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Electrical conduction in some $(C_nH_{2n})(NH_3^+)_2FeCl_4$ compounds

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The d.c. conductivity, a.c. conductivity and thermoelectric power of the compounds $H_3N^+(CH_2)^+NH_3FeCl_4$, where $n = 2, 3, 7$ and 10, have been studied over a temperature range of 150–500 K. The conductivity results confirm the presence of more than one structural phase transition for each compound investigated. The thermoelectric power measurements showed that electrons are the main charge carriers in all crystal phases. The conductivity results were explained on the basis of an electron hopping mechanism over the whole temperature range.

1. Introduction

Recently interest has increased in layer compounds with a general formula $(C_nH_{2n})(NH_3)_2MX_4$ where $M = Fe^{2+}, Mn^{2+}, \ldots$ and $X = Cl^-, Br^-, \ldots$ due to the large variety of structural and magnetic phase transitions they exhibit [1]. These series of compounds have the perovskite layered type of crystal structure. It is made up of metal halogen layers of MCl_6 octahedra each of which shares four corners with neighbouring octahedra in the layer. The layers are widely separated by alkylene diammonium ions.

X-ray studies showed that the sequence and the nature of the structural phase transitions are a function of n, M and X [2–6]. Many investigations on similar compounds [7] have shown that the alkylene ammonium ions which exist between the layers take up disordered orientations through many crystal phase transition processes.

Studies on these low-dimensional materials will lead to a greater understanding of the physics of conductivity and other phenomena.

The present research is a part of a programme to study:

(1) The nature of charge carriers and the mechanism of its transfer through the perovskite layer and

(2) the effect of the disorder of the crystal, caused by heating each of the types, and on the transport mechanism of the charge carriers. The present paper reports the results for $H_3N^+(CH_2)_nN^+H_3FeCl_4$, where n has values of 2, 3, 7 and 10.

2. Experimental

All chemicals used were of analytical grade. The preparation of the complexes $H_3N^+(C_nH_{2n})N^+H_3FeCl_4$, where $n = 2, 3, 7$ and 10, was, as previously reported in the literature [8], carried out under a stream of oxygen-free nitrogen gas. The chemical analyses of the complexes are given in Table I.

The d.c. and a.c. electrical conductivity, σ, measurements were performed on compressed pellets using a two-electrode method. The d.c. conductivity ($\sigma_{\text{d.c.}}$) was measured using a Keithley electrometer and the a.c. conductivity ($\sigma_{\text{a.c.}}$) using the drop technique. The conductivity was measured at 10, 20 and 30 kHz. Seebeck measurements were made using a hot probe technique. All the above measurements were carried

TABLE I Chemical analysis of the compounds of the general formula $(CH_2)_n(NH_3)_2FeCl_4$, $n = 2, 3, 7$ and 10.

Compound	Carbon percentage found (calculated)	Hydrogen percentage found (calculated)	Nitrogen percentage found (calculated)	Chlorine percentage found (calculated)
$(CH_2)_2(NH_3)_2FeCl_4$	9.26 (9.24)	3.90 (3.85)	10.81 (10.78)	54.75 (54.65)
$(CH_2)_3(NH_3)_2FeCl_4$	13.20 (13.15)	4.36 (4.38)	10.21 (10.23)	51.88 (51.92)
$(CH_2)_7(NH_3)_2FeCl_4$	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)

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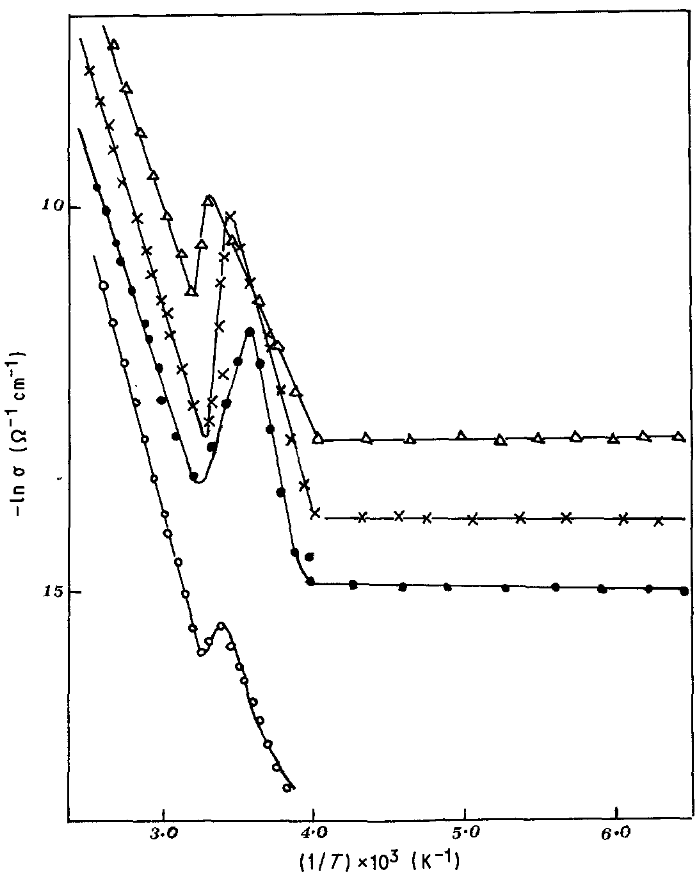

