DC electrical conductivity of $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{SO}_4$

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Abstract. D.C. electrical conductivity of single crystals of $(\text{NH}_4)_2\text{SO}_4$ and $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$ have shown conductivity jump near their respective structural transition temperature. Activation energy of $(\text{NH}_4)_2\text{SO}_4$ has been found to be consistent with the earlier data. However, $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$ has given prolonged aging effect due to dipolar relaxation and formation of space charge polarisation. σ_{true} and P_{max} have been measured. P_{max} has shown a negative maximum at the transition point. Activation energy of $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$ has been found to be comparable with $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$.

Keywords. Phase transitions; electrical conductivity; polarisation.

It has been observed from magnetic anisotropy (Majumdar and Datta 1965), specific heat (Dutta Roy *et al* 1971) and structural studies (Roy *et al* 1973) that cobalt fluosilicate hexahydrate undergoes a phase transition at $T_c \approx 246 \pm 1^\circ \text{K}$ during cooling which disappears at $T_c(h) \approx 259 \pm 1^\circ \text{K}$ during heating cycle. The effect of this structural transition on DC electrical conductivity of $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$ is the subject of investigation of the present work. $(\text{NH}_4)_2\text{SO}_4$ which has a protonic conduction (Schmidt and Uchling 1962; Schmidt 1963) and $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$ which is isomorphous with $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$ have been included for comparison.

The single crystals of cobalt and zinc fluosilicates were grown from metallic carbonate in fluosilicic acid. The clean solution was kept at 30°C in a desiccator. Crystals, of approximate size $5 \times 3 \times 2 \text{ mm}^3$ with well-developed prism faces, were obtained. The single crystals of ammonium sulphate were grown by slow evaporation of an aqueous solution of reagent grade ammonium sulphate. The DC electrical conductivity measurements were performed using an electrometer amplifier (ECIL model EA815). The sample holder was made of teflon with two spring-loaded copper electrodes. The sample assembly was put inside a grounded copper container for electrical shielding. The continuous flow cryostat was used to maintain any preselected temperature between 400–77 K.

Voltage current (V-I) characteristics of $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$ taken at a fixed time after the application of the external voltage shows that siller point contact produces non-linear V-I relation whereas aquadog contact gives linear characteristics up to 400 volts/cm. The charge-discharge characteristics have also revealed pronounced space charge polarisation effect. The true conductivity has therefore been measured

following the method suggested by Zheludev (1971). The maximum polarisation $P_{\max}$ is determined using the relationship,

$$I_1 I_2^{-1} = (V_1 - P_{\max})(V - P_{\max})^{-1},$$

where I_1 , V_1 and I_2 , V_2 are respectively the current and voltage before and after a change of applied voltage. Figure 1 shows $P_{\max}$, $\log \sigma_{\text{res}}$ and $\log \sigma_{\text{true}}$ as a function of T^{-1} along the direction perpendicular to the c -axis. It is seen that anomalous conductivity fluctuation of σ_{res} and σ_{true} occurs at the structural transition point. In addition, the maximum polarisation e.m.f. developed within the crystal $P_{\max}$ shows a minimum near the transition temperature T_s and at the transition point the calculated value of $P_{\max}$ becomes negative and ten times larger than the applied voltage. This sudden reversal of $P_{\max}$ and its large negative value at the transition temperature probably indicate the onset of spontaneous polarisation. Activation energy of the crystal along different direction is shown in table 1.

A typical plot of $\log \sigma$ as a function of T^{-1} for current parallel and perpendicular to the b -axis of the orthorhombic $(\text{NH}_4)_2\text{SO}_4$ single crystal is shown in figure 2. V-I characteristics with silver paste contact are ohmic up to 1000 volts/cm. Schmidt's (1963) data along b -axis of the crystal is also shown in the figure for comparison. The calculated activation energy is shown in table 1.

Figure 1. Conductivities (σ) and maximum polarisation ($P_{\max}$) of $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$ single crystal as a function of temperature along the direction to c -axis of the crystal.

For crystal A during cooling : $\bullet$ — σ_{true} (true conductivity), Δ — σ_{residual} (residual conductivity); for crystal A during heating : $\square$ — σ_{true} (true conductivity); For crystal B during cooling : $\blacktriangle$ — σ_{initial} (initial conductivity); Maximum polarisation voltage in crystal A during cooling and heating X— $P_{\max}$ and O— $P_{\max}$ respectively. The applied voltage is $V = 181.5$ V/cm.

Table 1. Activation energy E_T for $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{SO}_4$ and $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$ in different temperature range.

Sample	Crystal no. and direction of I	Cooling $E_{(T > T_c)}$ (eV)	Heating $E_{(T < T_c)}$ (eV)
$\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$	(1) $I_{\perp c}$ -axis (True conductivity)	0.64	0.45
	(2) $I_{\parallel c}$ -axis	0.72	..
$(\text{NH}_4)_2\text{SO}_4$	$I_{\parallel b}$ -axis Schmidt's data	0.74	0.45
	$I_{\parallel b}$ -axis	0.76	..
$\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$	$I_{\perp c}$ -axis	0.58	..

Figure 2. The conductivity of $(\text{NH}_4)_2\text{SO}_4$ single crystal as a function of temperature. For current along the direction $11c$ to b -axis of the crystal: ●—cooling cycle; ■—heating cycle. For current along the direction $1R$ to b -axis of the crystal: △—cooling cycle; Data of Schmidt for most pure crystal along the b -axis: ○—cooling cycle.

Figure 3 shows $\log \sigma_{\text{true}}$ and $\log \sigma_{\text{res}}$ vs T^{-1} plot for zinc fluosilicate, which is isomorphous with cobalt fluosilicate. The figure also shows linear dependence of $\log \sigma_{\text{true}}$ vs T^{-1} up to 230 K and shows no structural anomaly in the crystal within the temperature range 300–220 K.

Figure 3. Conductivity (σ) of $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$ as a function of temperature.

σ_{residual} —○ cooling; Δ heating
 σ_{true} —● cooling; $\blacktriangle$ heating.

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