

## Experimental Study of the Phase Transition in $(\text{CH}_2)_8(\text{NH}_3)_2\text{FeCl}_{4-x}\text{Br}_x$ ( $x = 0, 1$ and $2$ )

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### Abstract

The dielectric constant  $\epsilon$  and the pyroelectric current  $I_p$  for the compounds  $(\text{CH}_2)_8(\text{NH}_3)_2\text{FeCl}_{4-x}\text{Br}_x$  ( $x = 0, 1$  and  $2$ ) have been measured in the range from the liquid nitrogen temperature up to near the melting points. Measurements of the dielectric constant have been carried out at various frequencies. A calculation of the electric dipole moments at the background and transition points is given. Calorimetric measurements have also been carried out and the values of the enthalpy change  $\Delta H$  and entropy change  $\Delta S$  are also reported.

### 1. Introduction

Recently interest has arisen on layer compounds with the general formula  $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{MX}_4$  and  $(\text{C}_n\text{H}_{2n})(\text{NH}_3)_2\text{MX}_4$ ;  $n = 1, 2, 3, \dots$ ,  $M = \text{Fe}^{2+}, \text{Mn}^{2+}, \dots$ ,  $X = \text{Cl}, \text{Br}, \dots$  because of the large variety of structural and magnetic phase transitions they exhibit. The compounds of these two series show more than one commensurate phase transition (Sorge *et al.* 1986), in addition to incommensurate phases, in a certain temperature interval during measurements of their electrical properties. It is found that the sequence and nature of the structural phase transitions of these compounds vary with  $n$ ,  $M$  and  $X$  (Bocanger *et al.* 1975; Tello *et al.* 1977; Ahmed *et al.* 1986). Most of these compounds crystallise in the orthorhombic space group *Imma* at room temperature. The structure is made up of infinite sheets of corner-sharing divalent transition metal halogen octahedra, with a strong two-dimensional character similar to those of  $\text{K}_2\text{NiF}_4$  structure. The  $\text{NH}_3$  groups are expected to be halogen bonded to the  $M\text{-Cl}$  network. This results in a monoclinic unit cell at low temperature. Thus, these compounds are of importance in studies of electrical and magnetic properties.

In our laboratory (Mostafa *et al.* 1980, 1982) it has been found that the iron compounds of the diammine series show two-dimensional antiferromagnetism associated with weak ferromagnetism that appeared below the Néel temperature. This weak ferromagnetism is due to spin canting in the antiferromagnetically ordered state.

Calorimetric measurements on the layered compounds (Arriandiaga *et al.* 1978; Ahmed *et al.* 1986) show more than one peak. Some of these peaks are associated with the passage from a quasi-complete ordered to a complete disordered state through a

series of stable intermediate states. The rest of the peaks are associated with structural phase transitions.

In the present work, the compounds under investigation are simple dielectrics with spontaneous polarisation and they belong to the 10 out of 32 groups (Mitsui *et al.* 1976), i.e. they show pyroelectricity. So, it is of interest to study the dielectric constant and pyroelectric current of these compounds.

**Table 1.** Chemical analysis (in %) of the compounds  $(\text{CH}_2)_8(\text{NH}_3)_2\text{FeCl}_{4-x}\text{Br}_x$

The three rows correspond to compounds  $x = 0, 1$  and  $2$  respectively

C		H		N		Cl		Br	
Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
27.87	27.91	6.38	6.40	8.21	8.14	41.31	41.30	—	—
24.87	24.73	5.59	5.67	7.35	7.21	27.45	27.43	20.55	20.88
22.21	22.19	5.03	5.08	6.50	6.47	16.40	16.41	36.90	36.94

