

Electrical conduction of sodium acetylacetonate

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Abstract. The temperature dependence of DC electrical conductivity σ of sodium acetylacetonate compound Na(ac,ac) is studied for fresh and polarized samples. Both samples show semiconductor behaviour, but the value of σ for the fresh sample is higher than that of the polarized sample. Three distinct regions are observed in the temperature conductivity curves. The conduction mechanism of each region is discussed. Anomalous conductivity phenomena are observed above 105°C and attributed to unidirectional intermolecular or phase transformation. The results are discussed on the basis of ionic conduction and some conduction parameters such as conduction energy E_c , transport energy E_t , ion mobility μ , free ion density n , are calculated.

Keywords. Activation energy; electrical conductivity; phase transformation; sodium acetylacetonate.

1. Introduction

Metal acetylacetonate compounds $M(\text{ac,ac})_x$ are of increasing importance in many applied and industrial scientific fields. They are mostly used as catalysts or chemical activators. A number of investigations (Kamel *et al* 1975; Amin *et al* 1980; Sahai and Verma 1981; Kadry *et al* 1984; Molokhia 1986) has been made for some of these compounds to determine their electrical properties such as dielectric constant, dielectric loss, pyroelectric behaviour and electrical conductivity, but the available data is still far from being complete.

The aim of the present work is to study the temperature dependence of DC electrical conductivity of one of the most important metal acetylacetonate compounds which is sodium acetylacetonate Na(ac,ac), to collect more data and knowledge about the possible phenomena and the conduction behaviour of this compound.

2. Experimental technique

Sodium acetylacetonate compound Na(ac,ac) was prepared according to standard procedures given in the literature (Fernelius 1949; Lowis *et al* 1948). Recrystallization of the products was carried out in ethyl-alcohol and the samples were dried under vacuum. The purity of the sample was tested by measurement of melting point (203°C) and infrared spectra which agreed well with the reported values in the literature. For the electrical conductivity measurements, equal weights of the samples in powder form were placed in a special die. The die is placed in hydraulic press for 15 min under 10,000 kg in vacuum (Beckman 00–25 Glenrothes, Fife, Scotland), to form a disc 1.2 cm in diameter and 1.7 mm thick. The disc was sandwiched between two optical quality surfaces of a copper electrode using a specially designed holder to eliminate contact resistance. The I - V characteristics

indicate that the assembly of sample and electrodes is ohmic in character (Sawaby *et al*, unpublished).

A high impedance electrometer (VA-J 52, Dresden DDR) and a multiflex Galvanometer Type MG2 were used through a conventional electrical circuit. The measurements were carried out in a dry atmosphere keeping all experimental parameters unaltered in order to obtain comparable values.

Polarization of samples was carried out by first heating them to a specific polarizing temperature T_p and then applying an electric polarizing field E_p for a known polarizing time t_p . Subsequently, the samples were cooled to room temperature under the applied field and the field then reduced to zero.

3. Results

It was noticed that the time dependence of the current at voltages less than 12 V cm^{-1} is negligible. Therefore, to avoid the polarization effect on the conductivity behaviour of Na(ac,ac) sample, field strengths of value less than 12 V cm^{-1} should be used.

Figure 1 shows the relation between $\log \sigma$ and reciprocal absolute temperature over the temperature (20–160°C), for fresh and polarized Na(ac,ac) samples. For the heating curves, it can be seen from this figure that the electrical conductivity σ of fresh sample is higher than that of the polarized sample. However, the curve can be divided into three regions—the first region from 20 to 105°C, the second region from 105 to 125°C and the third region from 125 to 160°C. For the first region, it was noticed that the relation between $\log \sigma$ and $10^3/T$ gives straight parallel lines for fresh and polarized samples, i.e. obeys the well-known Arrhenius relation:

