

## Li<sup>+</sup> ION CONDUCTION IN COBALTOUS COBALTICYANIDE DOPED WITH LITHIUM CHLORIDE

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*(Date of receipt : 28.08.86)*

*(Date of acceptance : 17.11.86)*

**Abstract :** Cobaltous cobalticyanide (a Prussian Blue type of solid with large interstitial cavities) doped with lithium chloride is found to exhibit Li<sup>+</sup> ion conduction. The data on temperature variation of conductivity at different concentrations of LiCl are presented.

### 1. Introduction

Prussian Blue (Fe<sub>4</sub>(Fe(CN)<sub>6</sub>)<sub>3</sub>) and related heavy metal hexacyanides form a class of crystalline solids with complex ions whose structure is well understood.<sup>1,2,3</sup> They have similar face-centered cubic arrangement of metal cations at the corners of unit cubes linked by cyanide ions placed along the edges. A peculiar property arising from this structure is that the unit cells are unusually large (lattice constant  $\sim 10 \text{ \AA}$ ).<sup>1,2,3</sup> As the result the crystal can accommodate foreign molecules and ions as interstitial impurities.<sup>1,2,3</sup> We have noted that Prussian Blue type compounds doped with Li salts exhibit ionic conduction. Electronic conductivity (30°C) of Prussian Blue is  $\sim 3 \times 10^{-6} \Omega^{-1} \text{ m}^{-1}$ . However, it was found that compound with identical structure cobaltous cobalticyanide (Co<sub>4</sub>(Co(CN)<sub>6</sub>)<sub>3</sub>) has smaller electronic conductivity (30°C)  $\sim 4 \times 10^{-8}$  and high stability towards thermal degradation. Consequently this material is more suitable for studying Li<sup>+</sup> ion transport in metal hexacyanides doped with lithium salts. In this note we report our observations on Li<sup>+</sup> ion conduction in Co<sub>4</sub>(Co(CN)<sub>6</sub>)<sub>3</sub> doped with LiCl.

## 2. Experimental

$\text{Co}_4(\text{Co}(\text{CN})_6)_3$  was prepared by adding potassium cobalticyanide (Aldrich) solution (0.1 M) dropwise to a solution of cobalt nitrate (0.5 M). (Cobalt nitrate kept in excess to avoid formation of double salts containing potassium). The pink precipitate of  $\text{Co}_4(\text{Co}(\text{CN})_6)_3$  separated by filtration was washed with distilled water until the filtrate is free from potassium. The powder was dried in vacuum at  $140^\circ\text{C}$  for several hours to remove water of hydration. (Anhydrous material has a deep blue colour). The doping with LiCl was done by the following method.  $\text{Co}_4(\text{Co}(\text{CN})_6)_3$  was mixed with the desired amount of LiCl, the mixture homogenized and then dried in vacuum at  $140^\circ\text{C}$  to remove all moisture. The dried powder was compacted between carbon electrodes in a glass tube (diameter  $\sim 0.6$  cm) to a pressure of 800 psi until a pellet (length  $\sim 0.5$  cm) was formed. Ends of the tube were sealed with epoxy resin, the sample immersed in a thermostatic oil bath and a.c. (40 Hz) conductivity measured. (Modified Electronic Instruments Conductivity Bridge Model MC - 1, operated at 9 V). The d.c. conductivity was also measured by the polarization (blocking electrode) method<sup>4,5</sup> and found to be of the same order as the a.c. values. The rapid decrease in conductivity with time approaching a limit comparable to intrinsic electronic conductivity of  $\text{Co}_4(\text{Co}(\text{CN})_6)_3$  clearly demonstrated that the charges carried are ionic.

## 3. Results and Discussion

Figure 1 gives a plot of  $\ln \sigma$  vs  $T^{-1}$  for different concentrations of LiCl ( $c$ , measured as a percentage by wt). In each case the graph is a straight line showing that the relation,

