

Communicaton

## A Study on Electron Irradiation Effects in Hydrated Cobalt Ferricyanide Using Mössbauer Spectroscopy

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Recent works<sup>1-4)</sup> on irradiation experiments with complexes have reported that low-spin  $\text{Fe}^{\text{III}}$  is reduced to  $\text{Fe}^{\text{II}}$  after the irradiation. The same effect has been obtained by heating the sample. In this report we give Mössbauer spectroscopic measurements with hydrated cobalt ferricyanide irradiated by electron beams.

The complex was prepared by mixing slowly 0.01 N cobalt chloride and potassium ferricyanide. The precipitation was filtered, washed by ethanol and dried. The complex powder of about 250 mg was packed in an aluminum ring of 20 mm diameter covered with aluminum foil. The samples were irradiated at liquid nitrogen temperature with 1 MeV electron beams of 90  $\mu\text{A}$  for 10 minutes and 77  $\mu\text{A}$  for 1 hour. The Mössbauer measurements were performed at liquid nitrogen temperature, a) just after the irradiation, b) after annealing the irradiated samples at room temperature for 50 days, and c) after exposing the annealed powder to fresh air for 1 hour.

Figures 1 and 2 show the observed spectra which are resolved into several Lorentzian peaks of low-spin  $\text{Fe}^{\text{III}}$  and  $\text{Fe}^{\text{II}}$  and high-spin  $\text{Fe}^{3+}$  by least-square fitting. The Mössbauer parameters obtained are listed in Table I. We can see the following results from Table I. The reduction to low-spin  $\text{Fe}^{\text{II}}$  is the main effect of the irradiation. However, a part of the remaining  $\text{Fe}^{\text{III}}$  species changes to high-spin  $\text{Fe}^{3+}$  by the annealing. The reason would be supposed that cyanide linkages connected to low-spin iron species become unstable by the irradiation and the cyanide complex ions are decomposed by the annealing. When the sample is irradiated with very high dose,  $\text{Fe}^{3+}$  ions come from, as well as all of  $\text{Fe}^{\text{III}}$ , a part of  $\text{Fe}^{\text{II}}$  species formed by the irradiation. This dose dependence of the annealing effect implies that, probably due to  $\text{H}^\cdot$  radicals formed by radiolytic decomposition of the water ligands<sup>2)</sup>, low-spin  $\text{Fe}^{\text{III}}$  is reduced to  $\text{Fe}^{\text{II}}$  at the first stage of the irradiation and the cyanide linkages become unstable with further irradiation. The instability of  $\text{Fe}^{\text{II}}$  only at the very high dose irradiation shows that the

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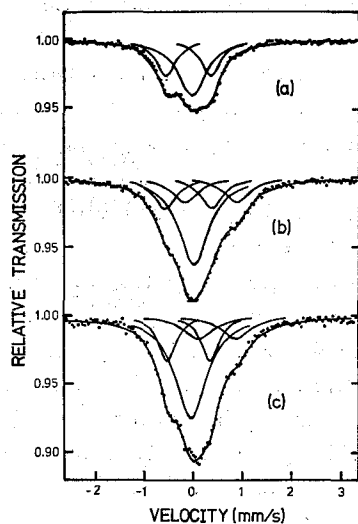


Fig. 1. Mössbauer spectra of cobalt ferricyanide irradiated with 90  $\mu$ A of 1 MeV electrons for 10 minutes. a) Irradiated. b) Annealed for 50 days after irradiation. c) Exposed to fresh air after irradiation and annealing.

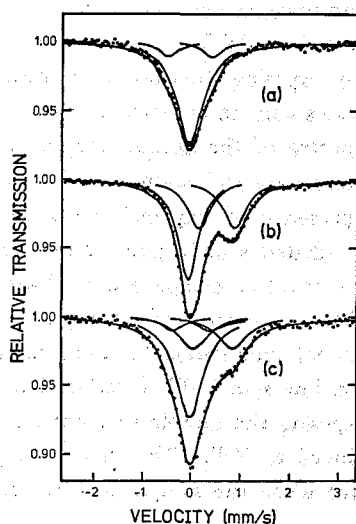


Fig. 2. Mössbauer spectra of cobalt ferricyanide irradiated with 77  $\mu$ A of 1 MeV electrons for 1 hour. a) Irradiated. b) Annealed for 50 days after irradiation. c) Exposed to fresh air after irradiation and annealing.

