

## The Influence of Interstitial Water on Electronic Conduction in Lead Ferrocyanide

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Water molecules present as an interstitial impurity in crystals of  $\text{Pb}_2\text{Fe}(\text{CN})_6 \cdot 2\text{H}_2\text{O}$  in excess of bonded water is found to activate electronic conduction with an activation energy of 0.32 eV. A quantitative explanation is given to show why lead and several other heavy metal ferrocyanides have approximately the same thermal activation energies.

### Introduction

The crystal structure of water-insoluble ferrocyanides of heavy metals are well studied (1-5). All these compounds have "Prussian blue"-type of structure (1-5) with  $\text{Fe}^{2+}$  and metal ions arranged on a cubic face-centered lattice. The cyanide ions lie along the edges of these cubes with  $\text{Fe}^{2+}$  ions coordinated to C and the other metal ions coordinated to N. A peculiar property arising from this structure is that the unit cells have large volumes (lattice constant  $\sim 10^{\circ}\text{A}$ ). Consequently these materials can accommodate foreign molecules, usually water, as interstitial impurities. The gravimetric and NMR studies indicate that  $\text{H}_2\text{O}$  molecules could be free or bound to the ionic sites (3, 6, 7). The author (8-11) and few other workers (7, 12) have noted that interstitial water enhances electronic conduction in ferrocyanides. Also the author has argued that this enhancement of conductivity is due to the lowering of the activation of energy of charge carriers by the high dielectric con-

stant of water (10). In this work we report our observations on electrical transport in lead ferrocyanide, that further elucidates the mechanism of electronic transport in these compounds.

### Experimental

Lead ferrocyanide was prepared by the double decomposition of lead nitrate with potassium ferrocyanide. The presence of nitric acid avoids the contamination of the product with lead hydroxide resulting from hydrolysis. The precipitate was washed with deionized water and dried under vacuum at  $115^{\circ}\text{C}$ . Chemical analysis confirmed that it corresponds to stoichiometric  $\text{Pb}_2[\text{Fe}(\text{CN})_6]$ . The anhydrous form readily absorbed moisture when exposed to the humid atmosphere. The data on thermal gravimetric analysis is indicated in Fig. 1. It is clear that in addition to free water, which is lost continuously, there is also bound molecules lost only at  $\sim 101^{\circ}\text{C}$ . When the compound dried up to  $\sim 90^{\circ}\text{C}$  it was heated to  $115^{\circ}\text{C}$  under vacuum, the weight loss ob-

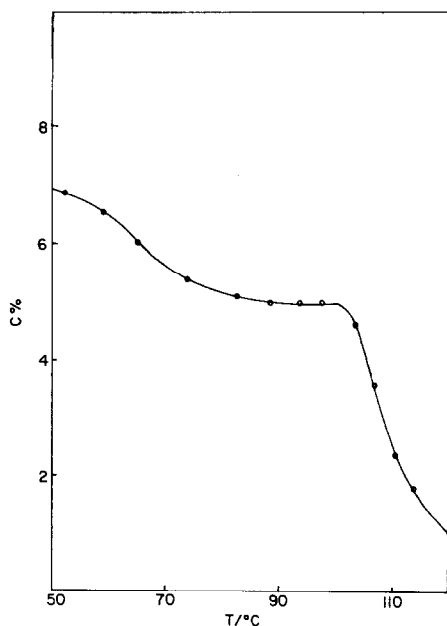


FIG. 1. Thermal gravimetric analysis data of a sample of lead ferrocyanide showing the percentage of loss of water (C%) when heated at a constant rate ( $2^{\circ}\text{C min}^{-1}$ ).

served indicated that the material dried at the above temperature has the stoichiometric composition  $\text{Pb}_2(\text{CN})_6 \cdot 2\text{H}_2\text{O}$ . Prolonged drying of moist samples in conc.  $\text{H}_2\text{SO}_4$  dessicators also yielded a product with the above hydration.

Single crystals of lead ferrocyanide were prepared by diffusing solution of  $\text{K}_4\text{Fe}(\text{CN})_6$  and  $\text{Pb}(\text{NO}_3)_2$  through two capillary tubes into a chamber of water (glass tube length = 12 cm, diameter = 2.5 cm). Crystals ( $\sim 2 \times 2 \times 2$  mm) was produced in a period of 5 months. Samples for conductivity measurements were made by pressing the crystals between stainless-steel electrodes in glass tubes. They were dried in vacuum at  $115^{\circ}\text{C}$  and exposed to the atmosphere until desired weight of moisture was absorbed (space between the electrodes and the tube permits moist air to enter). The ends of the tubes were sealed with epoxy resin, immersed in thermostatic oil

bath, and ac conductivity (40 Hz) was determined using a conductivity meter. Current (dc)-voltage characteristics were found to be linear and there was no appreciable difference between ac and dc conductivities. Pellets of the material made by pressing the polycrystalline powder between stainless-steel electrodes were also tested. The conductivity properties of pellets did not differ significantly from that of single crystals. The material was found to undergo decomposition at  $T \sim 140^{\circ}\text{C}$ , which explains the change in properties above that temperature.

