

A Correlation Study Between Electrical and Thermal Properties of Sodium Potassium Sulphate Crystals

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Abstract

Single crystals of sodium potassium sulphate, NaKSO₄, were grown by slow evaporation method from aqueous solution contained equimolar amounts of pure K₂SO₄ and Na₂SO₄. The temperature dependence of d. c. conductivity, $\sigma(T)$, specific heat at constant pressure, $C_p(T)$, and spontaneous strain, $\eta(T)$, have been measured for sodium potassium sulphate, NaKSO₄, crystals from 300 to 500 K. Over the temperature range of interest the conductivity exhibited two regimes; intrinsic above T_c and extrinsic below T_c . The thermal expansion coefficients were calculated from dilatometric measurements during heating and cooling and no hysteresis phenomena were detected. In the other hand DSC measurements of C_p showed a pronounced maximum at $T_c = 453$ K. The correlation between d. c. conductivity $\sigma(T)$ and specific heat $C_p(T)$ is clear. This behaviour is attributed to the dominating role of the nonlinearity in the temperature dependence of σ and C_p .

Introduction

Crystalline sodium potassium sulphate, NaKSO₄, is a member of the family of double sulphate crystals having the general formula $M^I M^{II} BX_4$ where M^I is Li or Na atom, M^{II} is Na, K, Rb, Cs atoms or NH₄, N₂H₅ groups, BX_4 is BeF₄, SO₄ or SeO₄. Their importance arises from the fact that some double sulphate crystals display ferroelectric and ferroelastic behaviour in different temperature ranges [1-4]. Studies of these ferroelectric and ferroelastic materials are important for their use as piezoelectric components and pyroelectric detectors, and in the memory of computers [5-7]. Sodium potassium sulphate crystals possess orthorhombic symmetry at 300 K and belong to an mmm point group [8]. Measurements on the electrical, thermal and elastic properties of NaKSO₄ in the temperature range 300 to 500 K show a structural

phase transition at 453 K [9-11]. Electrical conductivity measurements on NaKSO₄ crystal reveal high ionic conductivity values in the high-temperature range [12]. Order-disorder transitions and solid state kinetics in the same crystal were also studied [13].

The aim of the present work is to study the anomalous behaviour of thermal and electrical properties of NaKSO₄ crystal and report on the nature of conduction in the vicinity of the structural ferroelastic phase transition taking at 453 K.

Experimental

Sodium potassium sulphate crystals were grown isothermally at 315 K from aqueous solution. The initial substances used for the synthesis of NaKSO₄ were of chemical grade purity. The NaKSO₄ for crystal growth was subjected to five-fold slow recrystallization from water.

Specimens in the form of thin slabs (1x1x0.15 cm) were cut, with edge parallel to the crystallographic axes, from the single crystal using wet string saw. The lateral surfaces of the plate were polished to obtain thickness between 0.2-0.3 mm. Silver electrodes were deposited on the plane surfaces by evaporation in vacuum at pressure of 10⁻⁵ mm Hg. The electrical measurements were carried out, using an electrical circuit, which consists of a d.c. power supply taken from a 6 volt battery connected to a high resistance potential divider, which enables the potential across the specimen to be varied and to be kept at constant voltage (2V) during the period of experiment. The potential difference taken from the potential divider is applied to a circuit consisting of a Keithly digital multimeter for measuring current with a sensitivity of 10⁻⁹ A. The temperature of the sample was controlled from 300 to 500 K with accuracy ±0.2 K. It is worth of mention that electrical measurements were carried out over a sufficiently long time to allow the decay of polarization effects. Conductivity values were recorded during the heating and cooling, the recorded values agreeing very well for both forward and backward directions of voltage.

The specific heat under constant pressure, C_p, was determined by using a differential scanning calorimeter (DSC) technique, a Heraeus DSC cell being connected to a Heraeus DTA 500 thermal analyzer. Measurements were performed by applying the base line method [14]. A Pt 100 thermocouple was used as a temperature sensor, and a heating rate of 2 degree per minute was applied.

Results and Discussion

Electrical Conductivity

The conductivity data for, NaKSO₄, are obtained during raising the temperature from 300 to 500 K and also during cooling to 300 K. The conductivity was calculated using the formula:

$$\sigma = \frac{I}{V_c} \frac{t}{bL}$$

where I is the current in Ampere, V_c is the potential drop across the sample, b is the width of the sample, L is the cross-section of the sample, and t is the thickness of the sample.

