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Li^+ ION CONDUCTION IN COBALTOUS COBALTICYANIDE DOPED WITH LITHIUM CHLORIDE

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

1. Introduction

Prussian Blue ($Fe_4(Fe(CN)_6)_3$) and related heavy metal hexacyanides form a class of crystalline solids with complex ions whose structure is well understood.[1,2,3] 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 A°).[1,2,3] As the result the crystal can accommodate foreign molecules and ions as interstitial impurities.[1,2,3] We have noted that Prussian Blue type compounds doped with Li salts exhibit ionic conduction. Electronic conductivity (30°C) of Prussian Blue is $\sim 3 \times 10^{-6}\ \Omega^{-1}\ m^{-1}$. However, it was found that compound with identical structure cobaltous cobalticyanide ($Co_4(Co(CN)_6)_3$) 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^+ ion transport in metal hexacyanides doped with lithium salts. In this note we report our observations on Li^+ ion conduction in $Co_4(Co(CN)_6)_3$ doped with LiCl.

2. Experimental

$Co_4(Co(CN)_6)_3$ 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 $Co_4(Co(CN)_6)_3$ separated by filteration was washed with distilled water until the filterate is free from potassium. The powder was dried in vacuum at 140°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. $Co_4(Co(CN)_6)_3$ was mixed with the desired amount of LiCl, the mixture homogenized and then dried in vacuum at 140°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[4,5] 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 $Co_4(Co(CN)_6)_3$ clearly demonstrated that the charges carried are ionic.

3. Results and Discussion

Figure 1 gives a plot of ln σ 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,

$$\sigma = \sigma_o e^{-E/kT} \tag{1}$$

is satisfied, both E and σ_o are found to depend on the degree of doping (ie, c). The plots of E vs c and σ_o vs c are shown in Figures 2 and 3. The conductivity was found to be maximum ($\sigma_{30} \simeq 2.5 \times 10^{-3} \ \Omega^{-1}m^{-1}$) when c $\simeq$ 34% wt (Figure 4) and minimum value of E also corresponds to this value of c. Again the minimum value of σ_o 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 Co^{2+}, Co^{3+} and CN^-) and density of solid LiCl indicate that the cavities get completely filled when c $\simeq$ 41%. The Li^+ ion mobility probably results from ionization of LiCl into Li^+ and Cl^- ions by the crystal field of $Co_4(Co(CN)_6)_3$. The smaller Li^+ ion become mobile and move through the interstices. Cl^- ions could also have some mobility, but we did not succeed in detecting this experimentally.

