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MÖSSBAUER SPECTROSCOPIC STUDIES ON IRON THIOCYANATE

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Mössbauer spectra of iron thiocyanate crystals prepared from iron(III) compounds show the presence of iron(II) species. It was found that some reduction of iron(III) species was taking place both in aqueous and ethereal phases.

Mössbauer spectroscopy can provide a quantitative measure of the oxidation state of iron atom. Mitchell and Macdonald have pointed out[1)] that pure crystalline iron(III) thiocyanate was not obtained, contrary to the results reported by Schlesinger and Van Valkenburgh.[2)] Since then, there seems no investigation so far on the oxidation state of iron atoms in this compound, whereas a number of investigations have been done in the field of solution chemistry of iron(III) thiocyanate species. We have undertaken the present studies to clarify this contradiction by using Mössbauer spectroscopy.

Repeated experiments were carried out to prepare pure crystalline iron(III) thiocyanate by following Schlesinger and Van Valkenburgh's method (slow evaporation of a solution made from barium thiocyanate and iron(III) sulphate, or from iron(III) hydroxide and thiocyanic acid prepared by distillation). All the procedures were carried out in the dark. The crystals were used as a Mössbauer absorber against a ^{57}Co(Pt) source moving in a constant acceleration mode at room temperature.

A typical spectrum is shown in Fig. 1. The spectrum is decomposed into two pairs of large quadrupole split lines ascribed to two kinds of iron(II) species and a pair of small quadrupole split lines due to iron(III) species. The facts

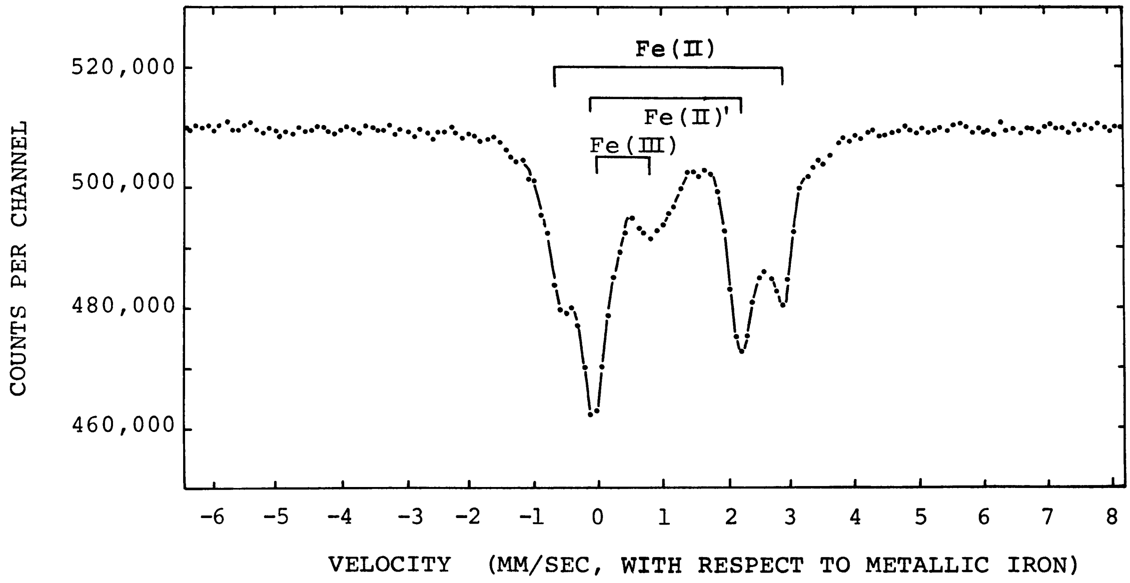

Fig. 1. The Mössbauer spectrum for iron thiocyanate at 78°K prepared from iron(Ⅲ) hydroxide and thiocyanic acid by following Schlesinger and Van Valkenburgh's method. I. S. [Fe(Ⅱ)]: 1.11 mm/sec, Q. S. [Fe(Ⅱ)]; 3.57 mm/sec; I. S. [Fe(Ⅱ)']: 1.06 mm/sec, Q. S. [Fe(Ⅱ)']: 2.35 mm/sec; I. S. [Fe(Ⅲ)]: 0.42 mm/sec, Q. S. [Fe(Ⅲ)]: 0.75 mm/sec.