$$\sigma = \sigma_0 \exp \left[-E_c/kT \right] \quad (1)$$

where σ is the conductivity corresponding to a temperature T and E_c is the apparent activation energy, σ_0 is a constant and k is the Boltzman's constant. The energy of the conduction E_c was calculated from the slope of the straight line of the first region and is found to be 1.68 eV. For the second region, slight decrease in the conductivity values are observed by increasing the temperature, followed by fast decay in the conductivity curve at the third region for both samples. On the other hand, it is also noticed that the values of σ are strictly reproducible at all temperatures of the first region for both samples, while the reproducibility of σ is not indicated for the second and third regions. However, as the sample is taken over the heating-cooling cycle from the first region to the second region, the break-point between the two regions appears only during the heating process. On the contrary, the reproducibility of σ is greatly impaired and the break-point between the first and second regions disappears completely during the heating-cooling cycle from the first to the third region and vice versa as shown in figure 1. The irreproducibility and decay process of σ which take place at the second and third regions may be attributed to possible existence of an irreversible intermolecular change starting slowly at the second region. Therefore it can be considered that this region is the transition region between the two straight lines of the first and third regions. However little inference can be drawn from figure 1. Therefore, for complete identification of the anomalous phenomena, several

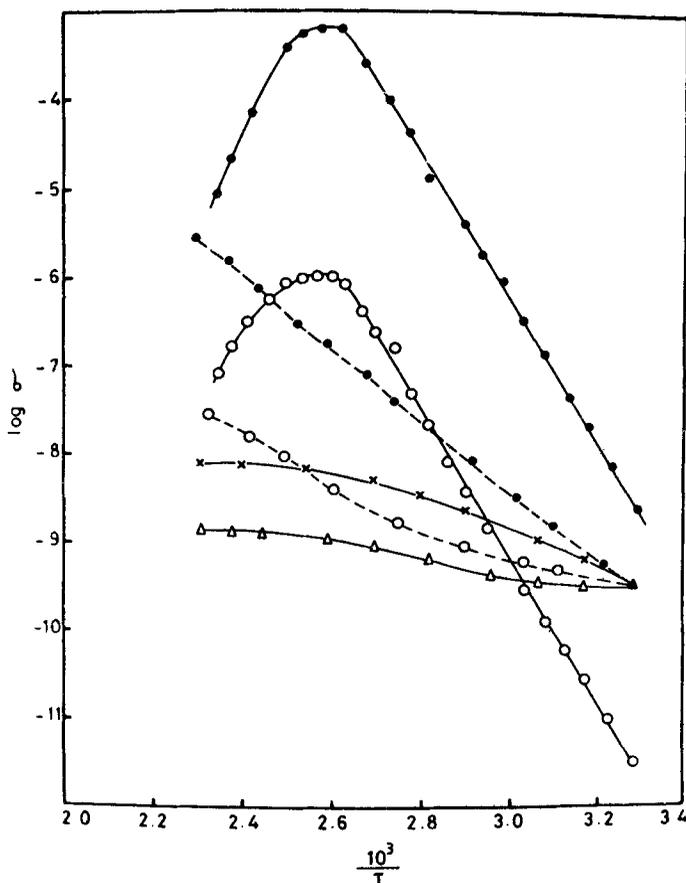


Figure 1. The electrical conductivity of Na(ac,ac) as a function of the reciprocal temperature. Solid line for heating, dotted line for cooling (●) fresh sample; (○) polarized sample, $T_p = 60^\circ\text{C}$, $E_p = 30 \text{ V cm}^{-1}$, $t_p = 30 \text{ min}$; (×) reheating the unpolarized sample; (△) reheating the polarized sample.

experimental runs were carried out at different temperatures corresponding to the transition region (105, 110, 115, 120 and 125°C), to study the isothermal annealing effect on the conduction current of Na(ac,ac) for different applied fields. Figure 2 represents one of these experiments at 115°C . It can be seen from this figure that the time dependence of the current at an applied field of 10 V cm^{-1} is nearly negligible, but it becomes conspicuous at fields above 12 V cm^{-1} and the gradient tends to increase with the applied field. Similar plots were made at 105, 110, 120 and 125°C but are not presented here. It was also noticed that the decay in the conductivity at this region not only depends on the applied field but is also affected by the annealing temperature. Therefore, the isothermal annealing effect was also studied at different annealing temperatures for a constant applied field strength of 30 V cm^{-1} as shown in figure 3. It can be seen from this figure that the values of the current density generally decrease with heating time. At higher temperatures, shorter heating periods are needed to reach a minimum value of the current density which reflects the temperature dependence of the current decay.