Fig.(1) shows the temperature dependence of the ionic conductivity (σ) expressed as $\log \sigma$ vs. $1/T$ for both a and b axes. over the temperature range of interest the conductivity exhibited two regimes. In regime I ($T > T_c$) the conduction is known to be intrinsic [15] and the value of the activation energy, as obtained from Fig.(1) is:

$$E_I = 1.98 \pm 0.02 \text{ eV}$$

In regime II ($T < T_c$) the conduction is known to be extrinsic [15] and the value of activation energy is:

$$E_{II} = 0.25 \pm 0.02 \text{ eV}$$

It is clear that the value of the activation energy in regime I is always greater than that in regime II; this is due to the fact that E_{II} is the activation energy in the structural phase orthorhombic which differs from that E_I , the activation energy, in another structural phase probably monoclinic [16]. The change in the activation energies at the transition point from phase II to phase I may be due to the large scale availability of the carriers released during the rearrangement process of the crystal lattice.

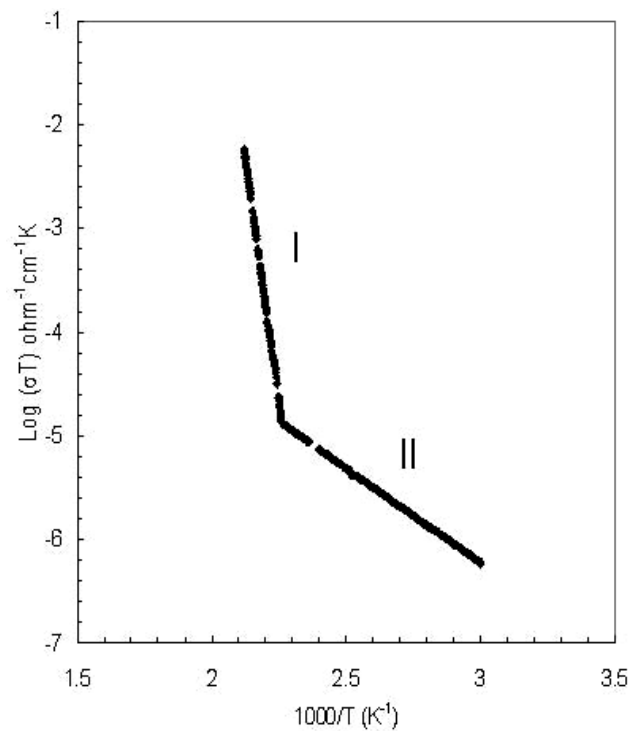


Figure 1: Temperature dependence of the conductivity

Thermal Expansion

The thermal expansion coefficients for, NaKSO_4 , were calculated from dilatometric measurements. The measurements were carried out when the temperature was increasing and once more when the temperature was decreasing and no hysteresis phenomena were detected. Table (1) shows the average values of the linear expansion coefficients α_{ii} in different temperature ranges. Fig.(2) revealed, for the first time, that, NaKSO_4 , exhibits major thermal expansion anomalies in the immediate vicinity of the temperature 453 K.

Table 1:

Temperature range	$\alpha_{11} (\text{K}^{-1})$	$\alpha_{22} (\text{K}^{-1})$	$\alpha_{33} (\text{K}^{-1})$
300-453 K	7.2×10^{-5}	6.8×10^{-5}	7.7×10^{-5}
453-460 K	-20×10^{-5}	-31×10^{-5}	-101×10^{-5}
460-500 K	4.3×10^{-5}	7.9×10^{-5}	4.3×10^{-5}

The thermal expansion is strongly anisotropic as shown by the large differences in contraction observed at temperature above $T_c = 453$ K. The sudden change in the thermal expansion coefficients may be due to a second order lambda transformation. The difference between the observed value of $\Delta L/L$ and that obtained by linear extrapolation from the high temperature side is regarded as the spontaneous part induced by the phase transition [17]. It is clear from Fig.(3), that the spontaneous strain η_{1s} , η_{2s} and η_{3s} along the x, y and z axes show linear temperature dependence.

