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THERMAL STUDIES ON THE DIELECTRIC CONSTANT OF SOME $(C_nH_{2n})(NH_3)_2FeCl_4$ COMPOUNDS ($n = 2$, 7 AND 10)

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ABSTRACT

The dielectric constant of the compounds $(CH_2)_2(NH_3)_2FeCl_4$, $(CH_2)_7(NH_3)_2FeCl_4$ and $(CH_2)_{10}(NH_3)_2FeCl_4$ is measured at temperatures from liquid nitrogen temperature up to near the melting point of each sample. The phase transitions obtained are confirmed by the DTA thermograph.

INTRODUCTION

In recent years there has been a renewed interest in the study of magnetic systems as a function of the magnetic field. The compounds of the series of the general formula $(C_nH_{2n})(NH_3)_2FeCl_4$ ($n = 1, 2, 3$, etc.) can be grouped as members of the perovskite layered type crystals. Compounds of the same series but with $n = 3$ and M = Mn, Cu, and Fe, have been determined [1,2]. Crystal structures of compounds where $n = 2$ and M = Ni, Cu, Cd, Pd and Mn, have also been determined [3–6].

The isomorphous compounds which are under investigation may be crystallized in the orthorhombic space group *Imma*. The structure is made up of metal halogen layers of MCl_6 octahedra each of which shares four corners with neighbouring octahedra in the layer. The metal ions occupy sites of $2/m$ symmetry. The metal–chlorine distances to the four bridging chlorine atoms are longer than the two terminal metal–chlorine distances. The M–Cl–M bridges are symmetrical with the non-linear bridging M–Cl–M angle. The octahedra are alternately tipped forward and backward to produce the well known puckering of the layers.

In our laboratory [7,8], it was found that the compounds with $n = 1$, 3 and 5 show two-dimensional antiferromagnetism associated with weak ferromagnetism. The weak ferromagnetism appearing below the Neél temperature is attributed to spin canting in the antiferromagnetically ordered state.

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One can safely say that the total structure is thus composed of alternate layers of $(C_nH_{2n})(NH_3)_2$ and an M–Cl network. The NH_3 groups are expected to be hydrogen bonded to the M–Cl network. This will result in a monoclinic unit cell structure if n is even and an orthorhombic unit cell if n is odd [3–6]. This rule applies when n is 1 to 6; exceptions occur when $n = 7$ and 8 when both have monoclinic unit cells.

In the present work, the compounds are simple dielectrics as is apparent from their different electrical properties. Since the dielectric constant of simple dielectrics increases with temperature due to lattice changes in the electronic structure caused by heating, one can expect heating to cause the samples to lose the bond structure which holds the ions in place, resulting in a large increase in their dielectric constants.

EXPERIMENTAL

The method of preparation of the compounds was reported by Remy and Laves [9]. The preparation was carried out by dissolving the stoichiometric amounts of amine hydrochloride and $FeCl_2 \cdot 2H_2O$ in aqueous or acidic solution under a stream of oxygen-free nitrogen gas. The mixture was heated in a nitrogen atmosphere for about one hour and then cooled slowly. Greenish-yellow plate-like crystals were obtained.

Chemical analysis of the samples was carried out before collecting the data and this is listed in Table 1.

After grinding the samples in a dry glove box under purified nitrogen gas, the finely powdered samples were compressed to pellet form with a diameter of 16 mm and a thickness of 1 mm. The pressure used for compression was fixed at 15 tons cm^{-2} for the three samples under investigation. The surface of each sample was polished and small equal areas on the two surfaces coated with liquid gold and checked to avoid contact effect. The sample temperature was measured using a calibrated copper–constantan thermocouple with the reference junction at 0°C.

The dielectric constant was measured using the bridge shown in Fig. 1. The data were collected at different frequencies (10, 20 and 30 kHz). The

TABLE 1

Chemical analysis of the compounds $(CH_2)_n(NH_3)_2FeCl_4$ ($n = 2$, 7 and 10)

Compound	C%		H%		N%		Cl%	
	found	calc.	found	calc.	found	calc.	found	calc.
$(CH_2)_2(NH_3)_2FeCl_4$	9.26	9.24	3.90	3.85	10.81	10.78	54.75	54.65
$(CH_2)_7(NH_3)_2FeCl_4$	25.51	25.47	6.10	6.06	8.37	8.49	43.13	43.05
$(CH_2)_{10}(NH_3)_2FeCl_4$	32.40	32.27	6.85	6.99	7.56	7.53	38.10	38.19

