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ELECTRICAL CONDUCTIVITY BEHAVIOUR IN $(C_nH_{2n})(NH_3)_2FeCl_4$ COMPLEXES (n = 2, 3, 7 AND 10)

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ABSTRACT

The d.c. and a.c. conductivity and the thermoelectric power of the compounds $H_3N^+(CH_2)_nN^+H_3FeCl_4$, where $n = 2$, 3, 7 or 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 show that electrons are the main charge carriers in all crystal phases. The conductivity results are explained on the basis of an electron-hopping mechanism over the whole temperature range.

INTRODUCTION

Recently increasing interest has been shown in layer compounds with the general formula $(C_nH_{2n})(NH_3)_2MX_4$, where $M = Fe^{2+}$, Mn^{2+}, etc. and $X = Cl^-$, Br^-, etc. owing to the large variety of structural and magnetic phase transitions that they exhibit [1]. This series of compounds has a crystal structure of the layered perovskite type, made up of layers of metal halogen (MX_6) octahedra, each of which share four corners with neighbouring octahedra in the layer. The layers are widely separated by alkylene diammonium ions.

X-ray studies have shown that the sequence and the nature of these structural phase transitions are dependent on n, M and X [2–6]. Many investigations on similar compounds [7] have shown that alkylene ammonium ions, which lie between the layers, cause disorientation of the structure during many crystal-phase transition processes.

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Studies of these two-dimensional materials should lead to a greater understanding of the physics of conductivity and other phenomena.

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

(1) the nature of charge carriers and the mechanism of their transfer through the perovskite layer;

(2) the effect of disorder within the crystal, and 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 the value 2, 3, 7 or 10.

EXPERIMENTAL

All chemicals were of analytical grade. The preparation of the complexes $H_3N^+(C_nH_{2n})N^+H_3FeCl_4$ were prepared as reported in the literature [8]. The preparation was carried out under a stream of oxygen-free nitrogen gas. The results of a chemical analysis of the complexes are given in Table 1.

The d.c. and a.c. electrical conductivity σ measurements were performed on compressed pellets using the two-electrode method. The d.c. conductivity σ_{dc} was measured using a Keithly electrometer; the a.c. conductivity σ_{ac} was measured using a drop technique. The conductivity was measured at 10, 20 and 30 kHz. Seebeck measurements were performed using the hot-probe technique. All the above measurements were carried out under a nitrogen atmosphere to avoid oxidation of the complexes.

RESULTS AND DISCUSSION

The a.c. electrical conductivity σ_{ac} of the investigated complexes was measured at 150–500 K. On plotting our results in the form ln σ_{ac} versus

TABLE 1

Results of chemical analysis (calculated values in parentheses) of the compounds of the general formula $(CH_2)_n(NH_3)_2FeCl_4$; $n = 2, 3, 7$ and 10 [a]

Compound	C (%)	H (%)	N (%)	Cl (%)
$(CH_2)_2(NH_3)_2FeCl_4$	9.26	3.90	10.81	54.75
	(9.24)	(3.85)	(10.78)	(54.65)
$(CH_2)_3(NH_3)_2FeCl_4$	13.20	4.36	10.21	51.88
	(13.15)	(4.38)	(10.23)	(51.92)
$(CH_2)_7(NH_3)_2FeCl_4$	25.51	6.10	8.37	43.13
	(25.47)	(6.06)	(8.49)	(43.05)
$(CH_2)_{10}(NH_3)_2FeCl_4$	32.40	6.85	7.56	38.10
	(32.27)	(6.99)	(7.53)	(38.19)

[a] The calculated values were obtained from the ratio of atomic weight of each element with respect to the molecular weight of the complex.