## 2. Experimental

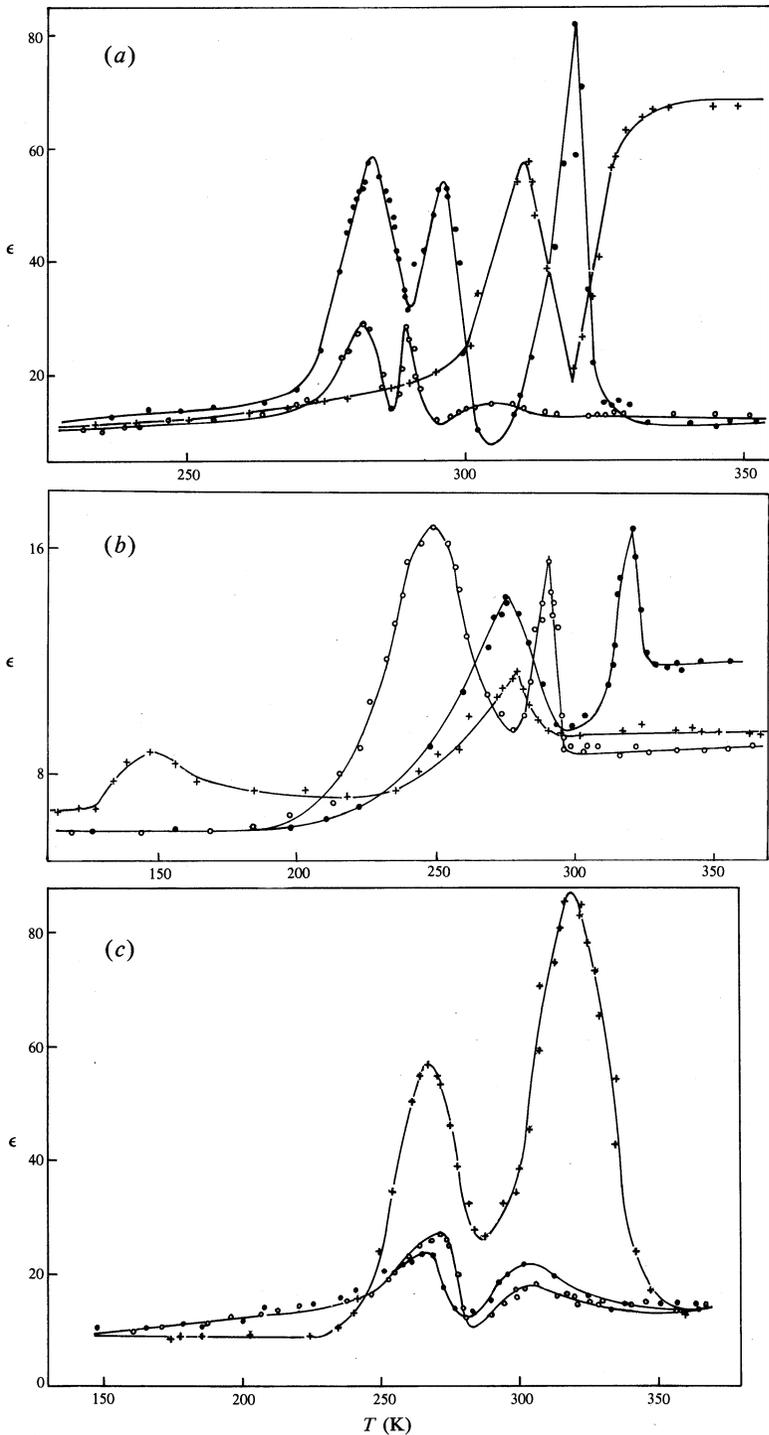
The compounds were prepared from starting products by dissolving a stoichiometric amount of ammine hydrochloride or hydrochloride and hydrobromide in an aqueous or acidic solution. The  $\text{FeCl}_2 \cdot 3\text{H}_2\text{O}$  was added under a stream of oxygen-free nitrogen gas. The mixture was then heated in a nitrogen atmosphere for about one hour and then cooled slowly, yielding crystals of greenish yellow colour. Chemical analysis by weight of the samples was carried out before data collection, as listed in Table 1. All samples used were in powder form, compressed into pellets with a diameter of 16 mm and thickness of 1 mm. The pressure used was  $2.18 \times 10^5$  psi (1 psi  $\equiv$  689.4 Pa). The two surfaces of each sample were coated with liquid gold.