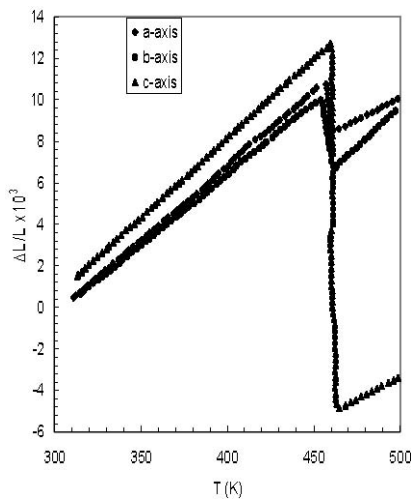


Figure 2: Thermal expansion versus temperature

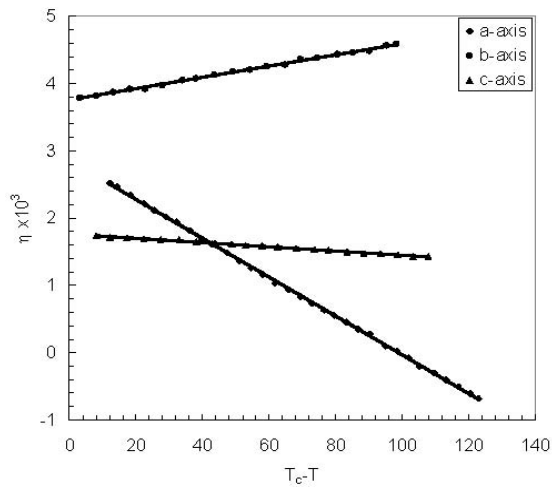


Figure 3: Spontaneous strain η_{1s} , η_{2s} and η_{3s}

Differential Scanning Calorimeter DSC

The DSC measurements of the specific heat at constant pressure, C_p , Fig.(4), showed a pronounced maximum at $T_c = 453$ K. This may indicate that the entropy change is continuous and therefore there is no latent heat. However, since specific heat peak was observed (anomalous specific heat) and have the shape given by Fig.(4), it could correspond to a second order lambda transition [18]. The changes in enthalpy (ΔH) and entropy (ΔS) at the phase transition 453 K is thus calculated. The change in enthalpy is estimated to be about 11.54 kJ/mole; while the value of change in entropy of phase transition is about 25.5 J/mole. K.

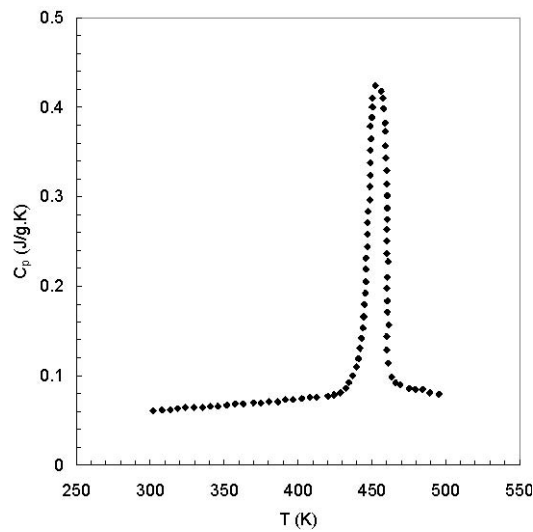


Figure 4: Specific heat versus temperature

The contributions to the specific heat near the phase transition could arise from the critical fluctuation which has been examined by fitting the specific heat C_p according to the power laws:

$$C_p = A (T-T_c)^{-\alpha} \quad \text{for } T < T_c$$

$$C_p = A^* (T-T_c)^{-\alpha^*} \quad \text{for } T > T_c$$

where α and α^* are critical exponents, A and A^* are constants. Fig (5) shows the relation $\ln C_p$ vs. $\ln |T-T_c|$ in the vicinity of the phase transition temperature T_c . The slope of the lines were found to be $\alpha = 0.73$ and $\alpha^* = 0.14$.