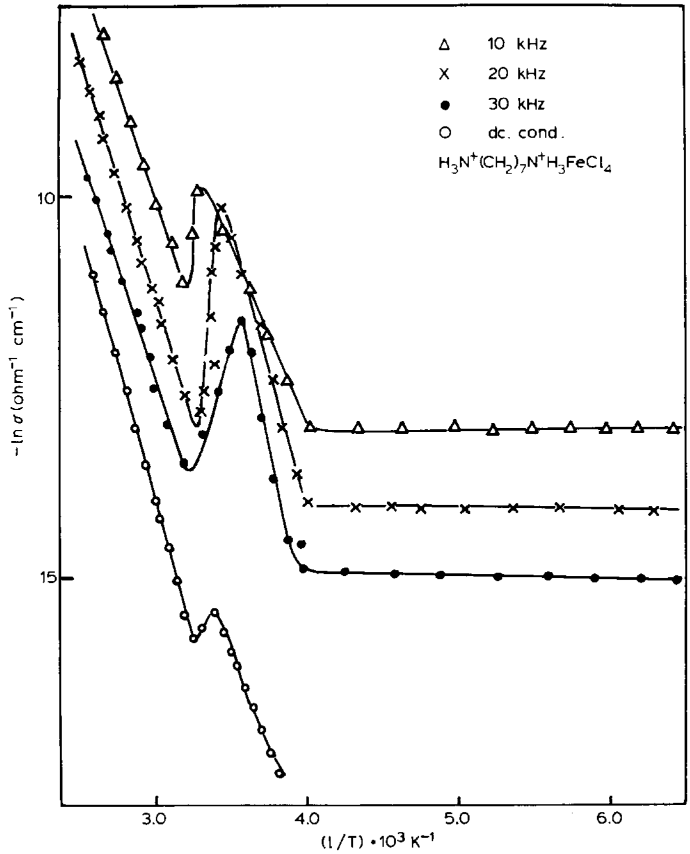

Fig. 1. Correlation between ln σ and the reciprocal of the absolute temperature at different frequencies.

$1/T$, the same behaviour was observed for all the complexes investigated. A typical plot is given in Fig. 1. On inspection of the conduction spectrum one can define three phase-transition temperatures, each corresponding to an abrupt change of σ and indicating a new structural modification of the sample. The temperatures at which these abrupt changes of σ occur are in good agreement with those obtained previously by DTA and dielectric constant measurements on the same chelated compounds [7]. Figure 1 also shows that away from these anomalies the function $\ln\sigma_{ac}=f(1/T)$ may be well represented by straight lines verifying the thermal activation formula $\sigma=\sigma_0\exp(-E_a/KT)$. The activation energies for conduction E_a for each phase of the complexes were calculated using the least-squares method and are given along with other conductivity data in Table 2.

The results for all of the complexes investigated show that at low temperatures, before the first phase transition, the conductivity σ_{ac} is almost independent of temperature (Fig. 1). Such behaviour has also been observed for some alloys such as Si–Au [9], which has attracted much attention in

TABLE 2

Conductivity data [a] (d.c. and a.c.) of the investigated chelated compounds $H_3N^+(CH_2)_nN^+H_3FeCl_4$, where $n = 2, 3, 7$ or 10

Compound	Temperature range (K)	30 kHz		20 kHz		10 kHz		d.c.	
		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	$9.4\ \times10^{-6}$	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	$6.1\ \times10^{-6}$	0.37	9.03×10^{-6}	0.36	$2.4\ \times10^{-8}$	0.48
	320–500	3.72×10^{-6}	0.19	4.84×10^{-6}	0.26	7.76×10^{-6}	0.25	$9.6\ \times10^{-7}$	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	$4.9\ \times10^{-6}$	0.36	6.22×10^{-11}	1.26
	330–500	2.90×10^{-5}	0.52	3.80×10^{-5}	0.52	$6.1\ \times10^{-5}$	0.51	$4.4\ \times10^{-6}$	0.95

[a] σ given at 270 K (upper) and 375 K.