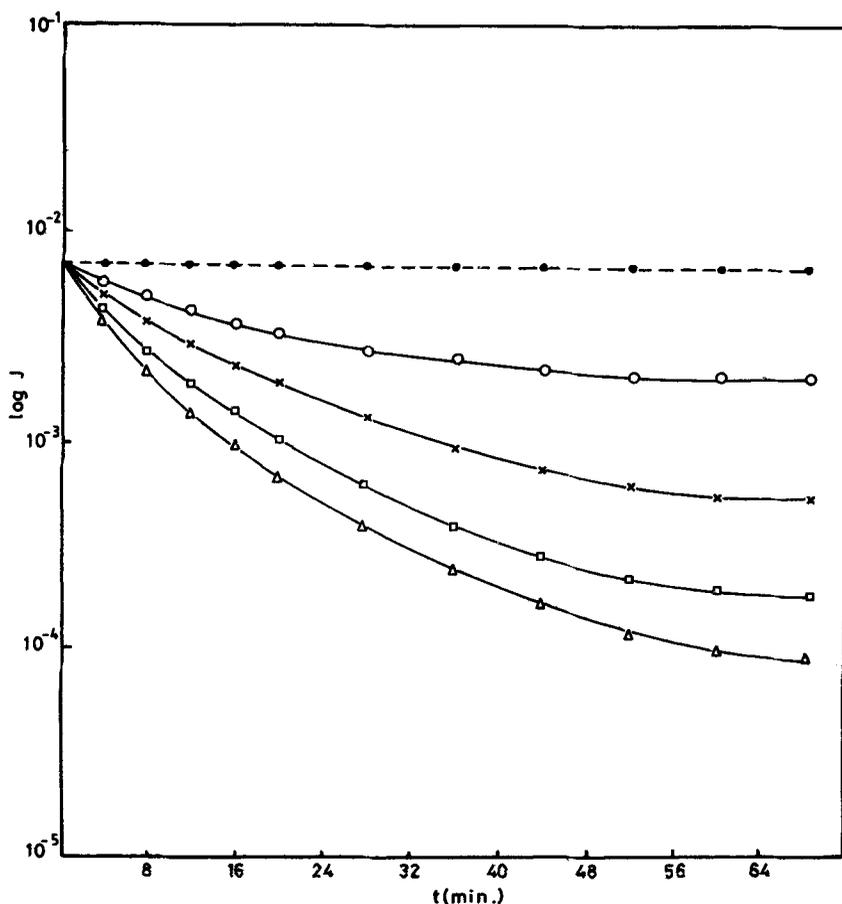


Figure 2. Isothermal annealing curves at different applied field ($\log J$ against time) at 115°C for applied field of: (●) 10; (○) 15; (×) 20; (□) 30; (△) 40 V cm^{-1} .

4. Discussion

The temperature dependence of the electrical conductivity σ of Na(ac,ac) shows semiconductor behaviour, when the values of the specific conductivity (which was measured under the present experimental conditions) are increased from $10^{-9} \text{ ohm}^{-1} \text{ cm}^{-1}$ at room temperature to about $10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 105°C as seen in figure 1. The apparent activation energy calculated from the straight line of the first region is 1.68 eV. It is sometimes assumed, as a general rule, that values for activation energies greater than 0.6 or 0.8 eV would normally be associated with ionic transport and values less than 0.2 eV should be considered as indicating undoubtedly electronic mechanism (Jonscher 1967; Jain *et al* 1978). Therefore the value of 1.68 eV may be taken in favour of an ionic conduction mechanism operating in the temperature range corresponding to the first region. On the other hand, the irreproducibility of σ observed at the second and the third regions of figure 1, may be attributed to possible existence of an irreversible phase