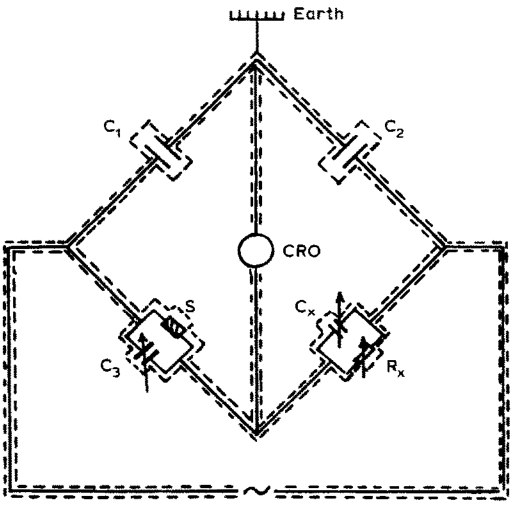

Fig. 1. Bridge designed for dielectric constant measurements. C_1, C_2, capacitors of equal value; C_3, C_x, decade capacitors; S, sample; R_x, decade resistance.

connecting wires of the circuit are completely shielded cables and are as short as possible to reduce wiring capacitance. The samples are inserted in a constant vacuum cryostat to avoid the effect of moisture.

RESULTS AND DISCUSSION

The results of the dielectric constant (ϵ) versus absolute temperature are shown in Fig. 2 for the compound $(CH_2)_2(NH_3)_2FeCl_4$. The data are collected from liquid nitrogen temperature up to 470 K. The dielectric constant (ϵ) averaged over a constant value gives an almost straight line up to 240 K. After that it increases gradually with temperature until 275 K when it increases suddenly to a frequency of 20 kHz. After passing the thermochromic phase transition (phase I) at $\simeq 300$ K (this thermochromic transition appears in the DTA thermograph Fig. 5a), the dielectric constant (ϵ) decreases sharply with temperature until it reaches a minimum at $\simeq 330$ K. Another phase transition (phase II) is detected by both dielectric constant (ϵ) measurement and DTA thermograph. The large spike at 20 kHz becomes a broad hump by changing the frequency to 10 kHz.

The temperature dependence of the dielectric constant (ϵ) for the compound $(CH_2)_7(NH_3)_2FeCl_4$ in the same range of temperature as that for the above compound is shown in Fig. 3. The same behaviour is obtained for ethylene-diammonium iron tetrachloride at low temperatures. Two phase transitions are obtained, one around 280 K (phase I) and another around 330 K (phase II). A slight shift in the phase transition temperature is observed by changing the frequencies from 10 to 30 kHz. The first phase

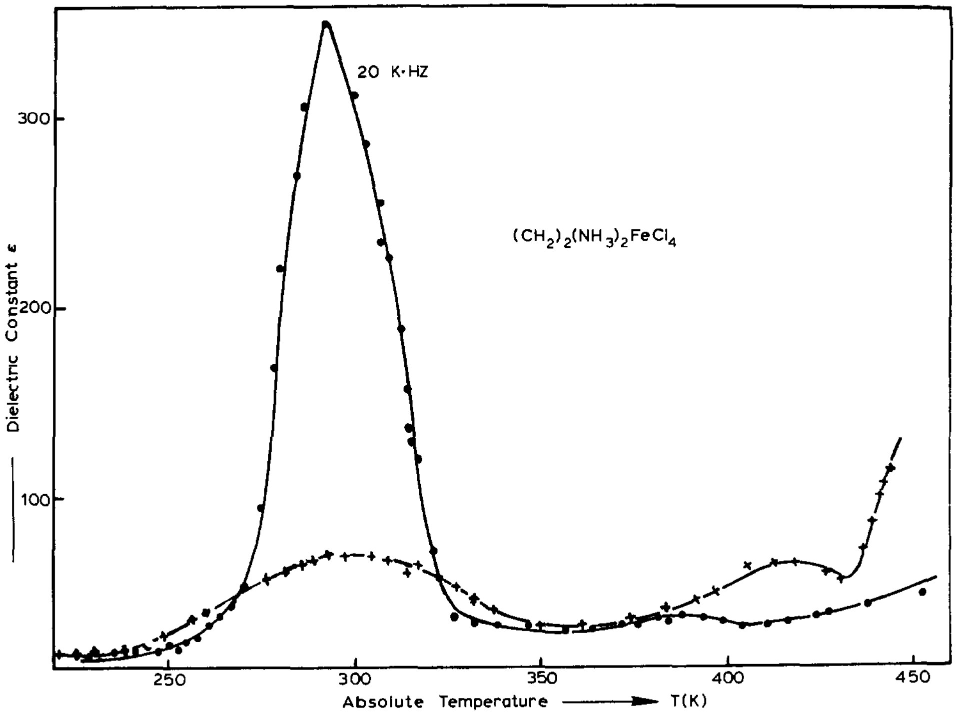

Fig. 2. Relationship between dielectric constant and absolute temperature at different frequencies for the compound $(CH_2)_2(NH_3)_2FeCl_4$; (+) 10 kHz, (●) 20 kHz.

transition which appeared just below room temperature is not detected by DTA (MOM Derivatograph system No. 975136) as this type of equipment only measures from room temperature and above, and is used for the two compounds in Figs. 5b and 5c. The peak value of the dielectric constant as a function of frequencies is given in Fig. 3b for the two phases.

