



Heat-induced charge transfer in cobalt iron cyanide

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Abstract

The heating of Co(2+) ferricyanide above 80 °C induces an inner charge transfer from Co(2+) towards Fe(III) to form the mixed valence system Co(2+)Co(III) ferri-ferro-cyanide. This charge transfer takes place preserving the material framework and forming a solid solution of the initial and final species. The cell edge of the cubic cell (Fm-3m) of this solid solution follows a regular variation with the material composition. This mixed valence system was characterized using X-ray diffraction, infrared, thermo-gravimetric, Mössbauer and magnetic measurements. Its formation is easily detected by the appearance of an intermediate $\nu(\text{CN})$ absorption band in the infrared spectra at around 2120 cm⁻¹, 40 cm⁻¹ below and above the observed frequency for this vibration in Co(2+) ferri- and ferro-cyanide, respectively.

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1. Introduction

Transition metal cyanides form a particular class of molecular materials where the metal centers remain strongly linked through CN groups, fact that allows a considerable spin coupling and, as a consequence, magnetic order in many of them. Owing to this characteristic, these compounds have been intensively studied as prototype of high temperature molecular magnets [1–5].

The occurrence of photo-induced transitions is a common feature to transition metals, involving changes of both electronic configuration and valence. When two of these metals remain linked through CN groups, these transitions could be related to a charge transfer between the metal centers through the CN bridges. Such is the case of low spin Co(III) ferrocyanide. This a non-magnetic species where an inner charge transfer can be induced, by

illumination, to form high spin Co(2+) ferricyanide. The formed species is a molecular magnet at low temperature [6]. In this sense that photo-induced charge transfer has been taken as a photo-induced magnetization. This fact has stimulated its study as a non-common or rare effect [7–9]. An analog charge transfer, but in an inverse sense, is observed when Co(2+) ferricyanide is heated above certain temperature. As far as we know, that heat-induced charge transfer has not been previously studied.

The thermal-induced spin crossover and charge transfer processes in transition metal salts are subjects that have received an outstanding attention [10]. Both, basic and practical interests have stimulated their study. In the heat-induced charge transfer in Co(2+) ferricyanide, to be discussed in this contribution, these two processes are present. The oxidation of the cobalt atom is accompanied of a change in its electronic configuration, from high spin Co(2+) to low spin Co(III). As end product of these heat-induced effects a Co(2+)Co(III) ferrocyanide is obtained. However, between this end species and the initial Co(2+) ferricyanide an intermediate solid solution of Co(2+)-Co(III) ferri-ferro-cyanide is formed. In this work that

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