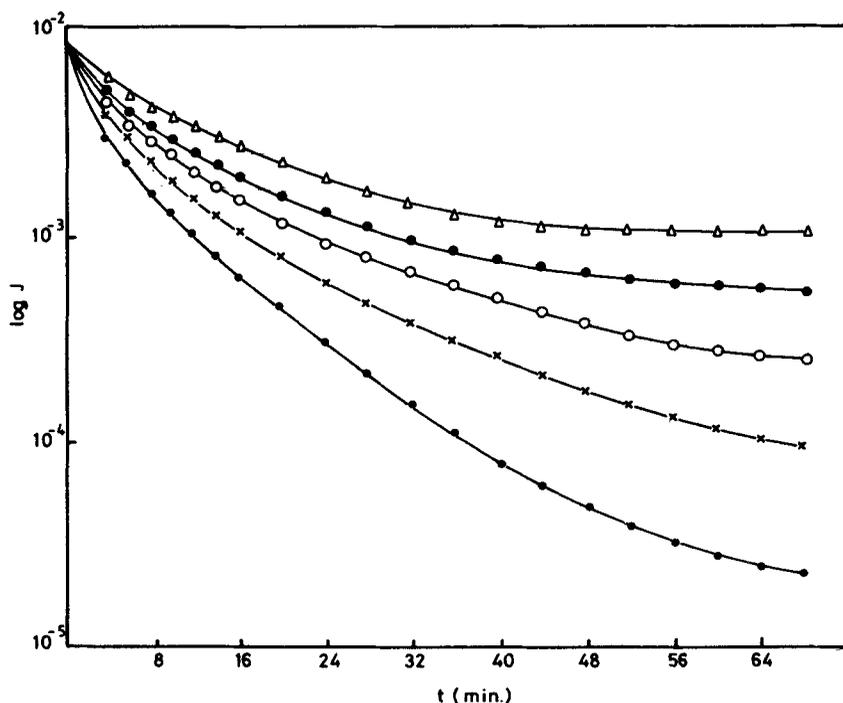


Figure 3. Isothermal annealing curves at different temperature and constant applied field of 30 V cm^{-1} ($\log J$ against time) (Δ) 105, (\bullet) 110, (\circ) 115, (\times) 120, (\cdot) 125°C.

transformation starting slowly in the transition region (second region) and completely altered in the third region.

The isothermal annealing study shows that the observed change is thermally and electrically activated.

It will be assumed here to a first approximation that the process in action is controlled by a chemical rate equation of type (Kamel and Attia 1961),

$$t \exp(-\Delta E/kT) = \text{constant}, \quad (2)$$

where k is the Boltzman's constant, t the time of change and ΔE the energy activating the process. The equivalent times and temperatures prescribing a particular degree of change were measured by the cross-cut method from the regular part of the isothermal annealing curves given in figure 3. The activation energy ΔE for this process was deduced from (2) by plotting the logarithm of the time versus the reciprocal of the absolute temperature. Figure 4 shows a parallel set of straight lines. The slopes of these lines give an average value of the ΔE amounting to 0.82 eV. On the other hand, more information about the current decay phenomena could be obtained by applying the following equations (Masamitsu *et al* 1970).

$$J = J_0 \exp[-\mu_i Et/l], \quad (3)$$

where J is the current density, μ_i the mobility, l the thickness of the sample and t the time.