The dielectric constant was measured using the bridge designed by Ahmed *et al.* (1986). The data were collected at the frequencies 10, 20 and 30 kHz. The pyroelectric current was measured by a multimeter level type TM9H, which is sensitive down to  $10^{-12}$  A, while the calorimetric measurements were carried out with a Mettler TA 3000 system.

## 3. Results and Discussion

Fig. 1a correlates the dielectric constant  $\epsilon$  and the absolute temperature  $T$  for the compound  $(\text{CH}_2)_8(\text{NH}_3)_2\text{FeCl}_4$  at the three frequencies 10, 20 and 30 kHz. The data give straight lines from liquid nitrogen temperature up to about 250 K, after which the dielectric constant increases gradually. At 270 K a sudden change in  $\epsilon$  occurs giving complicated phase transitions in the range 270–330 K. It is known that (Sorge *et al.* 1986) some of the peaks obtained are accompanied by a change in crystal symmetry, while others are accompanied by a transition from a complete crystalline ordered state to a complete disordered state.

Fig. 1b shows the temperature dependence of  $\epsilon$  for the compound  $(\text{CH}_2)_8(\text{NH}_3)_2\text{FeCl}_3\text{Br}$ . It is clear that  $\epsilon$  has a constant value from the liquid nitrogen temperature up to 200 K for the frequencies 20 and 30 kHz, while after 200 K a gradual increase is observed. At 250 and 290 K for the frequency 20 kHz, the thermochromic phases appear which are accompanied by slight reversible changes in the colour of the sample from faint to bright yellow. These two phases are shifted to  $\approx 275$  and 320 K when the frequency is changed to 30 kHz.



**Fig. 1.** Relationship between the dielectric constant  $\epsilon$  and absolute temperature  $T$  for the compound (a)  $(\text{CH}_2)_8(\text{NH}_3)_2\text{FeCl}_4$ , (b)  $(\text{CH}_2)_8(\text{NH}_3)_2\text{FeCl}_3\text{Br}$  and (c)  $(\text{CH}_2)_8(\text{NH}_3)_2\text{FeCl}_2\text{Br}_2$ . The crosses, open circles and solid circles are for the frequencies 10, 20 and 30 kHz respectively.

The values of the electric dipole moment at the background and the transition points are calculated using the Weiss model equation (see e.g. Mitsui *et al.* 1976)

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

and listed in Table 2. Here  $\chi$  is the electric susceptibility,  $N$  is the number of electric dipoles per unit volume,  $\beta = 4\pi/(2\epsilon + 1)$  and  $k$  is Boltzmann's constant.

**Table 2.** Electric dipole moment (in units of  $10^{-18} \mu\text{C cm}$ ) at the background and peak points for  $(\text{CH}_2)_8(\text{NH}_3)_2\text{FeCl}_{4-x}\text{Br}_x$

$(\text{CH}_2)_8(\text{NH}_3)_2\text{FeCl}_4$		$(\text{CH}_2)_8(\text{NH}_3)_2\text{FeCl}_3\text{Br}$		$(\text{CH}_2)_8(\text{NH}_3)_2(\text{NH}_3)_2\text{FeCl}_2\text{Br}_2$	
$T$ (K)	EDM	$T$ (K)	EDM	$T$ (K)	EDM
240	7.7	110	4.3	150	6.5
282	13.7	148	5.8	268	20.0
290	13.7	250	10.3	271	14.1
296	19.1	275	9.9	303	13.8
304	9.9	278	9.0	305	12.3
311	19.5	290	10.6	320	27.8
320	23.7	320	11.5	—	—

The temperature dependence of  $\epsilon$  for  $(\text{CH}_2)_8(\text{NH}_3)_2\text{FeCl}_2\text{Br}_2$  at 10, 20 and 30 kHz, over the same range of temperature as the above two compounds, is shown in Fig. 1c. It is clear that this compound has the same general features as the other two, with two structural phase transitions at 270 and 310 K. The values of the electric dipole moment at the background and peak points are also listed in Table 2.