Large dc currents were passed through thin disks of the material containing water (<8%) for long intervals of time. The absence of electrolytic effects proved that the ionic conduction was absent.

## Results and Discussion

The plots of  $\log \sigma$  vs  $T^{-1}$  for samples of  $\text{Pb}_2\text{Fe}(\text{CN})_6 \cdot 2\text{H}_2\text{O}$  containing different amounts of water (in excess of the two bound molecules) is depicted in Fig. 2. In all cases the conductivity rapidly diminishes above a critical temperature  $T_c \approx 109^{\circ}\text{C}$  and below  $T_c$  the relation

$$\sigma = \sigma_0 e^{-E/kT} \quad (1)$$

is found to hold with  $E \approx 0.32$  eV. The activation energy  $E$  is independent of the concentration  $C$  of water, but  $\sigma_0$  increases linearly with  $C$  (Fig. 3). The compound containing two molecules of bound water or less does not show measurable conductivity ( $\sigma \leq 10^{-9} \Omega^{-1} \text{cm}^{-1}$ ).

The sudden decrease of  $\sigma$  at  $T_c$  suggests that the bonding of water molecules near the ionic sites is essential for the generation of charge carriers.  $kT_c \approx 0.03$  eV has same order of magnitude as the energy of a hydrogen bonds that break at  $T \leq T_c$ , i.e., the  $\text{H}_2\text{O}$  molecules cannot remain bound to the ionic sites at temperatures above  $T_c$ .

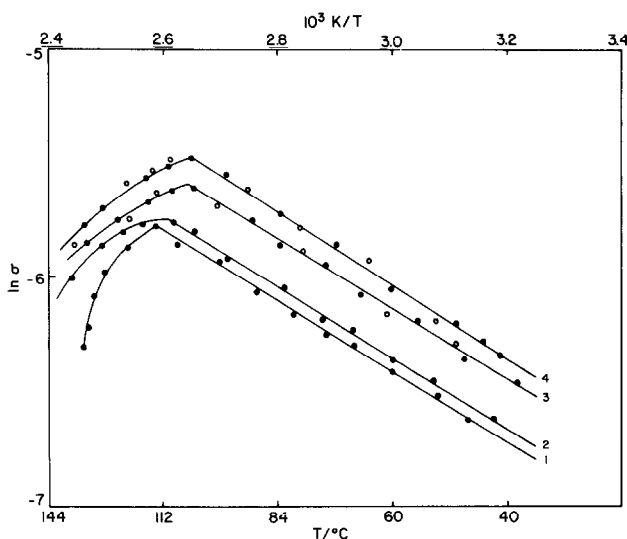


FIG. 2. The plot of  $\ln \sigma$  ( $\sigma$  in  $\Omega^{-1} \text{cm}^{-1}$ ) vs  $T^{-1}$  for samples of  $\text{Pb}_2(\text{CN})_6 \cdot 2\text{H}_2\text{O}$ . (○) Single crystals, (●) compressed pellets containing different concentrations of free water. (1) 0.12%, (2) 0.15%, (3) 0.21%, (4) 0.27%.

Our earlier observations have revealed that ferrocyanides with higher numbers of bonded water molecules, e.g., those of rare

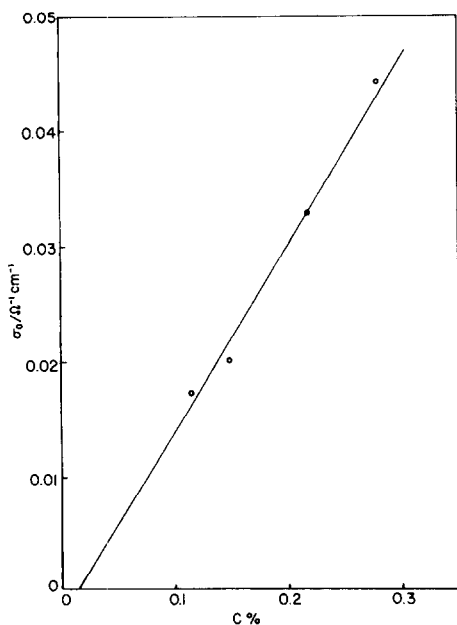


FIG. 3. The plot of  $\sigma_0$  vs concentration (C%) of free water.

earths  $\text{R}_4[\text{Fe}(\text{CN})_6]_3 \cdot 5\text{H}_2\text{O}$  behaves in the same manner with a significant difference. In these compounds, although the anhydrous form is an insulator, water in excess of bonded ones is not necessary for the onset of conductivity. However, the activation energies and the critical temperatures are comparable to that of lead ferrocyanide (Table I).