Figure 1 ln σ (σ is the conductivity) plotted against reciprocal of absolute temperature ($1/T$) at different frequencies (△ 10 kHz, × 20 kHz, ● 30 kHz, ○ d.c. conductivity) for $H_3N^+(CH_2)_7N^+H_3FeCl_4$.

out under a nitrogen atmosphere to avoid oxidation of the investigated complexes.

3. Results and discussion

The a.c. conductivity ($\sigma_{a.c.}$) of the investigated complexes was measured over a temperature range of 150–500 K. A plot of our results as ln $\sigma_{a.c.}$ against $1/T$ showed the same form of behaviour as that obtained for all complexes investigated. A typical plot is given in Fig. 1. From the conduction spectrum three phase transition temperatures can be defined; each corresponds to an abrupt change of σ and leads to a new structural modification characterizing the sample investigated. The temperatures at which the abrupt change of σ occurs are in good agreement with those obtained by DTA and dielectric constant measurements, on the same chelated compounds [7]. Fig. 1 also shows that above and below the anomalies, the function ln $\sigma_{a.c.} = f(1/T)$ could be well represented by straight sections verifying the thermal activation formula $\sigma = \sigma_0 \exp(-E_a/kT)$. The activation energies of conduction, E_a, for each phase of the complexes were calculated using the least squares method and given with other conductivity data in Table II.

The results for all complexes investigated show that at low temperatures, before the first phase transition, the conductivity $\sigma_{a.c.}$ is almost temperature independent, Fig. 1. This behaviour has been observed for some inorganic metals such as silicon and gold [9], which has attracted much attention in connection with the metal–insulator transition in a disordered system. The conductivity of this system in the low-temperature region could be interpreted on the basis of a hopping model [10], which describes the behaviour of a disordered system with an electron just below the Fermi level hopping to a distant state for which the required energy is as small as possible.

Electrical polarization has not been observed at the electrodes on using different electrodes such as silver,

TABLE II d.c. and a.c. conductivity data of the investigated chelated compounds $H_3N^+(CH_2)_nN^+H_3FeCl_4$, n = 2, 3, 7 and 10.

Compound	Temperature range (K)	30 kHz		20 kHz		10 kHz		σ_{dc}	
		σ‡	E_a§	σ‡	E_a§	σ‡	E_a§	σ‡	E_a§
$H_3N^+(CH_2)_2N^+H_3FeCl_4$	250–300	2.49×10^{-6}*	0.80	9.4×10^{-6}*	0.35	1.84×10^{-5}*	0.35	1.81×10^{-8}*	0.41
	300–500	2.63×10^{-6}†	0.40	3.45×10^{-6}†	0.41	5.53×10^{-6}†	0.42	6.00×10^{-7}†	0.62
$H_3N^+(CH_2)_3N^+H_3FeCl_4$	250–290	4.20×10^{-6}*	0.37	6.1×10^{-6}*	0.37	9.03×10^{-6}*	0.36	2.4×10^{-8}*	0.48
	320–500	3.72×10^{-6}†	0.19	4.84×10^{-6}†	0.26	7.76×10^{-6}†	0.25	9.6×10^{-7}†	0.57
$H_3N^+(CH_2)_7N^+H_3FeCl_4$	250–280	4.78×10^{-6}*	0.85	9.63×10^{-6}*	0.60	1.30×10^{-5}*	0.43	5.05×10^{-8}*	0.45
	310–500	3.36×10^{-5}†	0.37	9.61×10^{-5}†	0.56	4.52×10^{-4}†	0.55	2.11×10^{-6}†	0.69
$H_3N^+(CH_2)_{10}N^+H_3FeCl_4$	250–290	2.32×10^{-6}*	0.49	3.10×10^{-6}*	0.38	4.9×10^{-6}*	0.36	6.22×10^{-11}*	1.26
	330–500	2.90×10^{-5}†	0.52	3.80×10^{-5}†	0.52	6.1×10^{-5}†	0.51	4.4×10^{-6}†	0.95

*σ at 270 K.
†σ at 373 K.
‡σ in Ω^{-1} cm^{-1}.
§E_a in eV.

