

ELECTRICAL AND THERMAL CONDUCTIVITIES OF SOME SULPHATE COMPOUNDS

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The electrical conductivity σ and the thermal conductivity λ were investigated at varying temperature ($40 < T < 120^\circ\text{C}$) for two sulphate compounds, anhydrous mercury(II) sulphate HgSO_4 and cerous(III) sulphate $\text{Ce}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$. It seems likely that each of the two sulphate salts undergoes structural phase transition around 90°C . The differential thermal analysis thermogram was carried out as an aid for confirming of the observed phase transitions. The mechanism of the heat transfer is mainly due to phonons. Interpretation of the obtained data was given on the basis of the reorientational motion of the SO_4^{2-} ions.

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1. Introduction

Over the past several years the physical properties of the members of sulphate series, M_2SO_4 , and/or hydrogen sulphate family MHSO_4 where M is a monovalent ion or group ($\text{M}^+ = \text{Cs}^+, \text{Rb}^+, \text{K}^+, \text{Na}^+ \dots$ and/or NH_4^+), have been receiving much attention of several investigators owing to their interesting properties. These compounds undergo several structural phase transitions at low and high temperatures [1-7]. Some members of these two series show ferroelectric phase transitions [8].

To our surprise much less attention has been devoted to the related two series of sulphate compounds $DSO_4 \cdot xH_2O$ and $T_2(SO_4)_3 \cdot xH_2O$ where D is a divalent element (D = Hg(II), Pb(II), ... and T is a trivalent ion i.e. Ce(III) and x is the number of water molecules ($x = 0, 1, 2, \dots$).

The crystal structures of some members of the sulphate series were previously determined [9–12]. The most interesting group in the structures of these compounds is the sulphate group SO_4 which is usually found to arrange in tetrahedral or polyhedral symmetries. The existence of water molecules in these compounds leads to the formation of the hydrogen bonding of the type O–H...O.

In the previous work we investigated the phase transition in ammonium persulphate, $(NH_4)_2S_2O_8$ [13]. The persulphate group, S_2O_8 , consists of two sulphate groups ($2SO_4$). In this paper we report on the electrical conductivity σ , the thermal conductivity λ and the DTA thermogram for two sulphate compounds, $HgSO_4$ and $Ce_2(SO_4)_3 \cdot H_2O$, as a representation of the two mentioned series $DSO_4 \cdot xH_2O$ and $T_2(SO_4)_3 \cdot xH_2O$. To the best of our knowledge these properties have not yet been investigated. By studying the thermal conductivity one can propose the mechanism of heat transfer, e.g. whether the thermal conduction is mainly due to electronic or phonon processes.

2. Experimental

The materials used in the present work were manufactured by the British Drug Houses Ltd. The purity of each salt is about 99%, the product number of the $HgSO_4$ salt is 29174 and that of the $Ce_2(SO_4)_3 \cdot H_2O$ salt is 27662.

For electrical measurements, the fine-grounded powder of each salt was compressed under a pressure of $\approx 5 \text{ t/cm}^2$ to form discs (pellets) of diameter $\approx 1.5 \text{ cm}$ and of thickness $\approx 1.5 \text{ mm}$. The density of the compressed sample of $HgSO_4$ is 50 g/cm^3 while that of the $Ce_2(SO_4)_3 \cdot H_2O$ is 3.20 g/cm^3 (the standard densities are 6.47 g/cm^3 and 3.17 g/cm^3 respectively [14]).

The electrical resistance was measured using Keithley type 617 programmable ohmmeter. A sample holder with brass electrodes was specially designed to fit the present electrical measurements. Good contact was attained by painting both faces of the sample with air-drying conducting silver paste (type RC, made in the U.K.). Measurements of the sample temperature were performed using a thermocouple attached to the sample. The electrical conductivity σ was calculated from the value of resistance (R) and the geometry of the sample. The DTA measurements were carried out on the powdered samples to check the transition temperature.

The apparatus used for thermal conductivity measurements is shown in fig. 1. The details of this method were given elsewhere [15–16]. The temperature gradient across the sample was measured using NiCr–Ni differential thermocouple. The heat transferred through the sample from the lower surface to the upper face was controlled by the heating current of the furnace to maintain the desired temperature. The degree of vacuum inside the system is 10^{-3} mm Hg . The experimental error in the thermal conductivity measurement is about 3%.

