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Thermally stimulated currents of $(CH_2)_8(NH_3)_2Fe_{1-x}Cd_xCl_4$ ($x = 0.15$–0.80)

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Abstract

The thermally stimulated current (TSC) has been measured for diaminooctane–Fe–Cd tetrachloride compounds in the temperature range that includes their phase transition points. The dilution of the metallic layers by non-magnetic Cd ions (15, 27, 40, 50, 60, 70 and 80 mol%) decreases the TSC until the critical concentration (≈ 50 mol%) is reached, then it increases again.

Keywords: Cadmium compound; Iron compound; TSC

1. Introduction

As a general rule in transition metal complexes, there are multiple phases indicating some structural differences. In recent years much effort has been devoted to relating the electrical properties to structural changes in compounds of the general formula $(CH_2)_n(NH_3)_2MCl_4$ [1–6], where $n = 2, 3, 4, \ldots$; $M = Fe^{2+}$, Mn^{2+}, Ni^{2+} .... The structure of these complexes consists of an octahedral layer of $MCl_4{}^{2-}$ anions with the alkylenediammonium chain occupying positions between the metal-containing layers. The modular structure of these compounds is significantly deformed by an applied external electric field. High fields may induce corresponding regions inside the phase or additional phase transitions [7]. The presence of the organic group between the metal-containing layers leads to superexchange interaction between them. The weak hydrogen bond N–H···Cl between the

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layers will lead to a monoclinic unit cell, especially at low temperature. This weak bond is due to the presence of NH_3 groups between the layers. This study is therefore devoted to the influence of dilution using non-magnetic ions such as Cd on the thermally stimulated discharge current (TSC) of the main skeleton for the compound $(CH_2)_8(NH_3)_2FeCl_4$. The effect of applying an electric field at high temperature is to develop a charged sample, the so-called thermal electret. After formation, a charged electret shows two major types of behaviour [8]; on the one hand, the TSC is obtained even at constant temperature, and on the other hand, a pyrolelectric current is obtained by varying the temperature which has a magnitude proportional to the rate of change of temperature. Dipolar orientation and trapping of charge carriers generated in the bulk as well as injected from the electrodes are the mechanisms responsible for electret formation. The trapping of charges can take place at various trapping sites—surface states, chain foldings and molecular disorder [9].

2. Experimental

The samples under investigation were prepared using Analar reagents (B.D.H) with a 1:1 molar ratio of $(CH_2)_8(NH_3)_2Cl_2$ to $FeCl_2 \cdot 4H_2O$ or $CdCl_2 \cdot 6H_2O$ respectively. Acidified triply distilled water was used to dissolve the reagents. The materials were heated for ≈ 1 h with a passage of stream of oxygen-free nitrogen gas to prevent the oxidation of Fe^{2+}. Sudden cooling was used to obtain the samples. Recrystallization was carried out and the sample was washed with ether and ethanol having a ratio of 1:2. The samples were dried in a glove box, then ground and compressed under a pressure of 5 tons cm^{-2} into pellet form with diameter 1 cm and thickness ≈ 0.1 cm. The top and bottom surfaces of each sample were polished, coated with silver paint, and checked to assure ohmic contact.

The samples were polarized by heating to a polarizing temperature $T_p = 230°C$, after which the polarizing field (0.2 kV cm^{-1}) was applied and the temperature was kept constant at T_p for a polarizing time $t_p = 1$ h. The samples were subsequently cooled to $-15°C$ with the polarizing field on for TSC measurements. After removing the field the samples were earthed immediately, then heated at a constant heating rate (0.4 K min^{-1}). The temperature was measured using a type K thermocouple placed in contact with the sample. The TSC was measured by using a Multimeter, LEVEL Type TM9BP.

3. Results and discussion

Measurements of the thermally stimulated current (TSC) for diaminooctane–Cd–Fe tetrachloride samples with different cadmium concentrations (15, 27, 40, 50, 60, 70 and 80 mol%) reveal two or three maxima, designated by α, β and γ, in order of decreasing temperature, as shown in Figs. 1 and 2. The γ-peak which generally occurs at lower temperatures may be due to the thermal agitation of the dipoles.

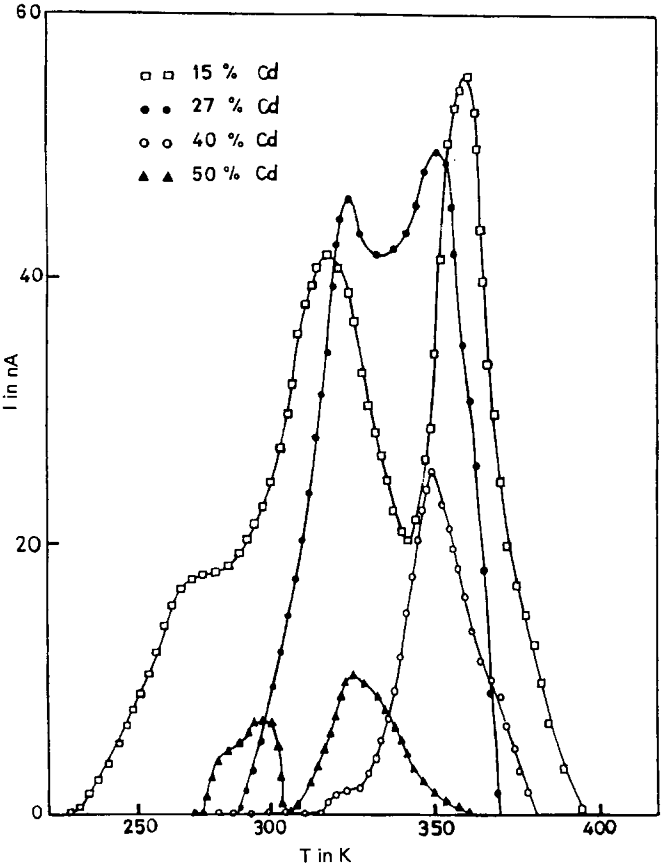

Fig. 1. Temperature dependence of TSC for samples of diaminooctane–Cd–Fe tetrachloride with different Cd concentrations (mol%): (□) 15%; (●) 27%; (○) 40%; (▲) 50%.