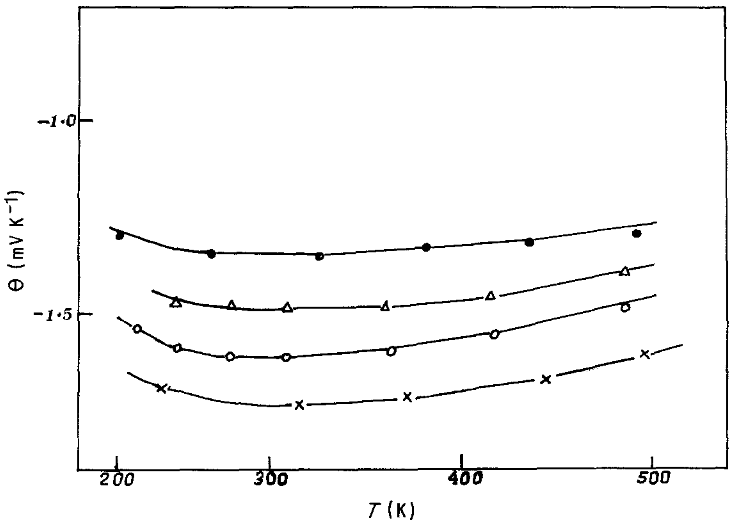

Figure 2 Dependence of Seebeck coefficient on temperature for the compounds $(CH_2)_n(NH_3)_2FeCl_4$, (● $n = 2$, △ $n = 3$, ○ $n = 7$, × $n = 10$).

platinum and copper. This behaviour suggests that the conduction is mainly electronic.

The Seebeck voltage measurements were carried out on the complexes under investigation at temperatures before and after each anomaly. The results are shown in Fig. 2. From the figure it can be seen that all complexes have a negative Seebeck voltage and the number of charge carriers are seemingly constant for each complex over the whole investigated temperature range. This means that the number of charge carriers is independent of the disorder formed in the crystal due to its crystal phase transition by heating. Therefore, one can say that the change in $\sigma_{a.c.}$ at phase transitions Fig. 1, should be attributed to the change in the mobility of the charge carriers. The ordering and disordering of alkylenediammonium cations between the layers during the phase transition process [1, 9] causes a change in the scattering of the diffusing electrons and in turn in its mobility values.

Fig. 1 also shows a slight decrease in the number of charge carriers as a result of increasing the number of carbon atoms in the complex. Therefore the change in σ; which is seemingly independent of the length of the diamine at lower temperatures, while it increases with length at higher temperatures, could be attributed to the decrease in the mobility of charge carriers with increasing length of the diamine. This interpretation is not unacceptable since the increase in the length of the diamine arises from the increase in the number of atoms between the layers. This will cause an increase in the probability of the collision of the hopping electrons with the atoms of diamine.

In the above mentioned conduction process the contribution of ionic conduction can not be totally excluded. The disappearance of the ionic current can be explained by considering the relative mobility of electrons and ions. It is well known that the mobility of electrons is generally about 6–10 orders of magnitude higher than the mobility of ions; therefore the ionic current is almost insignificant.

The d.c. conductivity ($\sigma_{d.c.}$) of the investigated complexes shows a similar trend to that obtained using a.c. measurements. Typical plots are shown in Fig. 1. The abrupt change in σ appears at temperatures which correspond to transition temperatures of the different structural phases observed by $\sigma_{a.c.}$, DTA and dielectric constant measurements. The d.c. conductivity data are summarized in Table II.

Our results show that the conductivities of the investigated complexes are high enough for a.c. measurements which indicate that the presence of barrier effects and crystal imperfections do not greatly influence the conductivity.

At higher temperatures our results show the dependence of $\sigma_{a.c.}$ on the frequency ω according to the following

$$\sigma_{a.c.} \propto \omega^{0.64}$$

This behaviour of the a.c. conductivity suggests a hopping conduction mechanism for the electrons at higher temperature.

4. Conclusion

The d.c. and a.c. conductivities of the complexes under investigation showed an abrupt change in the $\ln \sigma$ against $1/T$ plots. These results have been explained on the basis of structural arrangement of alkylenediammonium cations, $H_3N(CH_2)_nNH_3$ between the layers of octahedral $FeCl_6$ groups. The structural phase transition observed using this technique was found at the same temperatures observed on using DTA and dielectric constant measurements. Both conductivity and thermoelectric power measurements indicate that hopping transport of electrons through the crystals dominates the conduction process over the whole range of temperatures investigated.

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