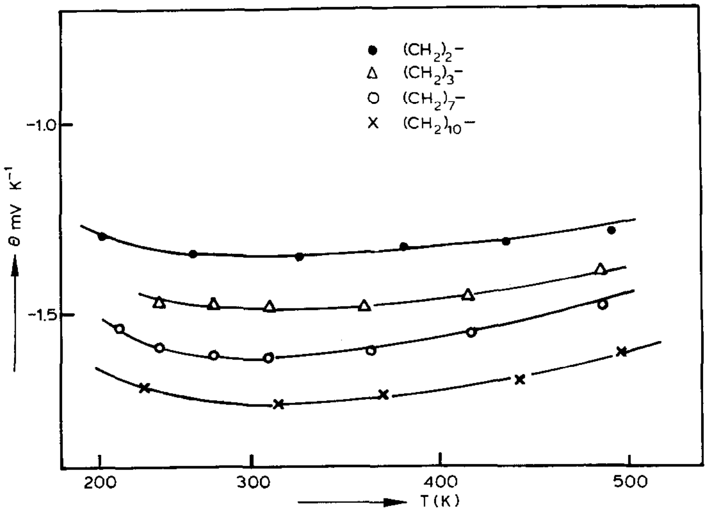

Fig. 2. Dependence of Seebeck coefficient on temperature for the compounds $(CH_2)_n(NH_3)_2FeCl_4$, where $n = 2$, 3, 7 and 10.

connection with the metal–insulator transition in a disordered system. The conductivity of this system at low temperatures could be interpreted on the basis of a hopping model [10], which describes the behaviour of a disordered system by postulating an electron just below the Fermi level hopping to a distant state for which the required energy is as small as possible.

Electrical polarization was not observed at the electrodes for any of the different metals used as electrodes (e.g. Ag, Pt and Cu). This suggests that the conduction is mainly electronic.

Seebeck voltage measurements were carried out on the complexes at temperatures, above and below those corresponding to each anomaly. The results are shown in Fig. 2. From the figure it can be seen that all the complexes have negative Seebeck voltages and that the number of charge carriers is seemingly constant for each complex over the whole temperature range investigated. This means that the number of charge carriers is independent of the disorder created in the crystal due to thermal phase transition. Therefore, one can say that the change in σ_{ac} at phase transitions (Fig. 1) can be attributed to a change in the mobility of the charge carriers. The ordering and disordering of alkylenediammonium cations between the layers during phase transition processes [1,9] causes a change in the scattering of the diffused electrons and, in turn, in their mobility.

Figure 1 indicates a slight decrease in the number of charge carriers with increasing number of carbon atoms in the complex. The change in σ, which is seemingly independent of the length of the diamine chain at lower temperatures but increases with the chain length at higher temperatures, may thus be attributed to a decrease in the mobility of the charge carriers with increasing chain length of the diamine. This interpretation is not unacceptable since an increase in the length of the diamine, coming from the increase in the number of atoms between the layer, will cause an increase in the probability of a collision of the hopping electrons with the atoms of the diamine group.

In the above-mentioned conduction process the contribution of ionic conduction cannot 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 about 6–10 orders of magnitude higher than the mobility of ions; therefore the ionic current is practically insignificant.

The d.c. electrical conductivity σ_{dc} of the complexes shows a similar trend to that obtained using a.c. measurements. Typical plots are shown in Fig. 1. The abrupt change in σ, appearing at temperatures corresponding to transition temperatures between different structural phases were followed by σ_{ac}, DTA and dielectric constant measurements. The d.c. conductivity data are summarized in Table 2.

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

At higher temperatures our results show the dependence of σ_{ac} on the frequency w according to

$$\sigma_{ac} \propto w^{0.64}$$

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

CONCLUSION

The d.c. and a.c. conductivities of the complexes under investigation showed an abrupt change in ln σ vs. $1/T$ plots. These results have been explained on the basis of the structural arrangement of alkylenediammonium cations, $H_3N^+(CH_2)_nN^+H_3$ between the layers of octahedral $FeCl_6$ groups. The structural phase transitions observed using this technique were found to occur at the same temperatures observed using DTA and dielectric constant measurements. Both conductivity and thermoelectric power measurements indicate that hopping of electrons through the crystals predominates as the main conduction process over the whole range of investigated temperatures.

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