

Nature of the Observed Asymmetry in Mössbauer Spectra of Iron (2+) Hexacyanometallates (III)

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The material under study belongs to the Prussian blue analogues family, which are coordination compounds with a porous framework appropriate for the storage of small molecules, among them hydrogen. The porous framework results from systematic vacancies for the octahedral building block, $[M(CN)_6]$, in a 3D structure. Mössbauer spectroscopy is a powerful tool to obtain structural information on the local environment for the iron nucleus in these materials. Mössbauer spectra of iron (2+) hexacyanometallates (III) show two slightly asymmetric quadrupole splitting doublets. These two doublets correspond to two non-equivalent structural sites for the iron atom in the framework related with a non-random vacancy distribution. The observed asymmetry was ascribed to a vibrational anisotropy for these iron sites. The asymmetry decreases on the sample cooling and for 7 K it practically disappears. The iron atom is found at the cavities surface with a mixed coordination sphere, $Fe(NC)_{6-x}(H_2O)_x$. Such anisotropic coordination environment could explain the presence of certain vibrational anisotropy detected as asymmetric quadrupole splitting doublets.

1. Introduction

Porous Prussian blue (PB) analogues have received a renewed attention in the last few years, particularly as prototype of porous solids for the hydrogen storage

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