

Effect of the water of crystallization on the Mössbauer spectra of hexacyanoferrates (II and III)

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Mössbauer spectra were recorded on hydrated, dehydrated and rehydrated hexacyanoferrate (II and III) samples including alkaline, alkaline-earth, transition metal and rare-earth salts. The location of the water molecules around the complex hexacyanoferrate anion has a decisive role on the quadrupole splitting of the low-spin Fe^{III} cation.

1. Introduction

The quadrupole splitting (Δ) in ⁵⁷Fe Mössbauer spectra has contributions from the relative electronic population of the 3d levels and the anisotropic effects of the surrounding atomic environment [1]. In low-spin Fe^{II} and Fe^{III} in an octahedral environment, such as in hexacyanoferrates, the d levels are split into lower t_{2g} and higher e_g levels. All d electrons are located in the lower t_{2g} levels, which is full for Fe^{II} and has a hole for Fe^{III}. Ferrocyanides have normally zero quadrupole splitting while ferricyanides, subject to a Jahn–Teller distortion in order to remove the degeneracy of the t_{2g} levels (d_{xy}, d_{xz}, d_{yz}), have generally quadrupolar doublets due to unequal electronic population of these levels (see fig. 1).

During the course of our research on ozonization of solid hexacyanoferrate (II and III) samples we have observed that the quadrupole splitting Δ of the products is not always the same as for the substance crystallized from solutions [2–4]. With time after ozonization process (aging), however, Δ changes to the normal value in most cases. We had interpreted the phenomena in terms of unstable species (O₃⁻, O⁻, OH⁻, OH[•], HO₂[•], etc.) formed during the ozonization process, which remain as integral part of the product. However, there is another important possibility, which is the influence on Δ of the water of crystallization which is abundantly present in most hexacyanoferrates. During ozonization, water can be decomposed according to the reaction [5]