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

is satisfied, both  $E$  and  $\sigma_0$  are found to depend on the degree of doping (ie,  $c$ ). The plots of  $E$  vs  $c$  and  $\sigma_0$  vs  $c$  are shown in Figures 2 and 3. The conductivity was found to be maximum ( $\sigma_{30} \simeq 2.5 \times 10^{-3} \Omega^{-1}\text{m}^{-1}$ ) when  $c \simeq 34\%$  wt (Figure 4) and minimum value of  $E$  also corresponds to this value of  $c$ . Again the minimum value of  $\sigma_0$  happens occur when the level of doping is  $\sim 34\%$ . It is possible that the critical point occurs when the interstitial cavities are nearly filled with LiCl. A simple calculation based on estimate of the volume of an interstitial cavity (using following data: lattice constant, ionic radii of  $\text{Co}^{2+}$ ,  $\text{Co}^{3+}$  and  $\text{CN}^-$ ) and density of solid LiCl indicate that the cavities get completely filled when  $c \simeq 41\%$ . The  $\text{Li}^+$  ion mobility probably results from ionization of LiCl into  $\text{Li}^+$  and  $\text{Cl}^-$  ions by the crystal field of  $\text{Co}_4(\text{Co}(\text{CN})_6)_3$ . The smaller  $\text{Li}^+$  ion become mobile and move through the interstices.  $\text{Cl}^-$  ions could also have some mobility, but we did not succeed in detecting this experimentally.