In comparing the two compounds  $-\text{Cl}_3\text{Br}$  and  $-\text{Cl}_2\text{Br}_2$  one can state that, since the size of the  $\text{Br}^-$  ion is larger than the  $\text{Cl}^-$  ion (the radius of  $\text{Br}^-$  is 1.96 Å and that of  $\text{Cl}^-$  1.81 Å), it is reasonable to assume that the  $\text{Br}^-$  ions will occupy the out-of-plane position and so force the  $\text{Fe}^{2+}$  ions towards the planes containing the  $\text{Cl}^-$ . Also, less puckering of the structure of  $\text{FeCl}_4^{2-}$  layers and, in turn, a smaller canting angle may be obtained. In other words, the introduction of  $\text{Br}^-$  ions in the out-of-plane position helps the moments to be oriented in the horizontal layers, leading to the observed features in these compounds.

The similarities in the transitions among the three compounds strongly suggest that there is a common mechanism responsible for the phase transitions, except for a small shift in the peak positions. Thus it is useful to compare the phase transition sequence in the three compounds. The dielectric constant measurements for the  $-\text{Cl}_4$  compound show a complicated phase transition: it has three peaks at 281, 290 and 305 K at 20 kHz, which are shifted to 284, 297 and 319 K when the frequency is changed to 40 kHz, while the measurements on the compounds containing Br give two phases only. This result agrees with Gesi (1983) and may be due to the larger size of the  $\text{Br}^-$  ions in these compounds.

One can safely say that the change in electronic configuration which is associated with the gradual structural change is due to the gradual increase in dielectric constant with temperature, which is also the case for the  $\text{NH}_4\text{SO}_4$  and  $\text{NH}_4\text{NO}_3$  family (Sawada *et al.* 1975; Lehner *et al.* 1975).

The temperature dependence of the pyroelectric current  $I_p$  for the compounds  $(\text{CH}_2)_8(\text{NH}_3)_2\text{FeCl}_{4-x}\text{Br}_x$  is shown in Fig. 2. It is observed that the phase transition

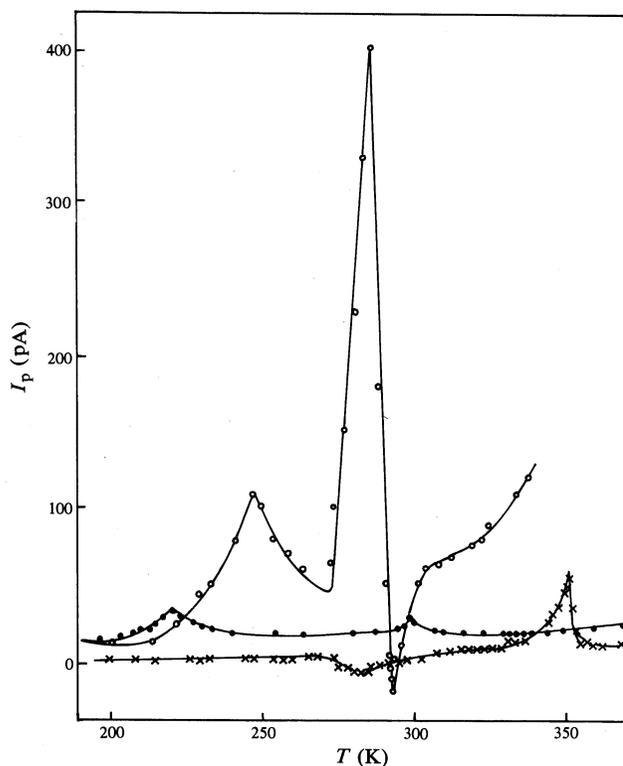


Fig. 2. Relationship between the pyroelectric current  $I_p$  and absolute temperature  $T$  for the compounds  $(\text{CH}_2)_8(\text{NH}_3)_2\text{FeCl}_{4-x}\text{Br}_x$ :  $x = 0$ , crosses;  $x = 1$ , open circles; and  $x = 2$ , solid circles.

points that appear in the dielectric constant are also present in  $I_p$ , with a slight shift in their positions. Experimentally, the polarisation which occurs in the pyroelectric sample is usually masked by the charges which are collected on the surface of the sample from the atmosphere. Changing the temperature of the sample will give a change in polarisation which can be detected in the form of a pyroelectric current. Theoretically, the measured pyroelectric current is usually the sum of the primary effect produced by clamping the sample plus the secondary effect produced from the free expansion of the sample. Recently it has been found (Ahmed *et al.* 1982; Sorge *et al.* 1986) that Cu and Zn compounds with the same general chemical formula give polarisation which increases by increasing the applied electric field, and when the field is turned off the polarisation still remains. This is known as the memory effect.

