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Electronic Transport in $K_3Fe(CN)_6$ Crystals

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Ionic crystalline solids generally have very small electronic dc conductivities ($<10^{-10}\ \Omega^{-1}\ cm^{-1}$) and very high thermal charge carrier activation energies (*1*) (several eV). This is especially the case with the salts of alkali metals, where the ionic character (*2*) of crystal bondings are larger. Here we report our observations on electronic conductivity of potassium ferricyanide, which is found to be an interesting exception to the above rule. The single crystals of $K_3Fe(CN)_6$ are found to have a room-temperature (30°C) conductivity $\simeq 2.1 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$ with a thermal activation energy 0.17 eV.

Single crystals of potassium ferricyanide were made by allowing seed crystals to grow in a saturated solution of the salt (Analar grade $K_3Fe(CN)_6$ was used), kept in a desiccator containing 75% H_2SO_4. The samples for conductivity measurements were made by cutting the monoclinic crystals into rectangular blocks ($\sim 10 \times 2.5 \times 2.5$ mm). Two copper wires were firmly fixed around the ends along the lengthwise direction and connected in series to a potentiostatically controlled voltage supply (kept at 50 V) and a calibrated microammeter. The sample was immersed in a thermostatic oil bath containing pure paraffin oil (conductivity $< 10^{-19}\ \Omega^{-1}\ cm^{-1}$) and the conductivity at different temperatures was determined by noting the current in the circuit. Before starting the measurements, the oil bath with the sample immersed is gradually heated to 110°C, kept at this temperature for about half an hour and allowed to cool to the room temperature. The above procedure and the method of mounting the crystal (that exposes its surface to oil) eliminates surface effects arising from moisture settling on the surface of the crystal. Four electrode measurements in sealed glass tubes were also carried out and any differences were not observed. We have found that if reasonably pure oil is used impurities do not get into the crystal and reproducible results (irrespective of the brand of the used) are obtained. Furthermore chromatographic and spectrophotometric tests indicated that there are no detectable differences between $K_3Fe(CN)_6$ kept heated in oil for several hours and fresh samples. At all temperatures (30–200°C) the current–voltage characteristics were found to be linear.

The plot of log σT vs T^{-1} fits into a straight line, indicating that the relation

$$\sigma T = Ae^{-E/kT} \qquad (1)$$

is satisfied with $E = 0.17$ eV and $A = 3.9 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$ K. Plots of log σ vs T^{-1} also

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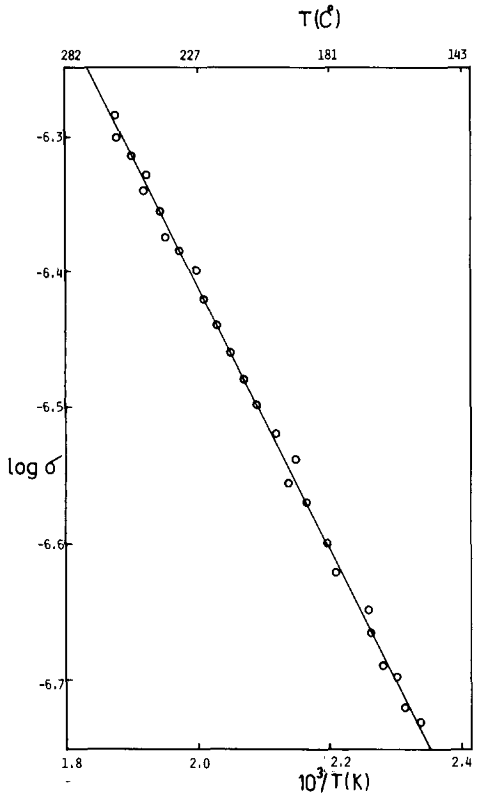

FIG. 1. Plot of log σT vs T^{-1} (σ in Ω^{-1} cm^{-1}).

gives good straight-line fits. But linear correlation analysis on five sets of data showed that the correlation coefficient is slightly better for the former plot. Conductivity properties were found to be isotropic to the accuracy of our experiments. Ionic conduction is negligible, no polarization or electrolytic effects were noted in dc measurements.

The crystal structure of ionic and covalent ferri- and ferrocyanides are well studied (*3–5*). It is known that $K_3Fe(CN)_6$ constitutes an ionic lattice of potassium ions and ferricyanide ions where CN^- are octahedrally linked Fe^{3+} ions (*3–5*). Conductivity properties reported above are probably intrinsic to the material and samples from different sources when purified by recrystallization give similar results. However, the possibility that a common undetected impurity is generating charge carriers cannot be completely ruled out. We have not succeeded in determining the sign of charge carriers or their mobilities.

Electronic transport in this material is most probably due to hopping (small polaron mechanism) (*6–7*). The observed temperature variation of conductivity favours this interpretation. However, it is difficult to understand why the conductivity in this case is much higher and the thermal activation energy is very small when compared with familiar ionic solids.

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