Figure 4 shows the relationship between dielectric constant (ϵ) and absolute temperature for the compound $(CH_2)_{10}(NH_3)_2FeCl_4$ in the same temperature region as the above two compounds. The DTA thermograph (Fig. 5c) is used to confirm the data obtained.

To a large extent, the shape of the curves for the three compounds are similar giving the well known picture to the dielectric constant of the two-dimensional systems, characterized by the presence of more than one phase transition above 200 K and the appearance of a gradual change in crystal structure.

The electric dipole moments below, at, and above the two phase transitions are calculated from the equations [10],

$$\chi = \frac{K}{N\mu^2}\left(T - \frac{N\mu^2\beta}{K}\right)$$

$$\chi = (\epsilon - 1)\epsilon_0$$

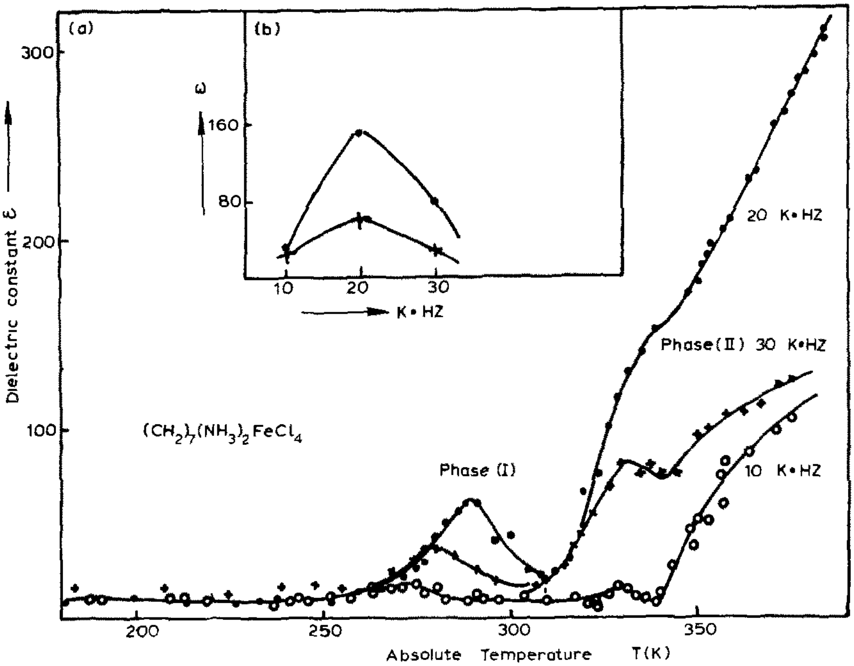

Fig. 3. (a) Relationship between dielectric constant and absolute temperature at different frequencies for the compound $(CH_2)_7(NH_3)_2FeCl_4$. (b) Peak value of dielectric constant versus frequencies: (●) phase (I), (+) phase (II).

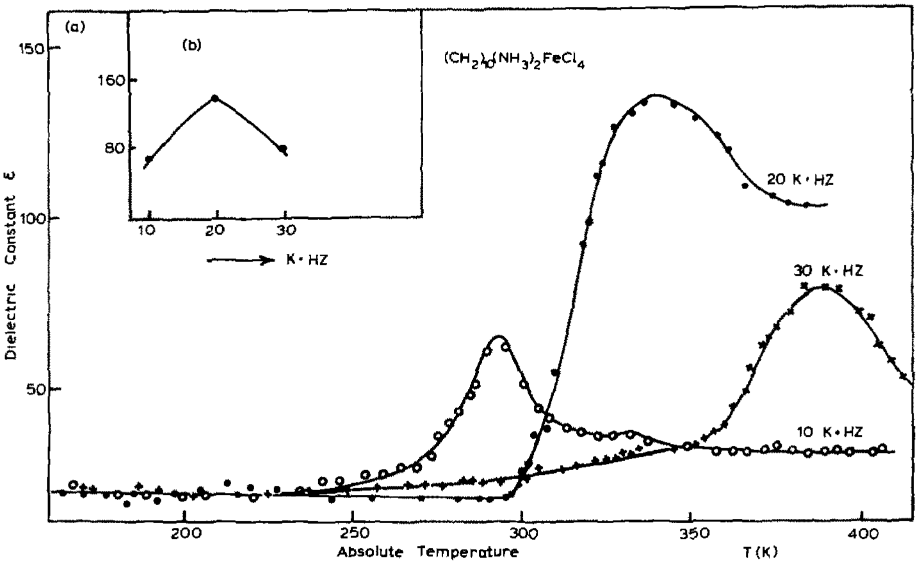

Fig. 4. (a) Relationship between dielectric constant and absolute temperature at different frequencies for the compound $(CH_2)_{10}(NH_3)_2FeCl_4$. (b) Peak value.

