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Mixed valence states in cobalt iron cyanide

R. Martínez-García[a], M. Knobel[b], J. Balmaseda[a,c], H. Yee-Madeira[d,1], E. Reguera[a,e,*,1]

[a]Institute of Materials Science and Technology, University of Havana, 10400 Havana, Cuba
[b]Institute of Physics "Gleb Wataghin", UNICAMP, Campinas, Brazil
[c]Institute of Materials Research, UNAM, Mexico, D.F.
[d]School of Physics and Mathematics of IPN, Mexico, D.F.
[e]Centre for Applied Science and Advanced Technology of IPN, Mexico, D.F.

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Abstract

Cobalt iron cyanide with both Co and Fe in mixed valence states were prepared and characterized. In this mixed valence system the cobalt atom is found both as high spin Co(2+) and low spin Co(III) while iron always appears in low spin state to form two solid solutions: Co(2+)Co(III) hexacyanoferrates (II,III), and Co(2+)Co(III) hexacyanoferrate (II). Such solid solutions have the following formula units: $(Co^{2+})_x(Co^{III})_{1-x}K[(Fe^{II})_{1-x}(Fe^{III})_x(CN)_6]\cdot\frac{1}{2}H_2O$ and $(Co^{2+})_{1.5x}(Co^{III})_{1-x}K[Fe^{II}(CN)_6]\cdot yH_2O$ ($0\leqslant x\leqslant 1$, $1\leqslant y\leqslant 14$). Compounds within these two series were characterized from Infrared, Mössbauer, X-ray diffraction and thermo-gravimetric data, and magnetic measurements at low temperature. A model for their crystal structure is proposed and the structure for a representative composition refined from XRD powder patterns using the Rietveld method. A simple and reproducible procedure to prepare these solid solutions is provided. Within hexacyanoferrates, such mixed valence states system in both metal centres shows unique features, which are discussed from the obtained data.

Keywords: A. Magnetic materials; C. Mössbauer spectroscopy; D. Crystal structure; D. Magnetic properties; D. Electronic structure

1. Introduction

Prussian blue analogues have been extensively studied in the last decade due to their interesting magnetic properties, e.g. high T_c magnet [1–3], magnetic pole inversion [4], spin glass behaviour [5], magnetic refrigeration [6], and so on. Within Prussian blue analogues, cobalt hexacyanoferrates (II, III) have received a particular attention, mainly due to the observed photo-induced magnetism in cobalt (III) ferrocyanide [7,8]. The illumination of this compound induces an inner charge transfer to form cobalt (2+) ferricyanide, which shows magnetic order at low temperature (below 20 K). The heating of cobalt (2+) ferricyanide, above 353 K, induces the inverse charge transfer, to form low spin cobalt (III) ferrocyanide [9]. These two charge transfer processes indicate that in cobalt hexacyanoferrates (II,III) the energy barrier between high spin Co(2+) and low spin Co(III) is relatively low. Such behaviour for cobalt iron cyanide suggests the possibility of obtaining solid compounds with both Co and Fe in mixed valence sates as stable phase at room temperature. However, as far as we know, such possibility has not been explored. The preparation and study of materials based in these mixed valence states is the aim of this contribution. Two stable solid solutions of Co(2+)Co(III) hexacyanoferrates were prepared and characterized from X-ray diffraction (XRD), infrared (IR), Mössbauer, thermogravimetry and magnetic data. A structural model is proposed for these solid solutions and the crystal structure refined for a typical composition from XRD powder patterns using the Rietveld method. The crystal structures of related cobalt iron cyanides are provided as Supplementary Information.

*Corresponding author. Institute of Materials Science and Technology, University of Havana, 10400 Havana, Cuba. Tel./fax: 53 7 2096653.
E-mail address: ereguera@yahoo.com (E. Reguera).
[1]COFAA Fellow.

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