The excess of specific heat ΔC_p can be expressed by [19]:

$$\Delta C_p = B t^{-\beta} \quad \text{for } T < T_c$$

$$\Delta C_p = B^* t^{-\beta^*} \quad \text{for } T > T_c$$

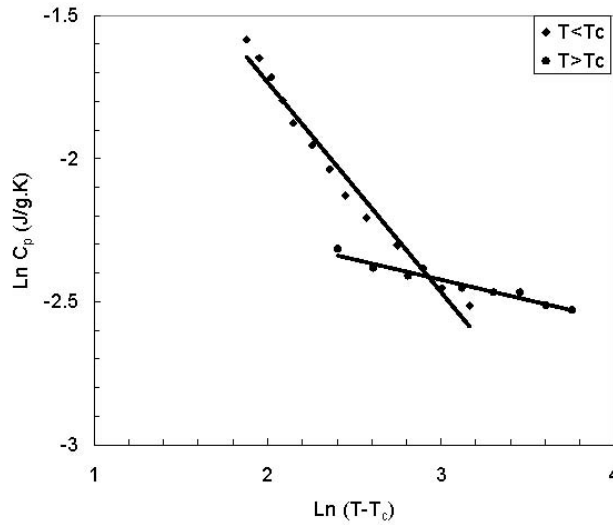


Figure 5: $\ln C_p$ versus $\ln |T-T_c|$

where $t = (T-T_c)/T_c$ is the reduced temperature, β and β^* are critical exponents describe the singularity in the specific heat at a second-order transition and B and B^* are constants. The relation between $\ln \Delta C_p$ vs. $\ln |t|$ in the vicinity of the phase transition temperature T_c is shown in Fig.(6). The value of the critical exponent β was approximately estimated from the slope of the linear section of the curve. For low temperatures $T < T_c$, the value of β was estimated to be equal to 0.35. In the temperature range $T > T_c$, the value of β^* was found to be 0.27. These values are not far from the theoretically expected value that expected for 3d Ising model ($\beta = 0.1 - 0.33$). The agreement between the theoretical and experimental value is rather good.

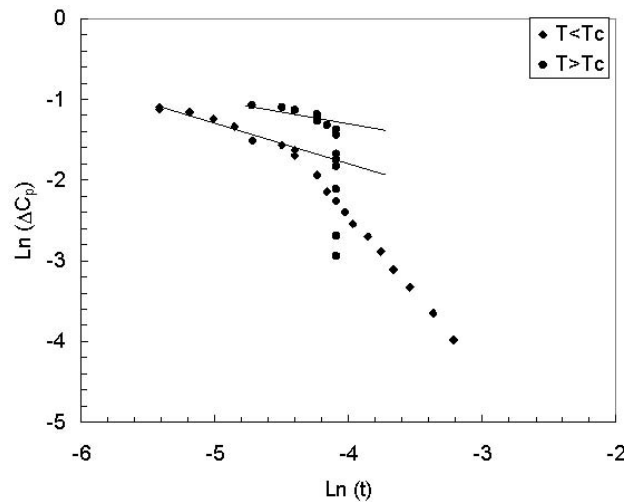


Figure 6: $\ln \Delta C_p$ versus $\ln |t|$

The temperature dependence of the specific heat near the phase transition obeys an experimental law [20]:

$$\Delta C_p = Z (NU^2/RT^2) \exp (-U/RT)$$

where N is the number of displaced atoms from the equilibrium position, U is the thermal activation energy, R is the universal gas constant and Z is the coordination number. By plotting the relationship between $\ln \Delta C_p T^2$ vs. $1000/T$ we obtain a straight line with slope $-U/R$ from which we can calculate U. Fig. (7) shows the dependence of $\ln \Delta C_p T^2$ on $1000/T$. The slope of the straight line gives the thermal activation energy of ordering transition which is 299 kJ/mole. The number of atoms displaced from the equilibrium position (N) could be obtained from the intersection of the line. Taking $Z = 4$ for the NaKSO₄ sample, the value of N is estimated to be 7.71×10^{28} .