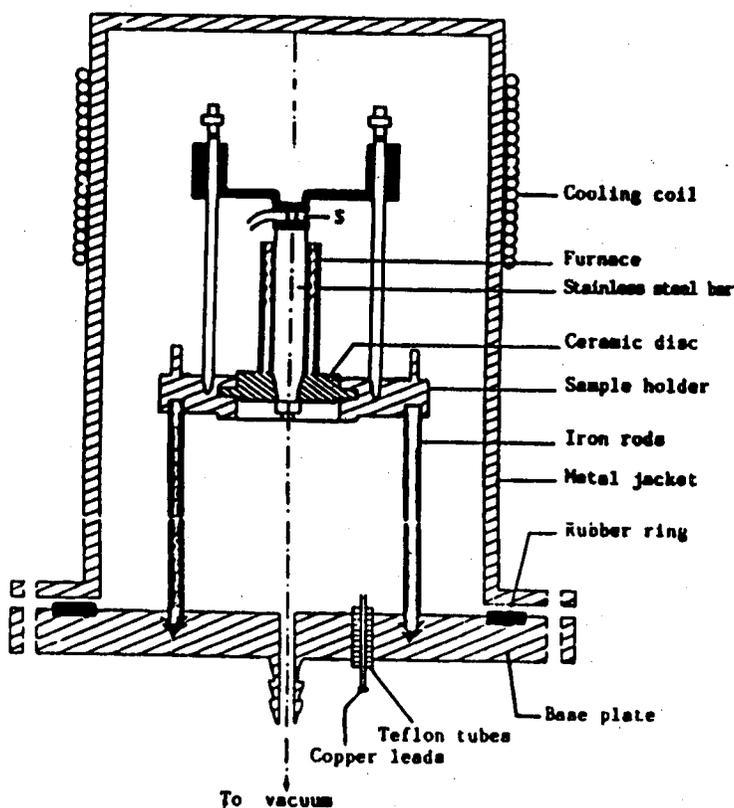


Fig. 1. The apparatus used for thermal conductivity measurements.

3. Results

Figure 2a shows the variation of the electrical conductivity σ with temperature $40 < T < 120^\circ\text{C}$ of HgSO_4 . As one can observe from Fig. 2a, the conductivity σ decreases sharply with increasing temperature up to $\approx 75^\circ\text{C}$. As the temperature exceeds this value, the rate of decrease in σ with temperature becomes very slow resulting in the minimum value of σ at temperature of about 90°C and then increases with temperature. The plot of σ vs. T suggests a structural phase transition at temperature of $\approx 90^\circ\text{C}$.

Figure 2b represents the same relation for the compound $\text{Ce}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$. The plot is characterized by a gradual increase in the values of σ as the temperature is increased up to 90°C where the electrical conductivity σ reaches its maximum value. A sharp decrease in σ values was observed as the temperature exceeds 100°C . This behaviour suggests a structural phase transition at $\approx 90^\circ\text{C}$.

Figures 3a and 3b show the Arrhenius plots ($\ln \sigma$ against $10^3/T$) for the HgSO_4 and $\text{Ce}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ respectively. Each plot is characterized by two straight lines of different slopes. From each plot we calculated the activation energy of