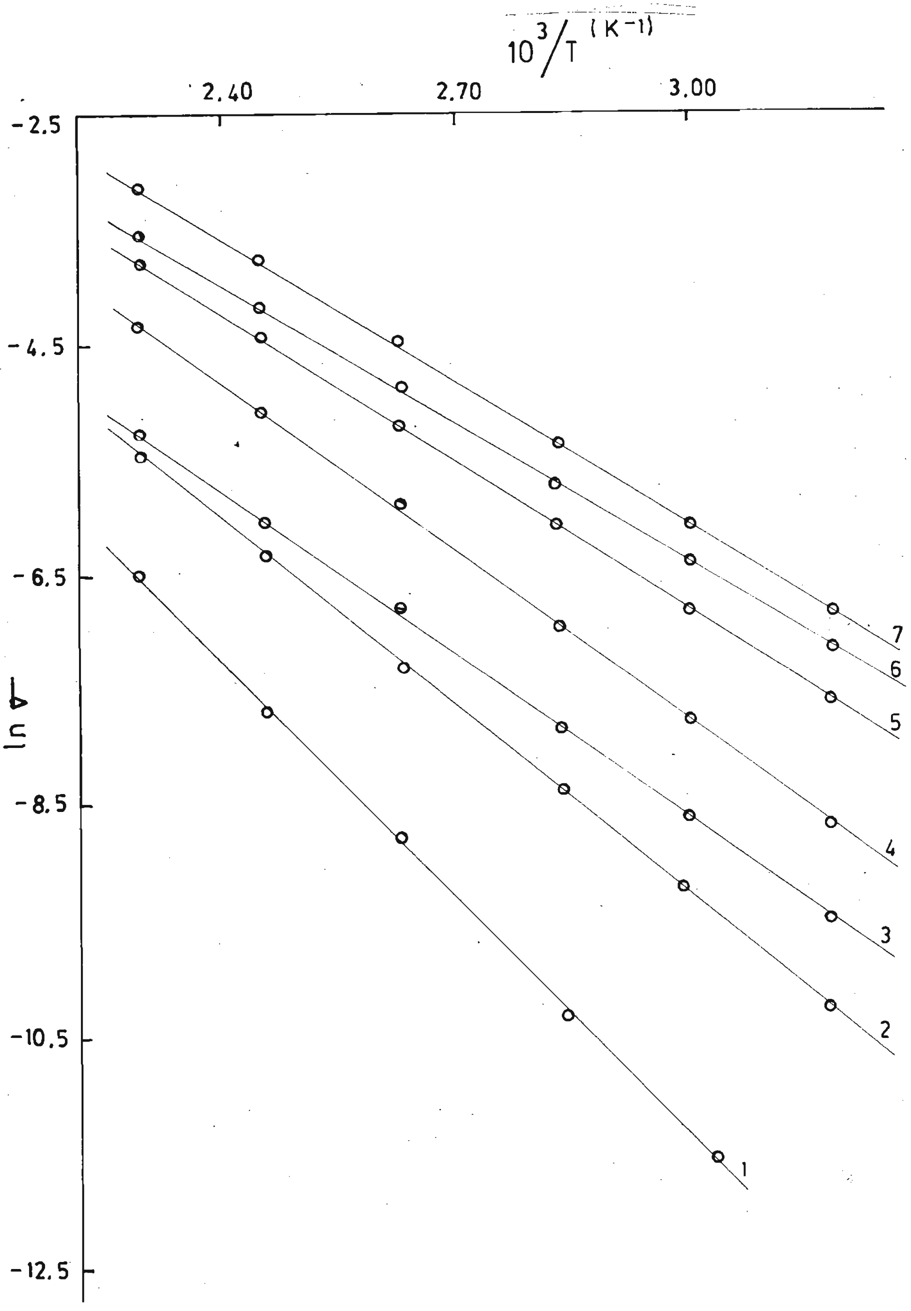

Figure 1. Plot of $\ln \sigma_0$ vs T^{-1} (σ in $\Omega^{-1}\ m^{-1}$). Level of deoping (ie, % of LiCl by wt).