The conclusion that we can draw from the above observations is that the bonding of several water molecules near an ionic

TABLE I  
THE VALUES OF  $E$  AND  $T_c$  FOR SEVERAL FERROCYNANIDES

Compound	$E$ (ev)	$T_c$ (°C)
$\text{HO}_4[\text{Fe}(\text{CN})_6]_3 \cdot 5\text{H}_2\text{O}$	0.38	130
$\text{Er}_4[\text{Fe}(\text{CN})_6]_3 \cdot 5\text{H}_2\text{O}$	0.36	130
$\text{Yb}_4[\text{Fe}(\text{CN})_6]_3 \cdot 5\text{H}_2\text{O}$	0.39	130
$\text{Eu}_4[\text{Fe}(\text{CN})_6]_3 \cdot 5\text{H}_2\text{O}$	0.39	128
$\text{Gd}_4[\text{Fe}(\text{CN})_6]_3 \cdot 5\text{H}_2\text{O}$	0.39	142
$\text{Pb}_2[\text{Fe}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$	0.32	110

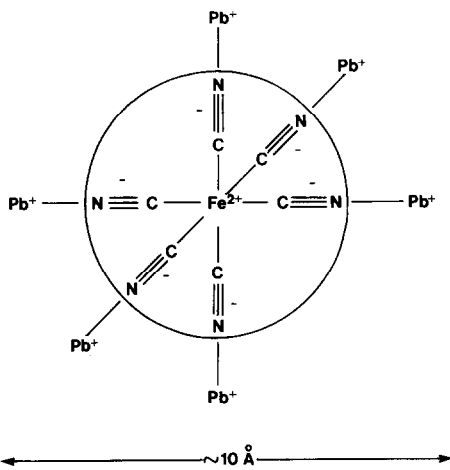


FIG. 4. The octahedral bonding of  $\text{CN}^-$  ions around  $\text{Fe}^{2+}$  ion in lead ferrocyanide. When the region encircled is "filled" with  $\text{H}_2\text{O}$  molecules the system behaves approximately as a ferrocyanide ion in aqueous solution.

site is necessary for the generation of charge carriers. In lead ferrocyanide most probable sites where water molecules get coordinated are  $\text{Pb}^{2+}$  ions and interstitial water molecules will get hydrogen-bonded to the coordinated ones (3). However, the following reasoning shows that all  $\text{Fe}^{2+}$  sites need not be unhydrated. If  $E_1, E_2, E_3$ , are the binding energies of  $\text{H}_2\text{O}$  molecules to  $\text{Pb}^{2+}$  ions, to each other, and  $\text{Fe}^{2+}$  ions, the assumption that  $\text{Pb}^{2+}$  ions are the most probable centers of hydration implies that  $E_1 > E_2 > E_3$ . Consider the thermal equilibrium between  $\text{H}_2\text{O}$  molecules near  $\text{Pb}^{2+}$  and those getting coordinated to  $\text{Fe}^{2+}$ . If  $n_1$  and  $n_3$  are the number of water molecules attached near  $\text{Pb}^{2+}$  and  $\text{Fe}^{2+}$ , respectively, we get

$$n_3/n_1 = e^{-(E_2-E_3)/kT} \quad (2)$$

Taking  $E_2 \sim 0.03$  eV, even in the limit  $E_3 \rightarrow 0$  we get  $n_3/n_1 \sim 4\%$  at  $T \sim 30^\circ\text{C}$ .  $\text{Fe}^{2+}$  centers coordinated with  $\text{H}_2\text{O}$  molecules can grow by hydrogen bonding of more  $\text{H}_2\text{O}$  molecules. Since  $E_2 > E_3$  this is a thermodynamically favorable process. Thus about

4% of  $\text{Fe}^{2+}$  sites could be fully hydrated. It is also interesting to note that a variation of  $n_1$  according to (2) will accurately preserve the form of the relation (1) with a very slight change in  $E$ . When a large number of  $\text{H}_2\text{O}$  molecules are bonded near a  $\text{Fe}^{2+}$  ion to form a cloud extending up to  $\text{CN}^-$  ions (Fig. 4). This ion and the octahedral arrangements of six  $\text{CN}^-$  ions is similar to an  $\text{Fe}(\text{CN})_6^{4-}$  ion in an aqueous environment the high dielectric constant of water reduces the energy needed to remove an electron to form  $\text{Fe}(\text{CN})_6^{3-}$



In ferrocyanides with smaller amounts of bonded water, the formation of such highly hydrated  $\text{Fe}^{2+}$  sites is less likely.

In the aqueous medium the process (3) requires 0.36 eV. Thus it is possible to understand why the thermal activation energy of large number of ferrocyanides is close to 0.36 eV. Thermally generated electrons from hydrated  $\text{Fe}^{2+}$  sites goes into a conduction band. Very small percentage of hydrated  $\text{Fe}^{2+}$  ions can generate charge carriers sufficient to give conductivities of the observed order of magnitude. This also explains why a small amount of water in excess of the coordinated molecules can activate electronic conduction.

Another question that might arise is, why hydrated  $\text{Pb}^{2+}$  sites are ineffective in activation of conductivity by the same mechanism. Here the activation energy, associated with a process similar to (3), would be much higher and hydrated structures disappear before the thermal activation of charge carriers could be observed.

Absorbed water can activate electronic conduction in ionic and molecular solids by other related but different mechanisms. They can reduce the binding energy of polarons or decrease the activation energy of hopping conduction (13, 14). The common feature is the role played by the hydrogen

bonding and the high dipole moment of water molecules.

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