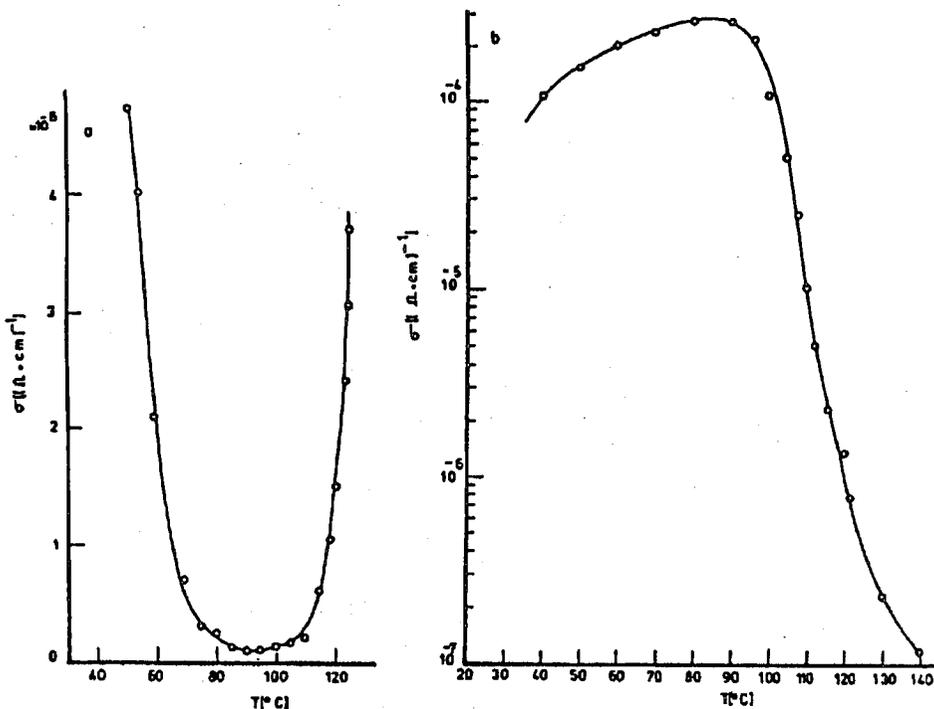


Fig. 2. Variation of the electrical conductivity σ with temperature for (a) mercury(II) sulphate, HgSO_4 , (b) cerous(III) sulphate $\text{Ce}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$.

each phase of the two salts. These calculations yield the values $E_1 = -1.8$ eV, $E_2 = 1.52$ eV for HgSO_4 , while for the $\text{Ce}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ the obtained values are $E_1 = 1.37$ eV and $E_2 = -0.24$ eV. These values agree quite well with that of other sulphate salts. For example, the values of the activation energies of Na_2SO_4 are 1.16 eV and 0.56 eV [17].

Among other things, the change of the values of E_1 and E_2 for each compound both in magnitude and sign is an indication for the occurrence of the structural phase transition. Furthermore, the negative sign of the activation energy means that the conductivity corresponding to this phase is not thermally activated. Another interesting fact is that the two lines of each plot intersect at $T \approx 90^\circ\text{C}$ ($10^3/T \approx 2.75$ or $T \approx 363.64$ K or $T \approx 90.47^\circ\text{C}$).

The variation of the thermal conductivity λ as a function of temperature $40 < T < 140^\circ\text{C}$ for the two compounds, HgSO_4 and $\text{Ce}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$, is shown in Figs. 4a and 4b respectively. The two plots have nearly the same general trends. In other words, the general feature of each plot is that there is a gradual decrease in the values of λ as the temperature increases up to a temperature of about 90°C , where the value of λ reaches its minimum value and then begins to increase once again. Among other things, the behaviour of the measured thermal conductivity λ for each of the two investigated compounds confirms and supports the