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

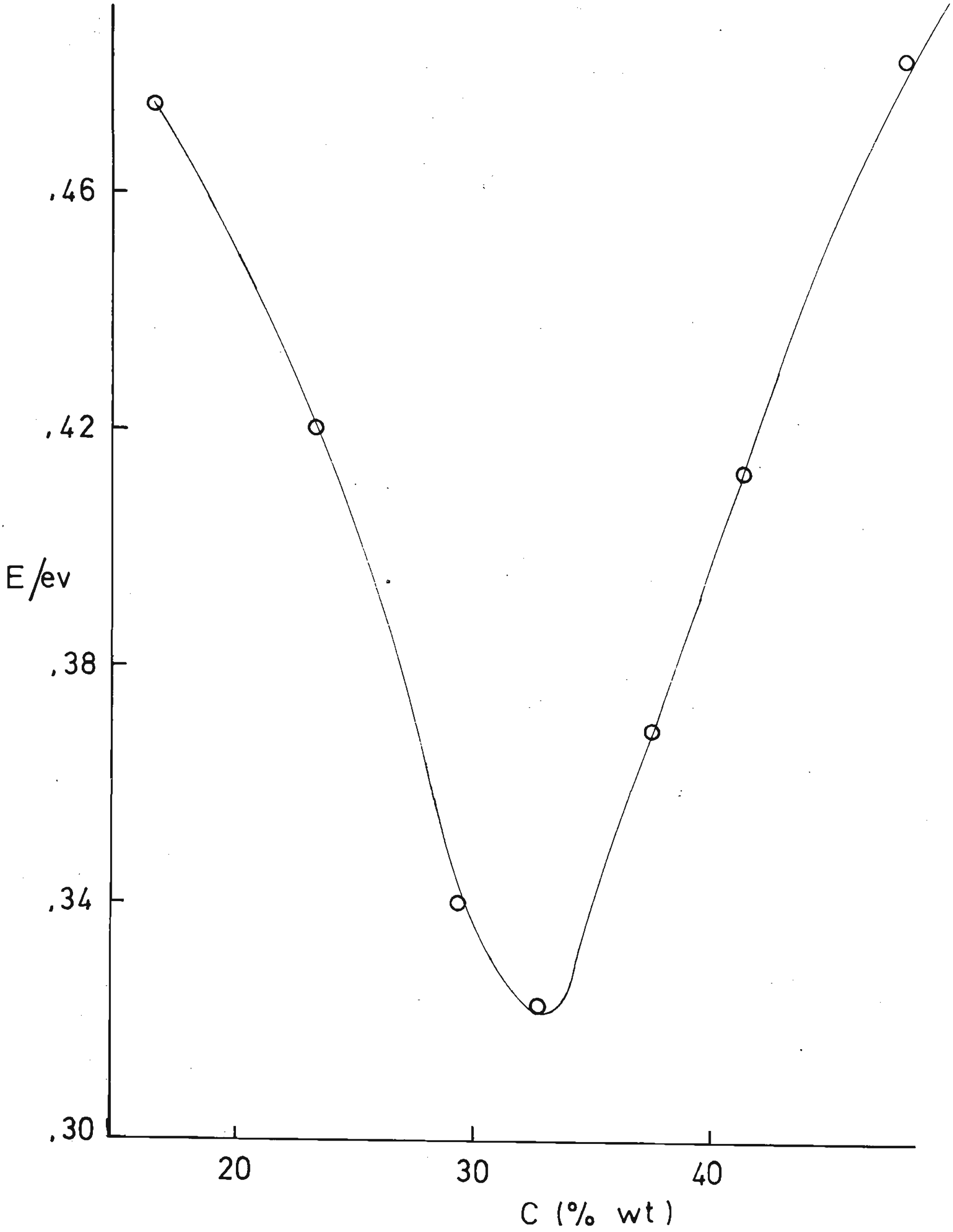

Figure 2. Plot of E vs C.

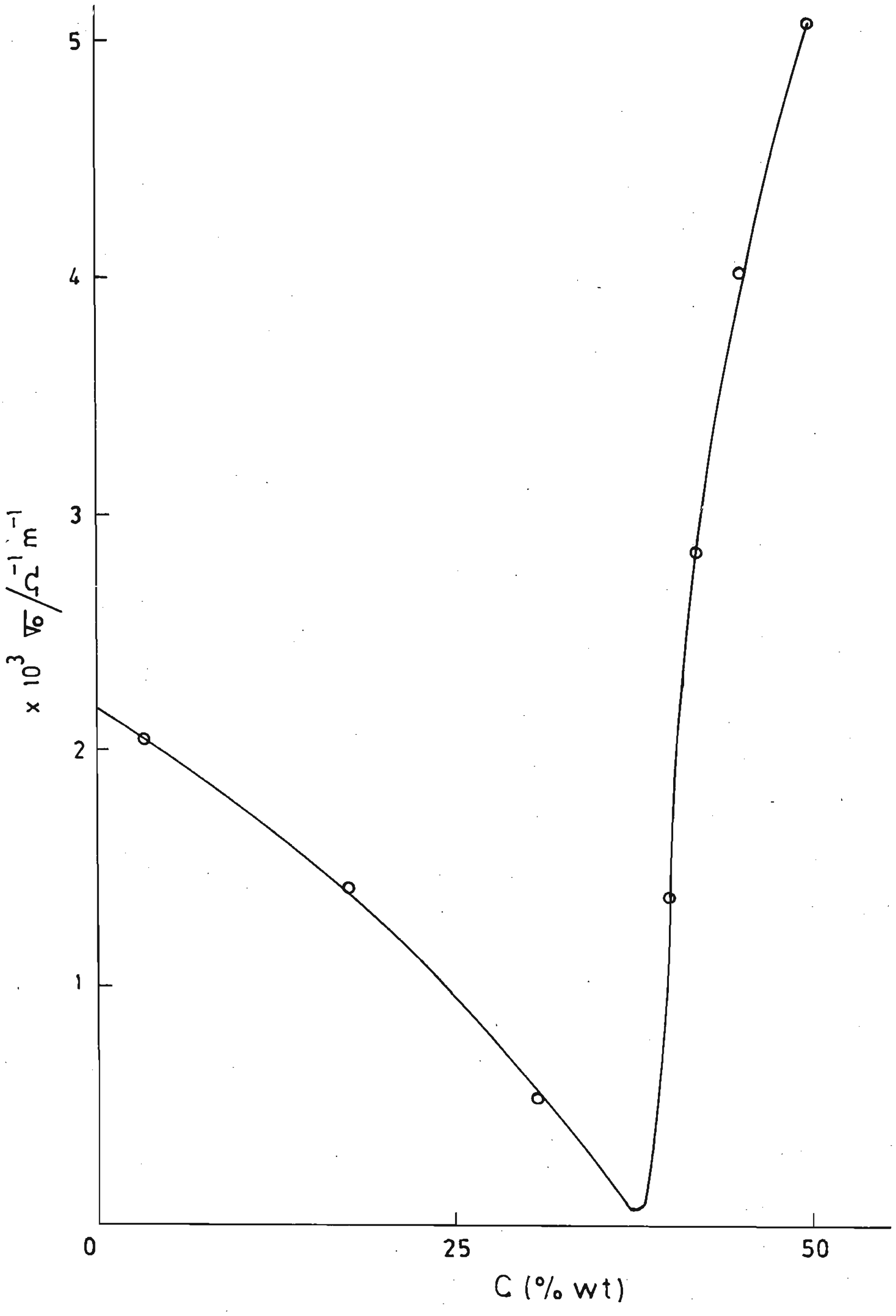

Figure 3. Plot of σ_0 ($\Omega^{-1}m^{-1}$) vs c.