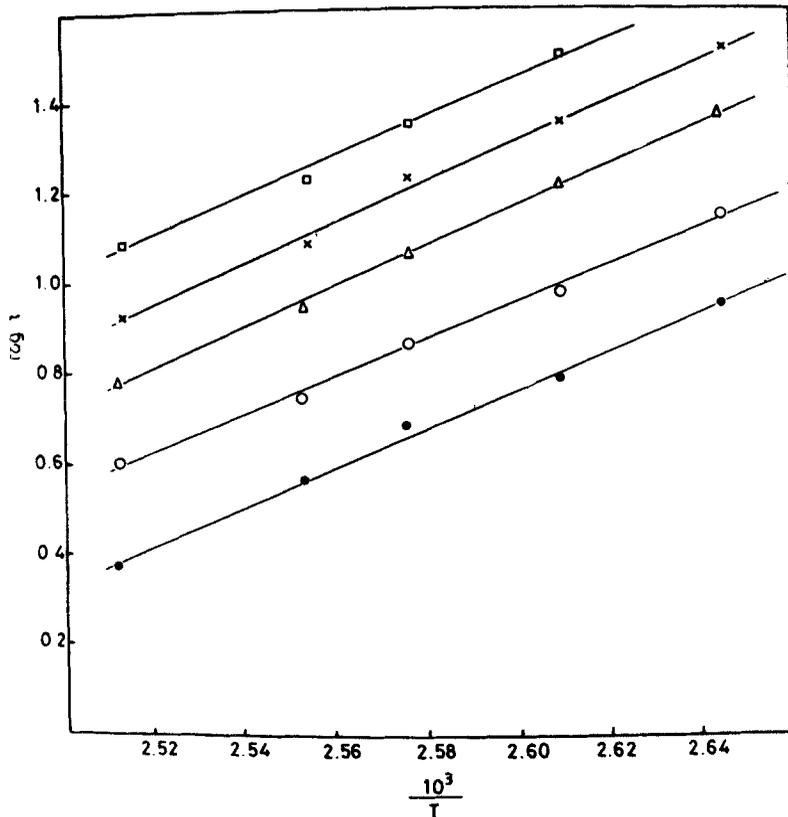


Figure 4. Equivalent time temperature curves for the observed decay in the current density during the isothermal annealing processes derived from figure 3.

$$J_0 = qM_0\mu E, \quad (4)$$

where q is the ion charge, E the electrical field and M_0 the density of the mobile ion at time $t=0$. However, the initial gradient of $\log I$ vs t curves in figure 3 at the maiden application of DC voltage may provide information on ion mobility μ_i from (3). The calculated ion mobilities μ_i at different temperatures are listed in table 1. The apparent activation energy concerning the transport phenomena E_μ is obtained by plotting $\log \mu_i$ vs $10^3/T$ as shown in figure 5. The value of E_μ which was calculated was found to be 0.80 eV. Since we have the DC conductivity of the unpolarized sample (the time dependence of the current in this case is negligible) and the ion mobility μ_i , it is possible to estimate the mobile ion density n from the following equation:

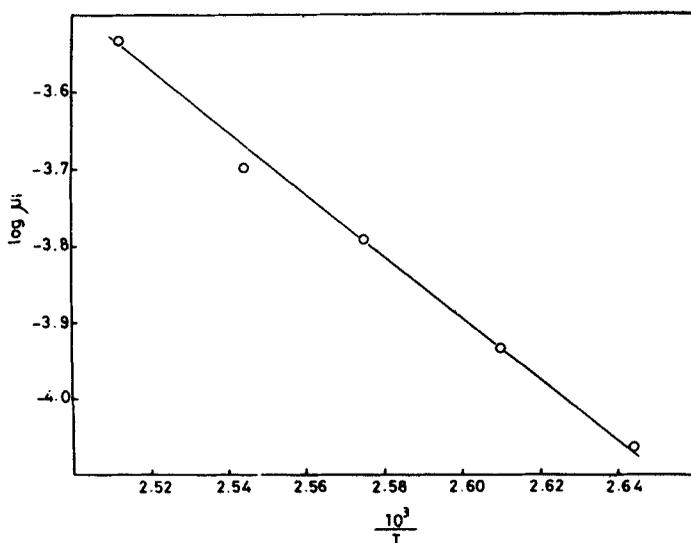
$$J = qn\mu E, \quad (5)$$

the numerically calculated values of n at different temperatures are listed in table 1.

The present data indicated that the activation energy of the slow phase transformation ΔE is equal to the transport energy E_μ . Therefore, it is believed that the two processes are linked. If this is true, the transformation of the phase should be associated with change in the conduction behaviour. The heating-cooling

Table 1. The calculated mobility and the number of mobile ion density.

Temperature (°C)	Ion mobility μ_i ($10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$)	Mobile ion density n (10^{16} cm^{-3})
105	8.7	11.5
110	11.5	9
115	16.1	7.29
120	19.5	6.4
125	28.9	4.84

**Figure 5.** Temperature dependence of mobility μ_i derived from the initial slope of current time curve of figure 3.

process either from the first region to the second region or from the first region to the third region, indicates the decrease of conduction after each cycle as seen in figure 1. Therefore, the phase transformation which is observed above 105°C usually leads to decrease in conduction of Na(ac,ac). Based on this, it is expected that the conductivity of the reheated sample for the second cycle becomes lower than that of the fresh sample which is experimentally found to be so. However, it was previously reported by using X-ray techniques that Na(ac,ac) undergoes an irreversible phase transition from orthorhombic to triclinic at temperatures above 82°C and the transformation is relatively slow (Kamel *et al* 1975). Therefore the electrical conductivity results of the present work can be considered as evidence and strong support for the presence of this slow phase transition. On the other hand, the determination of the activation energy of the phase transformation process and the transport energy of the charge carrier indicates the relation between this transformation and the electrical behaviour of Na(ac,ac).

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