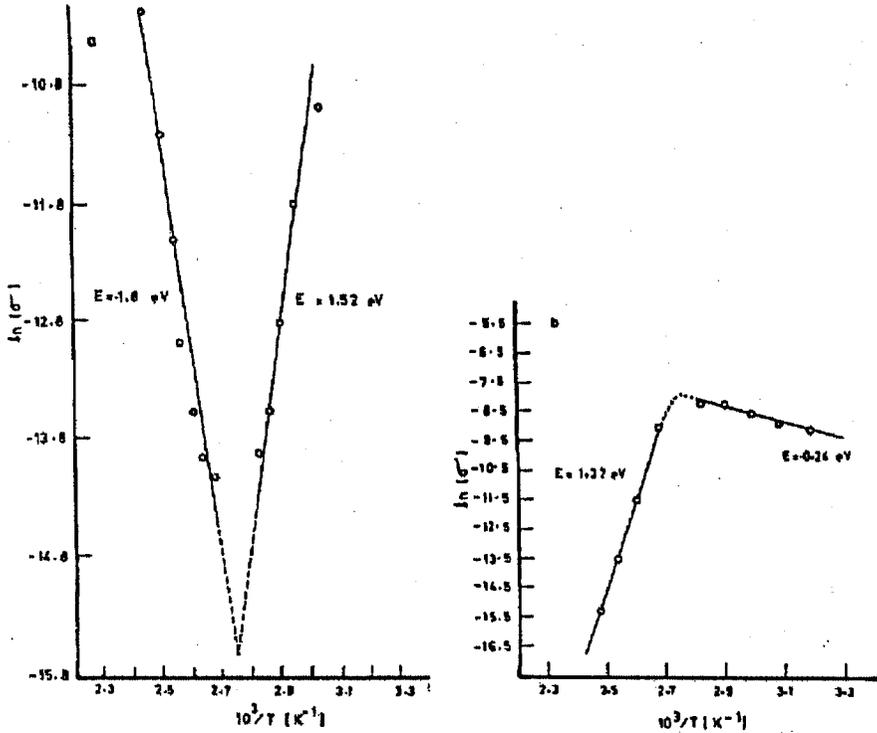


Fig. 3. Relationship between $\ln \sigma$ vs. $10^3/T$ for (a) mercury(II) sulphate, HgSO_4 , (b) cerous(III) sulphate $\text{Ce}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$.

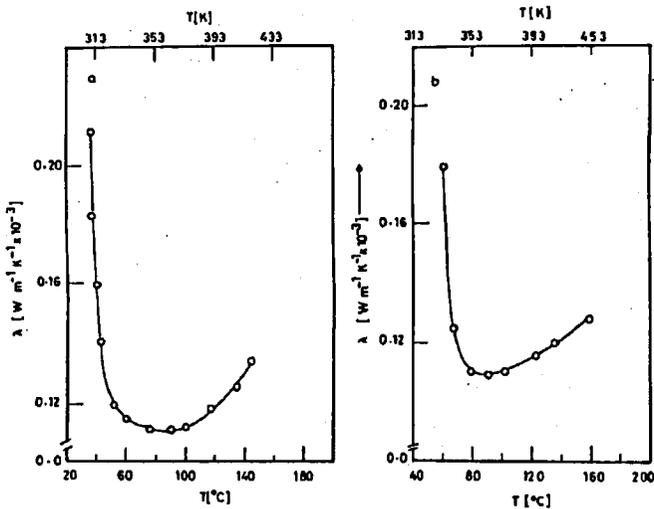


Fig. 4. Variation of the thermal conductivity λ with temperature for (a) mercury(II) sulphate, HgSO_4 , (b) cerous(III) sulphate $\text{Ce}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$.

possibility of the occurrence of phase transition at $\approx 90^\circ\text{C}$ which was observed from the measured electrical conductivity. Another interesting fact is that the order of magnitude of λ suggests that the two investigated salts behave almost as poorly conducting materials.

The proposed phase transitions in the two salts are confirmed by performing the differential thermal analysis in the same temperature range. The DTA thermograms resulting from such analysis are shown in Figs. 5a and 5b. The heating rate

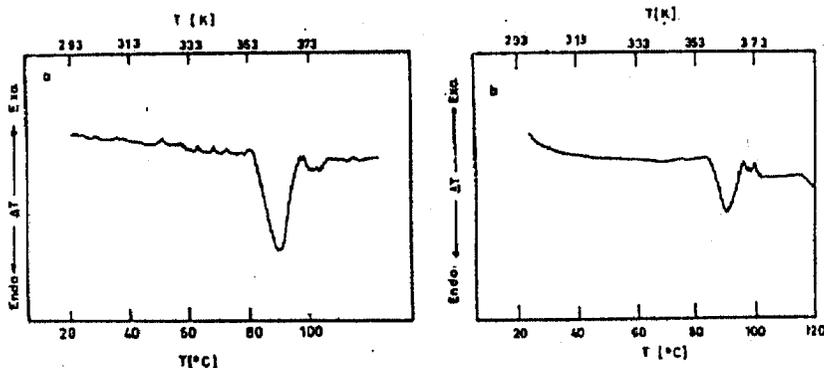


Fig. 5. The DTA thermograms for (a) mercury(II) sulphate, HgSO_4 , (b) cerous(III) sulphate $\text{Ce}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$.

is $10^\circ\text{C} \cdot \text{min}^{-1}$ and the sensitivity ΔT is $10 \text{ mV} \cdot \text{cm}^{-1}$. As one can observe, each thermogram is characterized by an endothermic peak centred at a temperature of $\approx 90^\circ\text{C}$. This can be considered as a good evidence and a final confirmation for the proposed phase transition.

4. Discussion

Based on the measured electrical and thermal parameters presented in this work, combined with the DTA thermograms, one can clearly suggest that each of the two salts undergoes structural phase transition at about 90°C .