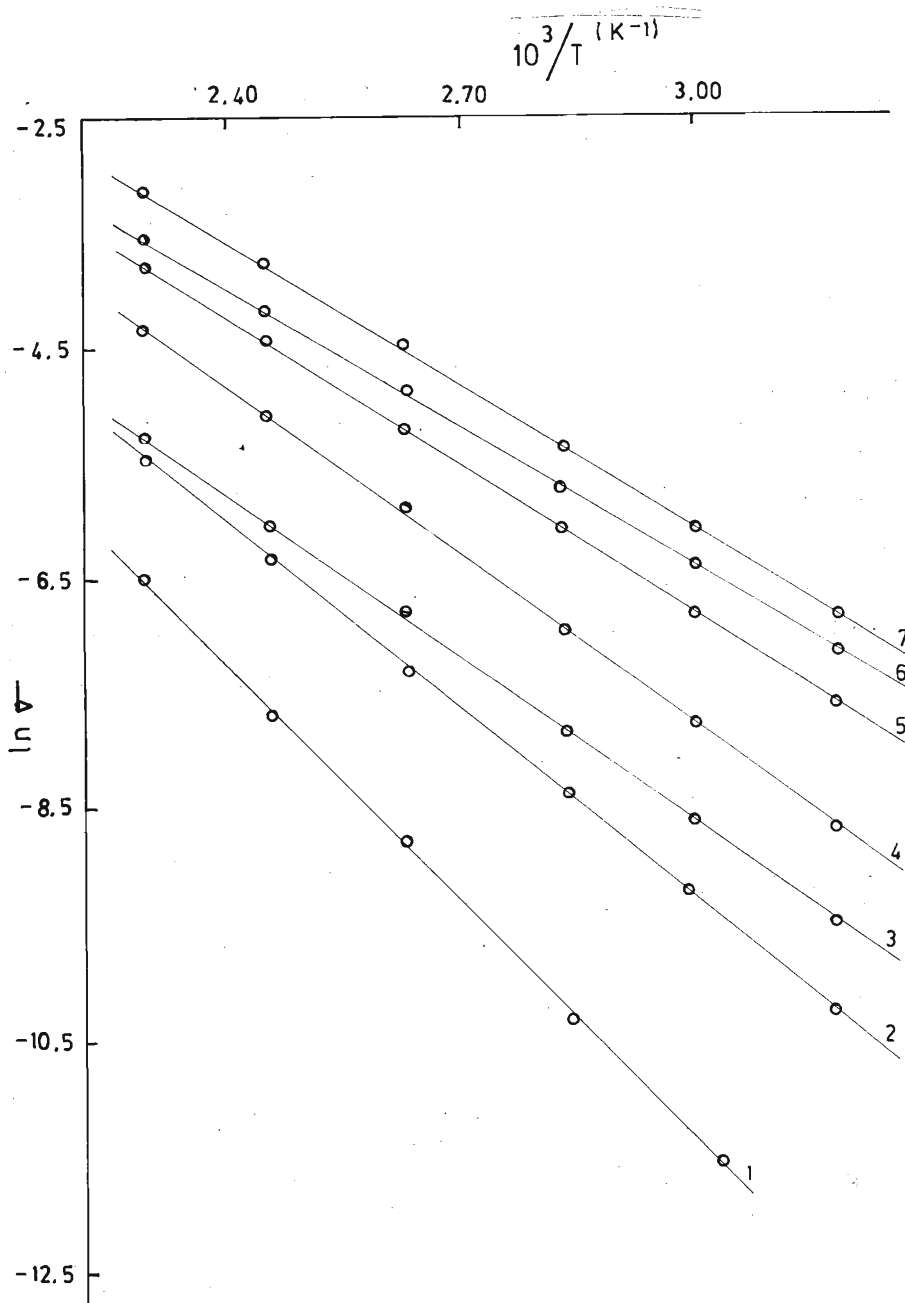


Figure 1. Plot of  $\ln \sigma_0$  vs.  $T^{-1}$  ( $\sigma$  in  $\Omega^{-1} \text{m}^{-1}$ ). Level of deoping (ie, % of LiCl by wt).

- |          |          |          |          |
|----------|----------|----------|----------|
| (1) 50   | (2) 16.7 | (3) 41.2 |          |
| (4) 23.1 | (5) 37.5 | (6) 28.6 | (7) 41.2 |

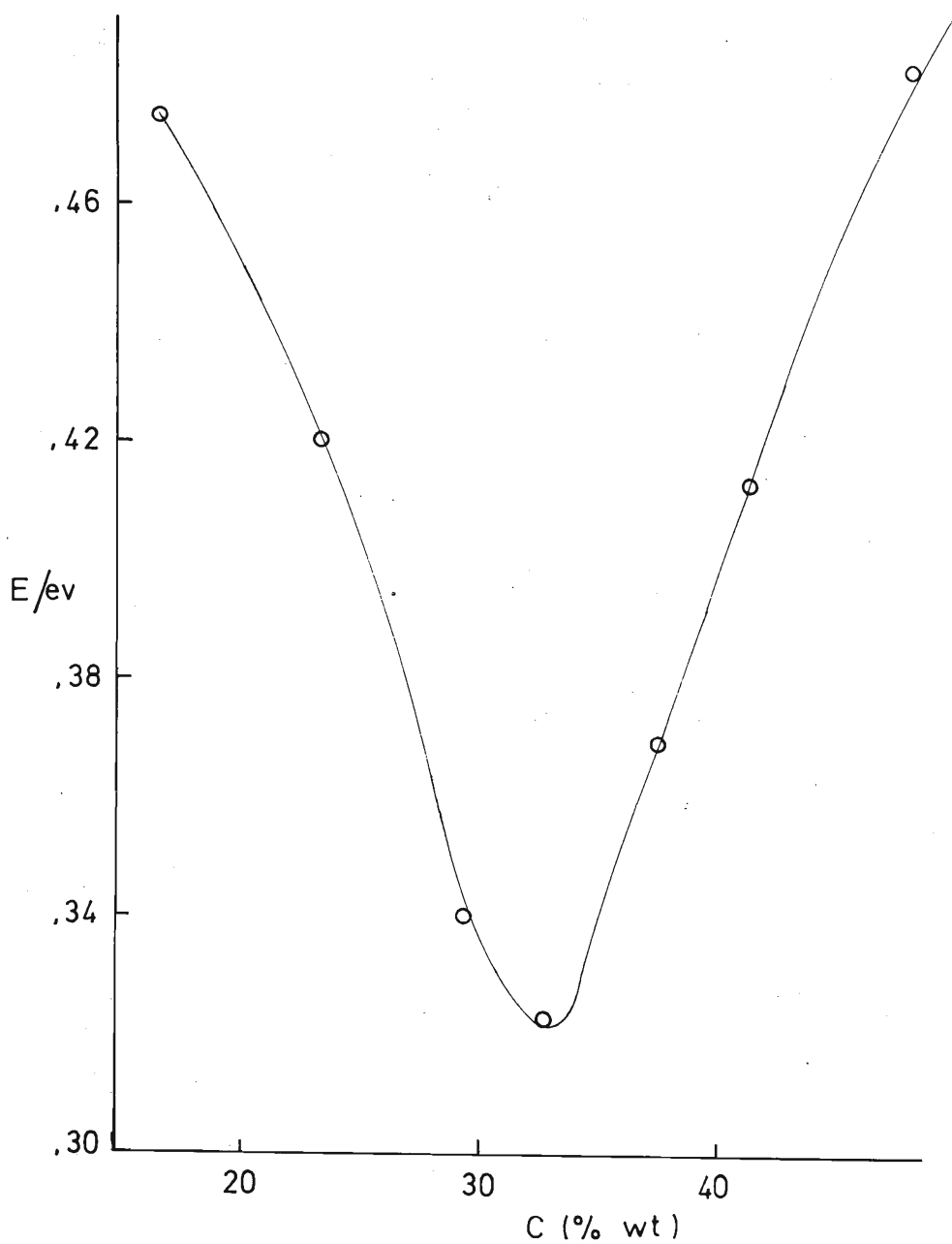


Figure 2. Plot of E vs C.