Table I. Mössbauer Parameters of the Irradiated Complex

| Species            | IS<br>(mm/sec)    | QS<br>(mm/sec) | Width<br>(mm/sec) | Intensity<br>(%) |      |
|--------------------|-------------------|----------------|-------------------|------------------|------|
| 90 $\mu$ A-10 min. |                   |                |                   |                  |      |
| a {                | Fe <sup>III</sup> | -0.10          | 0.92              | 0.48             | 47.4 |
|                    | Fe <sup>II</sup>  | -0.03          | —                 | 0.70             | 52.6 |
| b {                | Fe <sup>III</sup> | -0.09          | 0.95              | 0.53             | 25.8 |
|                    | Fe <sup>3+</sup>  | 0.37           | 1.06              | 0.61             | 24.1 |
|                    | Fe <sup>II</sup>  | 0.01           | —                 | 0.74             | 50.1 |
| c {                | Fe <sup>III</sup> | -0.09          | 0.88              | 0.43             | 25.9 |
|                    | Fe <sup>3+</sup>  | 0.49           | 0.77              | 0.73             | 22.0 |
|                    | Fe <sup>II</sup>  | -0.04          | —                 | 0.80             | 52.1 |
| 77 $\mu$ A-1 hour  |                   |                |                   |                  |      |
| a {                | Fe <sup>III</sup> | -0.03          | 0.90              | 0.44             | 16.9 |
|                    | Fe <sup>II</sup>  | -0.03          | —                 | 0.66             | 83.1 |
| b {                | Fe <sup>3+</sup>  | 0.50           | 0.72              | 0.60             | 52.9 |
|                    | Fe <sup>II</sup>  | -0.08          | —                 | 0.51             | 47.1 |
| c {                | Fe <sup>III</sup> | -0.02          | 0.76              | 0.55             | 12.1 |
|                    | Fe <sup>3+</sup>  | 0.44           | 0.81              | 0.70             | 34.9 |
|                    | Fe <sup>II</sup>  | -0.03          | —                 | 0.68             | 52.9 |

(a) Irradiated.

(b) Annealed for 50 days after irradiation.

(c) Exposed to fresh air after irradiation and annealing.

cyanide linkages connected to  $\text{Fe}^{\text{II}}$  are more stable against the irradiation than those connected to  $\text{Fe}^{\text{III}}$ .

By exposing the sample to fresh air, no conspicuous changes of the relative peak intensities can be recognized when the irradiation dose is not very high. However, as to the spectra of the sample irradiated with very high dose, approximately one third of  $\text{Fe}^{3+}$  ions vary to low-spin atoms. The above fact means that the presence of air, probably presence of oxygen, causes to coordinating of CN groups around iron atoms in the irradiated sample powder in which too much  $\text{Fe}^{3+}$  ions exist.

In order to compare the effects by irradiation with those by heating the complex, we observed spectra of a sample heated at  $200^\circ\text{C}$  for 1 hour as shown in Fig. 3. The Mössbauer parameters for the heated complex are shown in Table II. By heating the sample, low-spin  $\text{Fe}^{\text{III}}$  is reduced to  $\text{Fe}^{\text{II}}$ . The relative intensity of  $\text{Fe}^{3+}$  is rather small. By exposing the sample to fresh air for 1 hour, approximately half of the remaining  $\text{Fe}^{\text{III}}$  is reduced to  $\text{Fe}^{\text{II}}$ . This reduction process did not happen in the irradiated complex powder when the sample was exposed to fresh air, as mentioned above.

Table II. Mössbauer Parameters of the Heated Complex

| Species | IS<br>(mm/sec)    | QS<br>(mm/sec) | Width<br>(mm/sec) | Intensity<br>(%) |      |
|---------|-------------------|----------------|-------------------|------------------|------|
| a {     | Fe <sup>III</sup> | -0.03          | 1.35              | 0.90             | 61.6 |
|         | Fe <sup>3+</sup>  | 0.57           | 0.80              | 0.64             | 9.2  |
|         | Fe <sup>II</sup>  | -0.08          | —                 | 0.86             | 29.2 |
| b {     | Fe <sup>III</sup> | 0.05           | 1.10              | 0.85             | 28.4 |
|         | Fe <sup>3+</sup>  | 0.56           | 0.75              | 0.59             | 11.1 |
|         | Fe <sup>II</sup>  | -0.01          | —                 | 0.68             | 60.5 |

(a) Heated. (b) Exposed to fresh air after heating

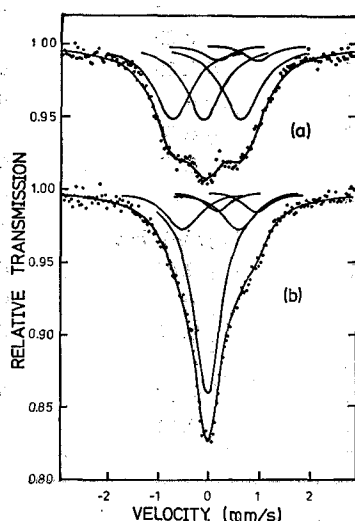


Fig. 3. Mössbauer spectra of cobalt ferricyanide heated at  $200^\circ\text{C}$  for 1 hour. a) Heated. b) Exposed to fresh air after heating.

#### Electron Irradiation Effects

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