For the anhydrous mercury(II) sulphate, HgSO_4 , the chemical formula does not contain any water molecules and the sample is not hygroscopic, in other words, the observed phase transition is not due to the loss of water (dehydration). For the cerous(III) sulphate no loss of weight was observed upon heating the samples from room temperature up to 70, 75, ... and 90°C . This means no loss of water (dehydration) at the above mentioned temperatures. Thus the observed phase transition in each of the two salts is of structural origin.

As mentioned before, the crystal structure of the HgSO_4 was determined [9]. The crystals are orthorhombic with $a = 4.785$, $b = 4.821$, $c = 6.581 \text{ \AA}$ and space group $Pn2_1m$. The bivalent (Hg) ion is surrounded by four oxygen atoms in the form of a very distorted tetrahedron [9]. To the best of our knowledge, the crystal structure of the $\text{Ce}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ has not yet been determined. However, the most interesting group in this salt is the SO_4 group in addition to water molecule. The

latter will result in the formation of hydrogen bond of the type O-H...O. The change in hydrogen bonding scheme is the primary cause of the phase transition in some sulphate and/or persulphate compounds [18, 13].

For the two compounds the common group is the SO₄ group. It is well known that this group is characterized by reorientational motion. Thus, as the temperature is increased from room temperature and is approaching 90°C, the thermal energy absorbed by the salt is high enough to activate the reorientational motion of the SO₄ group to another equivalent position. This reorientational motion will affect the arrangement of the molecule as a whole resulting in the observed phase transition. Another interesting problem is the mechanism of heat transfer.

In general, the thermal conductivity λ of such poorly conducting materials can be expressed by phononic and electronic modes of heat conduction. In other words

$$\lambda = \lambda_{ph} + \lambda_e,$$

where λ_{ph} is the contribution of the lattice vibrations (phonons) to the thermal conductivity and λ_e is the electronic part of the thermal conductivity. The latter depends on the electrical conductivity of the material.

Although the order of magnitude of λ may suggest that the two investigated salts behave almost as poorly conducting materials, yet the basic criterion for evaluation of electron contribution in heat transport is a comparison of the Lorenz number with the theoretical value $L_0 = 2.45 \times 10^{-8} \text{W} \cdot \Omega / \text{K}^2$. For further clarification we shall suggest first the validity of Weidmann-Franz law for these salts. According to this law, the electronic part λ_e is related to the electrical conductivity σ by the equation

$$\lambda_e = L_0 \sigma T,$$

where T is the absolute temperature. Using the measured σ values at different temperatures one can calculate the values of λ_e at the same temperatures. For the compound HgSO₄ the σ values at temperatures 333 K, 363 K and 393 K are $\approx 2 \times 10^{-8} (\Omega \cdot \text{m})^{-1}$, $0.15 \times 10^{-8} (\Omega \cdot \text{m})^{-1}$ and $1.5 \times 10^{-8} (\Omega \cdot \text{m})^{-1}$, respectively. Thus the corresponding λ_e values are

$$\lambda_e(333 \text{ K}) = 0.8 \times 10^{-12} \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1},$$

$$\lambda_e(363 \text{ K}) = 0.013 \times 10^{-12} \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$$

and

$$\lambda_e(393 \text{ K}) = 0.1 \times 10^{-12} \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}.$$

Similarly for the compound Ce₂(SO₄)₃·H₂O

$$\lambda_e(333 \text{ K}) = 0.8 \times 10^{-12} \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1},$$

$$\lambda_e(363 \text{ K}) = 13.3 \times 10^{-12} \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$$

and

$$\lambda_e(393 \text{ K}) = 0.90 \times 10^{-12} \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}.$$

From these calculations it is clear that the values of λ_e for any of the two salts are very small compared with the values of λ (see Figs. 4a, 4b) and/or the Lorentz number (L_0).

The conclusion we could arrive at is that the two salts behave almost as poorly conducting materials and therefore the mechanism of the heat transport is due to phonons and thus

$$\lambda \sim \lambda_{ph}.$$

Finally, X-ray structural analysis of the $Ce_2(SO_4)_3 \cdot H_2O$ and the study of other properties of these two sulphate salts such as optical spectroscopy and light scattering experiments are needed in order to give a clear view of the reorientational motion of the SO_4 group.

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