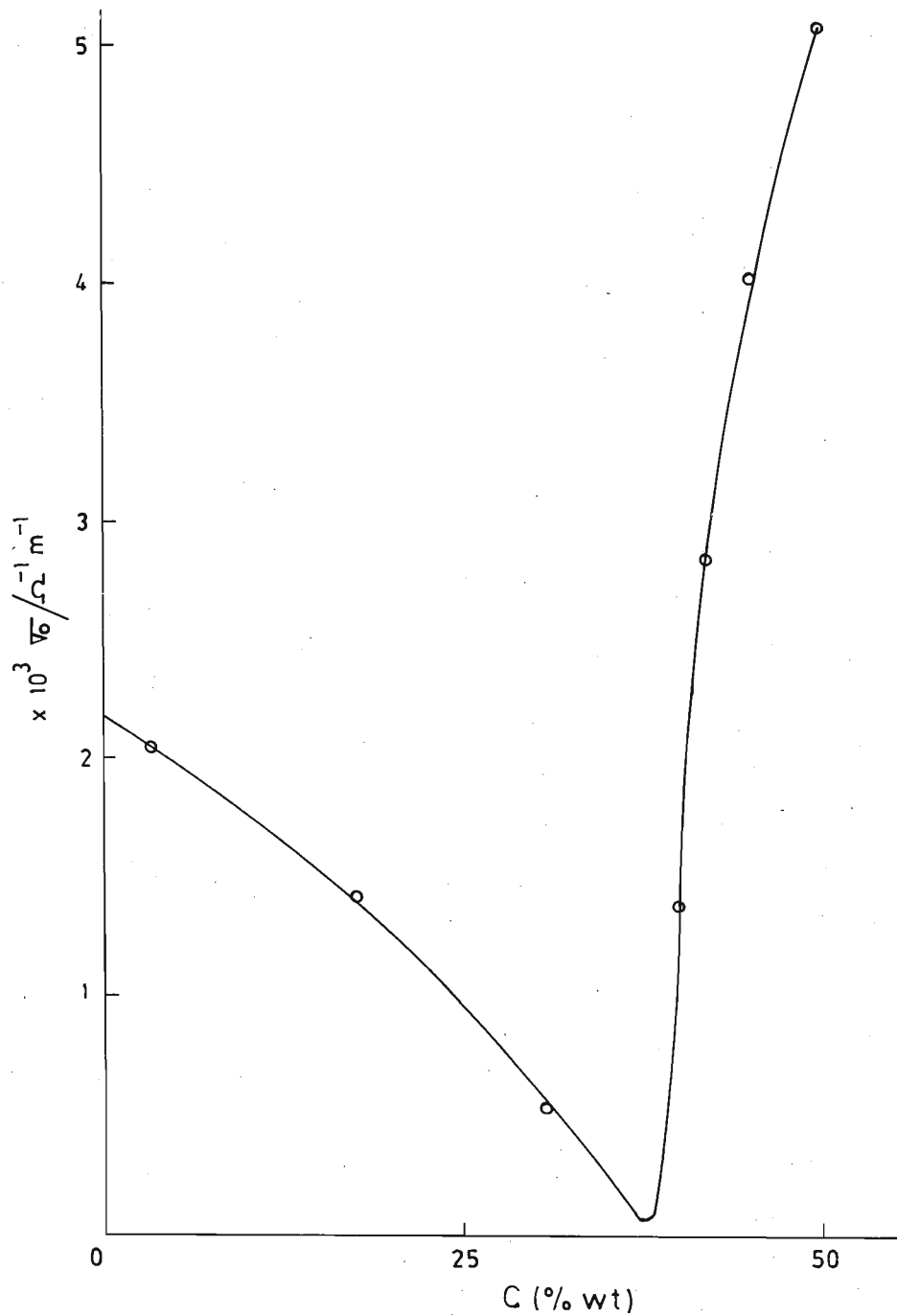


Figure 3. Plot of  $\sigma_0$  ( $\Omega^{-1}m^{-1}$ ) vs  $c$ .