Calorimetric measurements in the high temperature region were performed on  $(\text{CH}_2)_8(\text{NH}_3)_2\text{FeCl}_4$ , as shown in Fig. 3. The heating run was taken at a rate of 20 K per min. Similar studies have been carried out on isomorphous compounds (Landi and Vacatello 1975; Kind *et al.* 1979; Socias *et al.* 1980). Fig. 3 gives three transition peaks with a total transition enthalpy of  $744.46 \text{ kJ mole}^{-1}$ , corresponding to a total change in entropy of  $\Delta S = 1417.66 \text{ J mole}^{-1} \text{ K}^{-1}$ . The data obtained give an endothermic peak at  $125^\circ\text{C}$  and three exothermic peaks at  $225.8$ ,  $384.7$  and  $438.2^\circ\text{C}$ . The change in enthalpy  $\Delta H$  and entropy  $\Delta S$  for the three exothermic peaks are listed in Table 3. The values of  $\Delta S$  vary drastically from one peak to another.

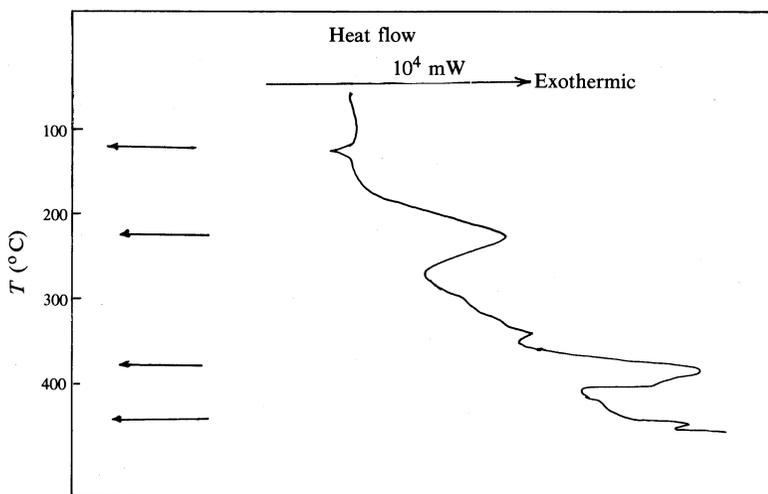


Fig. 3. Differential scanning calorimeter chart on heating the compound  $(\text{CH}_2)_8(\text{NH}_3)_2\text{FeCl}_4$ . The arrows show the temperature of each transition.

Table 3. Enthalpy change  $\Delta H$  and entropy change  $\Delta S$  for  $(\text{CH}_2)_8(\text{NH}_3)_2\text{FeCl}_4$

Peak temp. ( $^{\circ}\text{C}$ )	$\Delta H$ ( $\text{kJ mole}^{-1}$ )	$\Delta S$ ( $\text{J mole}^{-1} \text{K}^{-1}$ )
225.8	90.68	401.59
384.7	378.90	984.92
438.2	13.65	31.15

From direct observation one can assume that at  $384.7^{\circ}\text{C}$  a complete disordered chain is obtained. This means that we have an order-disorder phase transition of the rigid chain between two equivalent sites. Also, the resulting values of enthalpy and entropy change are of the same order of magnitude as the values reported for the two-dimensional system (Vacatello and Corradini 1973; Landi and Vacatello 1975; Kind *et al.* 1979). Finally, we can state that the anomalies appearing in both the dielectric constant and pyroelectric current, at the transition points, are related to the ordering in the system.

The effect of pressure on the size of the unit cell and the memory effect will be the subject of a future investigation.

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