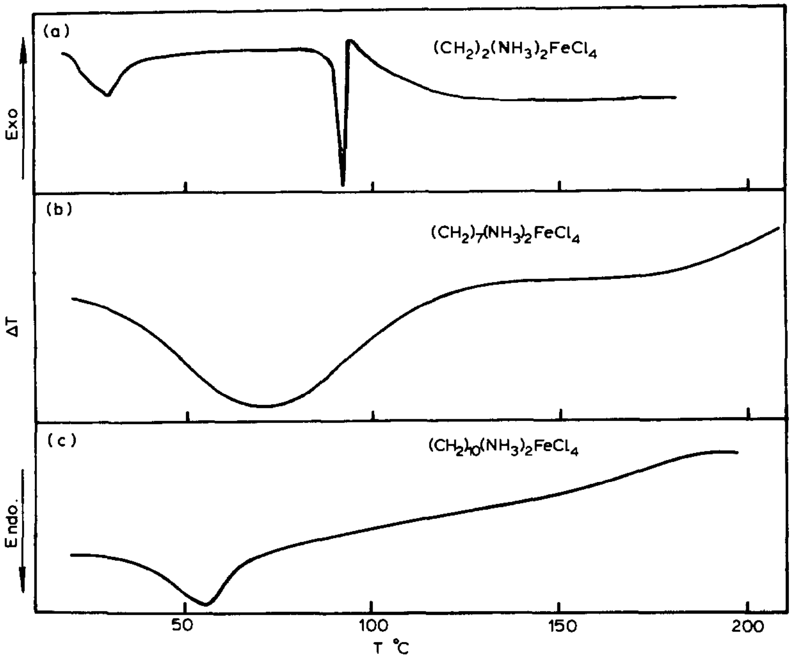

Fig. 5. DTA thermograph: (a) $(CH_2)_2(NH_3)_2FeCl_4$, (b) $(CH_2)_7(NH_3)_2FeCl_4$, (c) $(CH_2)_{10}(NH_3)_2FeCl_4$.

where χ is the electric susceptibility, N is the number of electric dipoles per unit volume, μ is the electric dipole moment, $\beta = 4\pi/(2\epsilon + 1)$, is the dielectric constant, K is the Boltzman constant, T is the absolute temperature and ϵ_0 is the permittivity of free space. The values of the electric dipole moments are listed in Table 2.

From the data obtained (dielectric constant and electric dipole moments) one can safely say that the gradual increase in dielectric constant before the

TABLE 2

Values of the electric dipole moments (μ) for the compounds $(CH_2)_n(NH_3)_2FeCl_4$ ($n = 2, 7$ and 10), below, at and above each phase transition

T (K)	μ of $(CH_2)_2(NH_3)_2FeCl_4$ (C cm$\times 10^{-18}$)	μ of $(CH_2)_7(NH_3)_2FeCl_4$ (C cm$\times 10^{-18}$)	μ of $(CH_2)_{10}(NH_3)_2FeCl_4$ (C cm$\times 10^{-18}$)
200	10.24	6.35	9.58
280	37.78	13.16	9.75
300	54.39	12.99	13.38
320	26.77	16.72	25.92
336	18.62	25.98	31.43
375	19.68	40.47	22.38
390	22.40	42.34	30.91
440	25.46	–	–

first phase transition of each sample may be due to the change in electronic configuration which is associated with the gradual structural changes. This result is enhanced by the endothermic peaks obtained from DTA thermographs. Also, one of the interesting features which appeared during the collection of the data, is the reversed polarity of the pyroelectric current, which is similar to that found for $(NH_4)_2SO_4$ [11] and NH_4NO_3 [12]. This phenomenon is attributed to the gradual change in symmetry above the thermochromic phase transition which is in agreement with the results. Finally one can expect the three compounds to crystallize at room temperature in a monoclinic unit cell after taking into consideration the exception of $n = 7$. This rule is found in the isomorphous compounds [12] when M = Cd, Cu and Mn.

Detailed analysis of the crystal structure, electrical conductivity and pyroelectric current for these compounds will be published later.

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