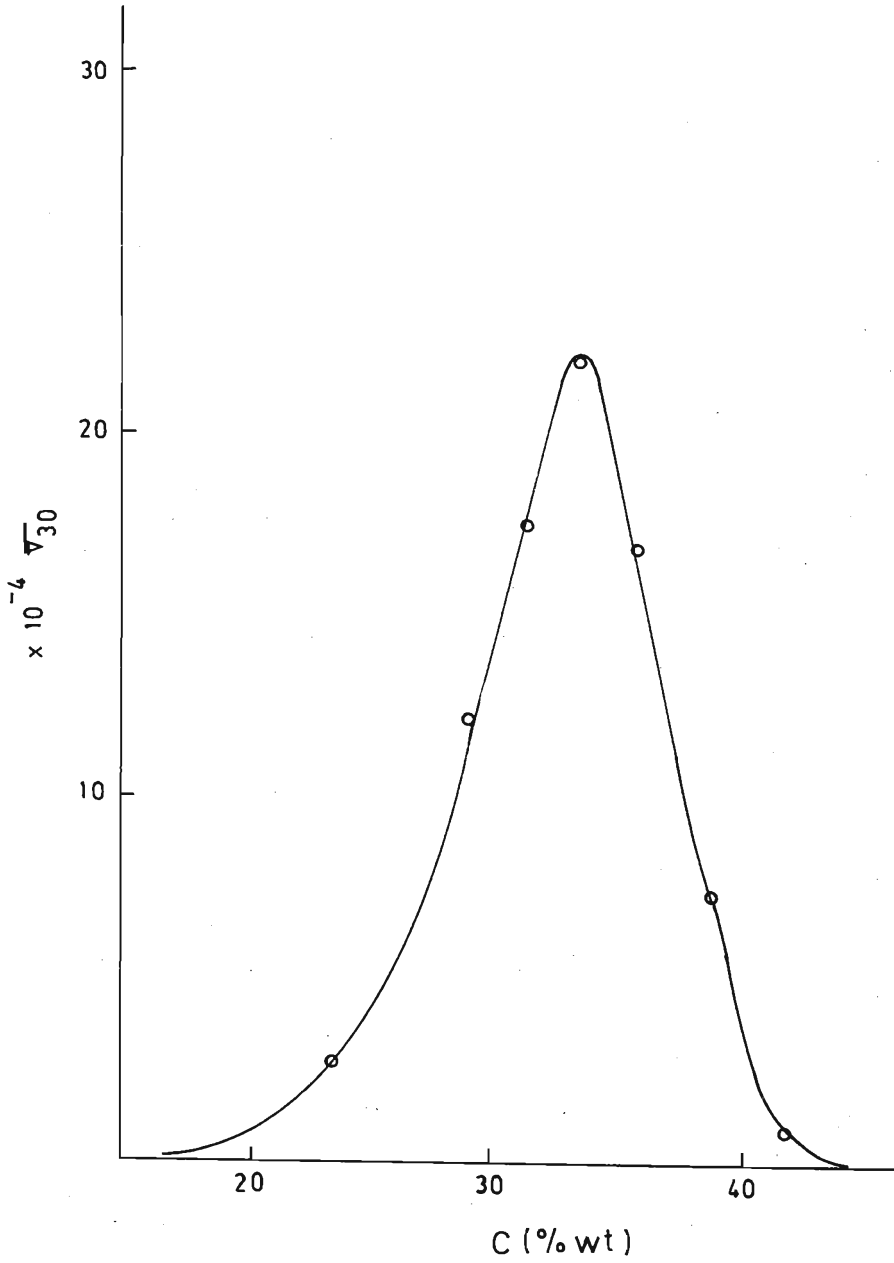


Figure 4. Plot of  $\sigma_{30} (\Omega^{-1} \text{m}^{-1})$  vs  $c$ .

#### 4. Conclusion

Further experimental work is necessary to elucidate the exact nature of Li<sup>+</sup> ion transport in this material. As interstitial cavities are large, it is very likely that Cl<sup>-</sup> ions also have some mobility in this material. Measurement of Cl<sup>-</sup> mobility would assist in understanding the mechanism of ionic conduction in Prussian Blue type materials. Unfortunately we did not have facilities for determination of the mobilities of Li<sup>+</sup> and Cl<sup>-</sup> ions separately.

#### References

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