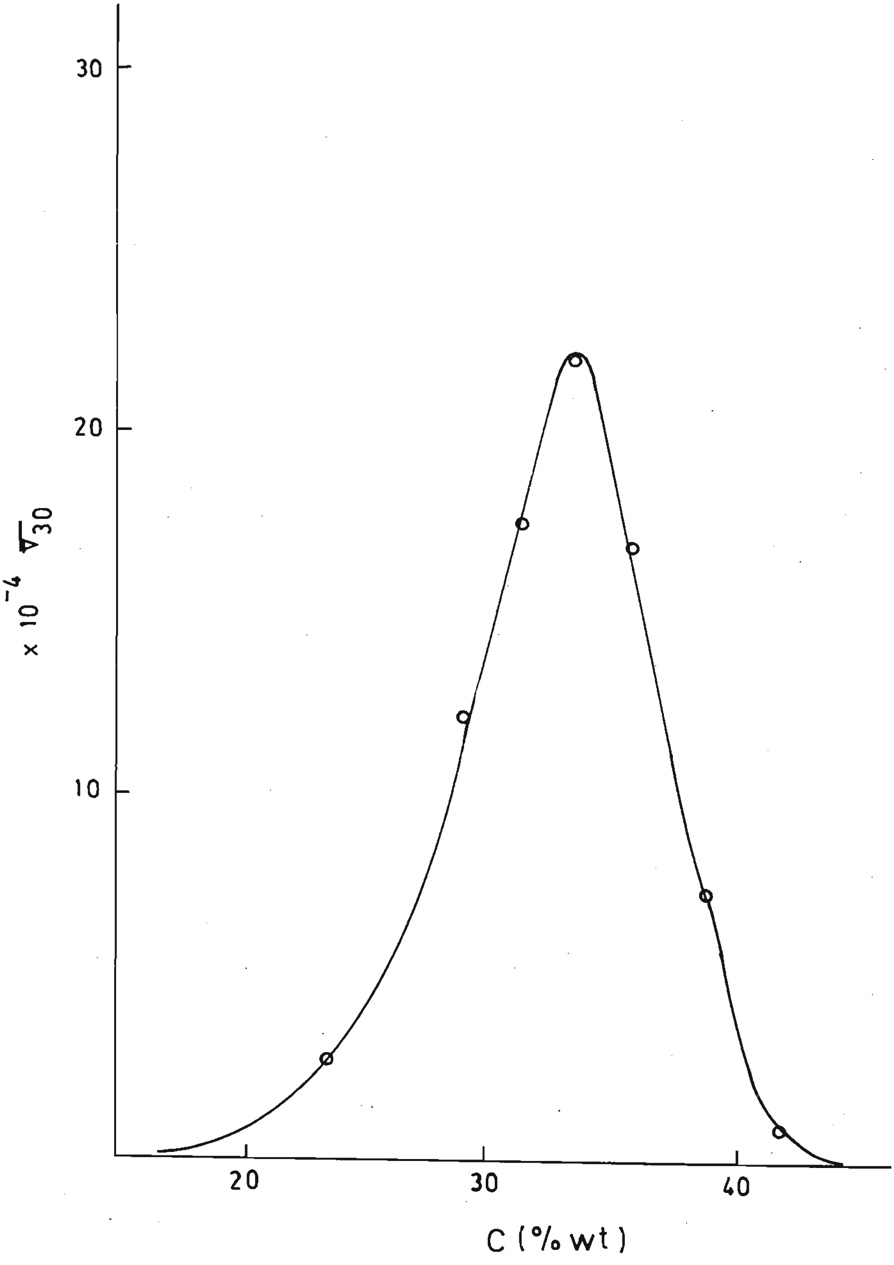

Figure 4. Plot of σ_{30} ($\Omega^{-1}m^{-1}$) vs c.

4. Conclusion

Further experimental work is necessary to elucidate the exact nature of Li^+ ion transport in this material. As interstitial cavities are large, it is very likely that Cl^- ions also have some mobility in this material. Measurement of Cl^- 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^+ and Cl^- ions separately.

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