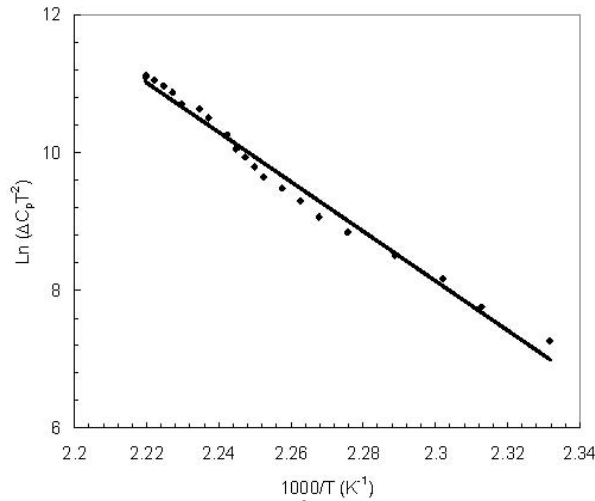


Figure 7: $\Delta C_p T^2$ versus $1000/T$

A Correlative A.C. Conductivity-Specific Heat

Nernst equation gives directly the conductivity, from which the correlation between the electric conductivity, σ , and specific heat, C_p , could be obtained [21]. Fig.(8) shows the variation of C_p as well as $d \ln \sigma / dT$ with temperature.

The relationship between σ and C_p is given by [21]:

$$\frac{d \ln \sigma T}{dT} = 2(1 - \mu) \frac{C_p}{RT} + B$$

where B contains all non-singular contributions and μ is a constant. The variation of $d \ln \sigma T / dT$ with molar C_p is shown in Fig.(9). The value of μ was calculated to be equal to 0.664, while B is equal to 0.006. The obvious correlation between the a. c. conductivity $\sigma(T)$ and specific heat $C_p(T)$ is clear. This behaviour is attributed to the dominating role of the nonlinearity in the temperature dependence of σ and C_p .

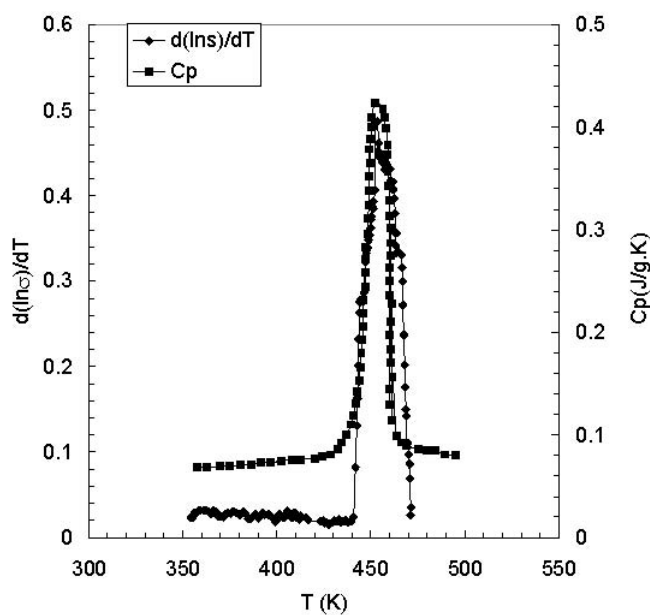


Figure 8: Variation of C_p and $d\ln\sigma / dT$ with temperature

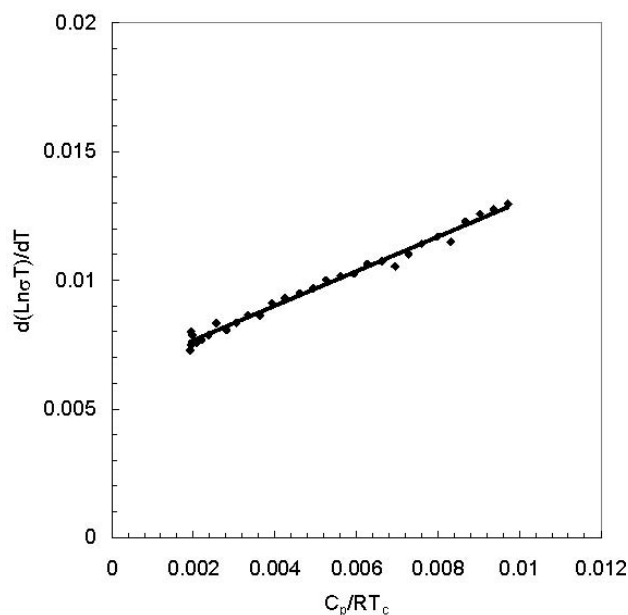


Figure 9: Variation of $d\ln\sigma T / dT$ with C_p

Conclusions

The anomalous behaviour of the thermal expansion coefficients, specific heat and conductivity observed during the study of NaKSO_4 crystals through the temperature range 300-500 K suggests that the crystal may present a structural phase transition at $T_c = 453$ K.

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