This is small and the probability of the alignment of the dipoles due to the previously applied field is still large. The gradual increase of the sample temperature will create some distortion in the metal-containing layers, and this will be accompanied by a change in the symmetry of the system. One may thus expect this change in symmetry to play a role in the occurrence of the γ-peak. During the experimental work, it was observed that the phase transition γ is accompanied by a reversible colour change that resembles the thermochromic character of many organic complexes [10]. Continually increasing the temperature will increase the thermal agitation and disturb the ordering of the organic groups bound between the metal-bearing layers. This disordering results in another transition called order–disorder; this appears in the form of the β-peak in Figs. 1 and 2. At the same time, weakening of the hydrogen bonding between the NH_3 group and the MCl_4^{2-} layers, and also the change in puckering of the system caused by heating, will both help to induce such a transition.

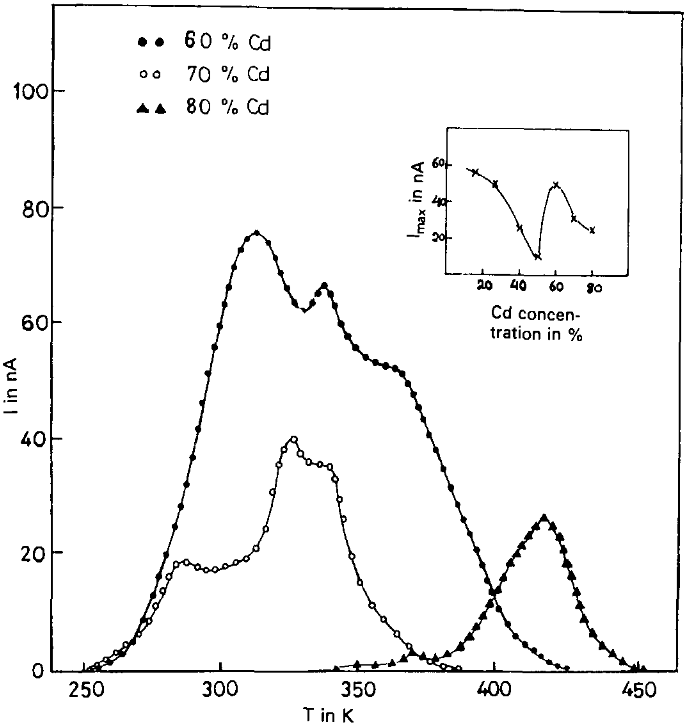

Fig. 2. Temperature dependence of TSC for samples of diaminooctane–Cd–Fe tetrachloride with different Cd concentrations (mol%): (●) 60%; (○) 70%; (▲) 80%. Inset: the dependence of the maximum TSC on the Cd concentration.

Going on through the TSC spectrum, the thermal energy increases, resulting in an increase in the movement of the organic groups. This contributes the conduction process, causing an increase of the TSC at the α-peak. The decrease of the TSC after the α-peak may be attributed to chain melting, which increases the degree of freedom of the electric dipoles to a limit which may overcome the reverse effect of the electric field, and to further weakening of H-bonding by heating.

Overall, from the experimental data, it is observed that the α, β and γ peaks are shifted to lower temperatures by increasing the Cd^{2+} ion concentration until that concentration reaches a critical value. At that point the trend is reversed. Considering the Cd ions as an impurity in the main lattice, one can attribute this behaviour to the increase of the impurity ions in the compound, thereby decreasing the nearest neighbour interaction between the Fe ions. Because of the change in the interlayer and interlayer interaction between the electric dipoles, the phase transition may be expected to occur at lower temperatures. This is supported by the experimental data in Figs. 1 and 2. Past the critical Cd^{2+} concentration, the main skeleton of the complex exhibits a new perturbation such that the iron ions will be considered as the impurity ions and the main lattice will be the cadmium ions. Therefore the phase transitions take place at higher temperatures.

Correlating the values of the TSC with different concentrations of cadmium ions, it is clear that on increasing the cadmium concentration the TSC is sharply decreased. This may be due to the interstitial position of cadmium ions in the lattice causing resistance towards the polarization process.

A closer look at Figs. 1 and 2 reveals that the effect of this dilution of the metallic layer by Cd^{2+} ions is to decrease the TSC. This decrease is observed up to certain concentration of Cd inside the Fe layer. Beyond this point the current increases again; see the inset in Fig. 2. We infer that the cadmium ions have as a separate unit cell on increasing their concentration up to ≈ 50 mol% (critical concentration). In this case the polarization may be due to the sum of two distinct processes, one of them related to iron ions and the other to cadmium ions. Above the critical concentration, the polarization begins to increase gradually due to the effect of predominantly cadmium ions in the lattice. In this case, the effect of the depolarization process due to iron ions is negligible in comparison with the polarization of cadmium ions in the lattice. At the same time some of the iron ions will be oxidized to Fe^{3+}, initiating an electron transfer reaction $Fe^{2+} \rightarrow Fe^{3+} + e^-$. These electrons will help in the conduction process and increase the TSC up to 60 mol% of Cd.

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