in temperature range 100K up to 300K.

In the low temperature range the ac conductivity shows extrinsic type conduction for the two compounds. In high temperature region, the conduction is intrinsic and is explained in terms of band gap. For the ECB compound, the results show that there is an anomaly at T~250K which is reflected in the real and imaginary parts of dielectric constant. This was confirmed by DSC thermograph and has been attributed to structural phase change.

The new two-dimensional compounds $(C_{27}H_{36}ON_2)_2MCl_4$, where M=Mn, Co, and Cu are prepared and the electric and magnetic studies in temperature range 290-470K are presented. X-ray powder diffraction pattern for the three compounds obtained at room temperature, showed that the compounds are isomorphous to each other with orthorhombic unit cell where a= 15.78A°, b=17.30 A° and c= 19.85A° for Mn, a= 15.57A°, b= 16.65A° and c= 19.96A° for Co and a= 15.89A°, b= 17.25A° and c= 20.01A° for Cu compound. Furthermore, x-ray diffraction patterns at high temperatures point to the existence of structural phase transitions.

The overall magnetic susceptibility results for the three compounds show a Curie-Weiss type behavior with small peaks occurring in the range of 378K-355K. Also a noticeable change in the rate of change of susceptibility has been observed at T = 430K-410K for the three compounds. The observed small peaks were found to reflect structural transition at 381±1K, 374±1K and

358±1K for the Mn, Co and Cu compounds respectively. The values of the magnetic moments for the three compounds above and below these transition temperatures were found to be 5.88 μ_B, 5.66μ_B for Mn, 4.58 μ_B, 4.30 μ_B for Co and 1.84 μ_B, 1.81 μ_B for Cu respectively.

The values of μ_{eff} obtained at T > 430K, > 420K and > 410K for Mn, Co and Cu compounds are found to be 2.97 μ_B, 2.54 μ_B and 1.13 μ_B, which is half the values obtained at lower temperatures indicating that dimerization occurs in the three compounds at these temperatures.

The ac conductivities for the three compounds measured as function of temperature at different frequencies (4Hz-10^4Hz) are characterized by three regions, region I (T<378K for Mn, T<367K for Co and T< 355K for Cu), region II (385K<T<432K for Mn, 378K<T<420K for Co and 365K<T<410K for Cu) and region III (T>430K for Mn, T> 420K for Co and T>410K for Cu).

The ac electrical parameters measured combined with the magnetic susceptibility results for the three compounds, reveals that each of the three compounds undergo two structural phase transitions at T_1= 385 ± 2K and T_2= 430±3K for Mn compound, T_1= 375 ± 2K and T_2= 420 ± K for Co compound and T_1= 365 ±3K and T_2= 410 ± 2K for Cu compound) and that dimerization occurs at high temperatures.

The magnetic properties and ac conductivity of the thermochromic compound $(C_3H_8O_2N)_2CuCl_4$ have been investigated in the temperature region 78K-320K. The magnetic susceptibility results show structural phase transition at 280 K. The conductivity measurement reveals a sudden change in the Arrehnius plot indicating the existence of the phase transformation. Thermal hystresis indicates that the transition is of first order. The results are related to the N..H-Cl hydrogen bonding in the system. This first order change

is also reflected in the optical properties of the compound as the compound shows thermochromism at ~280K

The last series in this studying is $(C_6H_{12})(NH_3)_2Fe_x\ Zn_{1-x}\ Cl_4$ compounds, where x = 1, 0.8, 0.5, and 0. The ac dielectric constant and conductivity in the temperature rang from T = 100K up to T = 420K at different frequencies (f= 0.1kHz- 20kHz) show that there are several anomalies at ~245K and ~ 310K for x =1.0. For x = 0.8 the anomalies occur at ~240K and 348K. For x = 0.5 the anomaly occur at 335K. Finally for x = 0 the anomalies appear at ~253K and ~335K.

The magnetic susceptibility for $(C_6H_{12})(NH_3)_2FeCl_4$(x = 1) measured at T= 78K up to 330K shows several anomalies at T~245K and ~310K. This agrees with results obtained from the electric measurements and was also confirmed by DSC thermograms.

The effect of the addition of the diamagnetic Zn^{+2} is reflected as a decrease in condctivity and the activation energies. A change in the transition temperature is also observed.