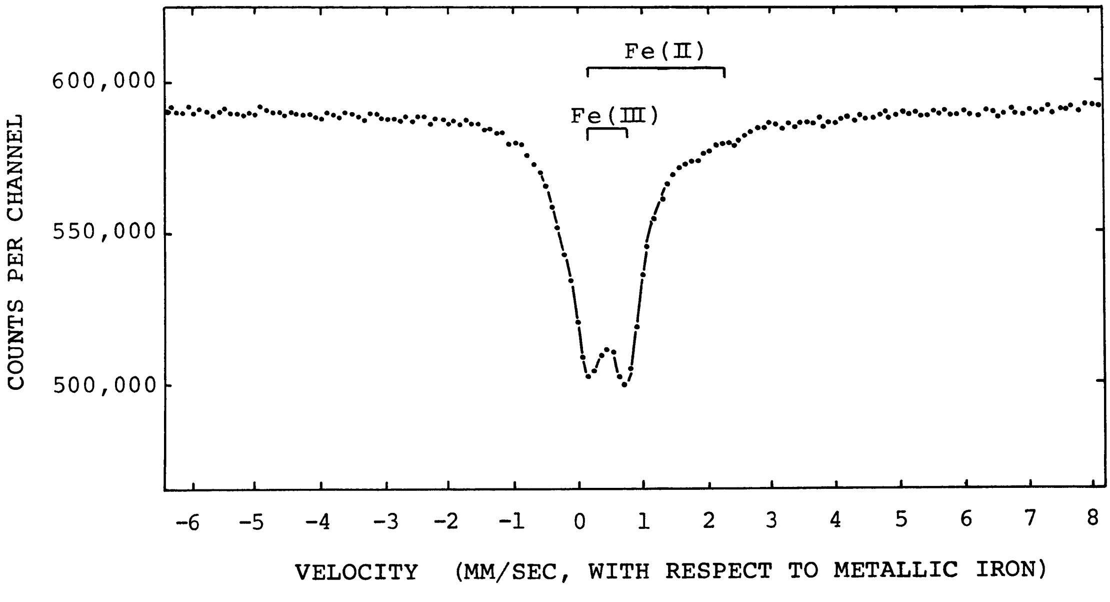

Fig. 2. The Mössbauer spectrum for iron thiocyanate at 78°K prepared from iron(Ⅲ) hydroxide and thiocyanic acid made by ion exchange method. I. S. [Fe(Ⅲ)]: 0.45 mm/sec, Q. S. [Fe(Ⅲ)]: 0.56 mm/sec.

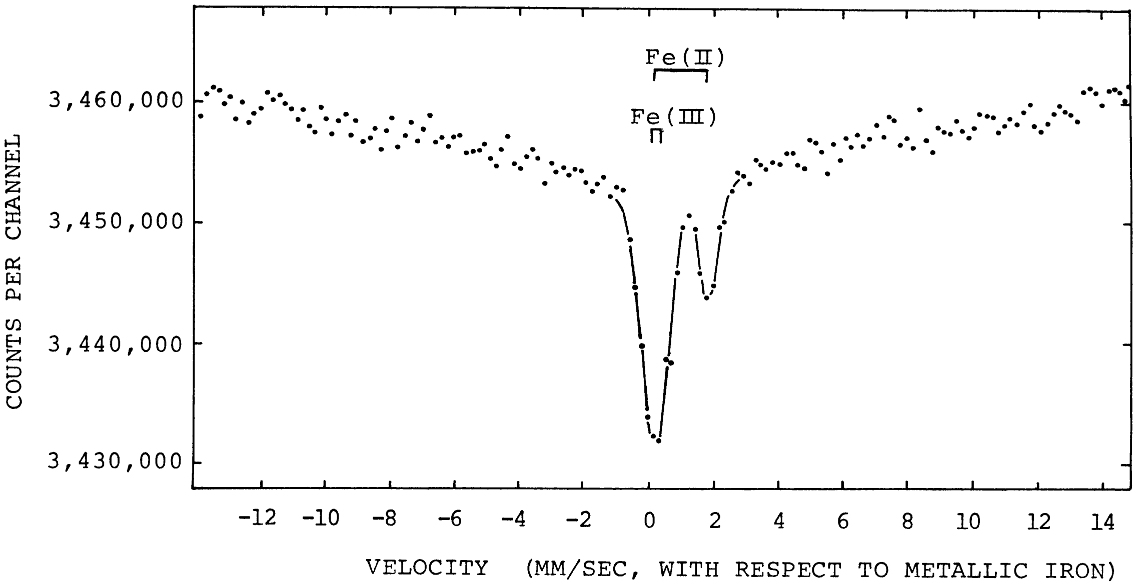

Fig. 3. The Mössbauer spectrum at 78°K for aqueous frozen solution of ^{57}Fe-iron(III) hydroxide dissolved into thiocyanic acid. I. S.[Fe(II)]: 1.23 mm/sec, Q. S.[Fe(II)]: ~1.5 mm/sec; I. S.[Fe(III)]: ~0.3 mm/sec.

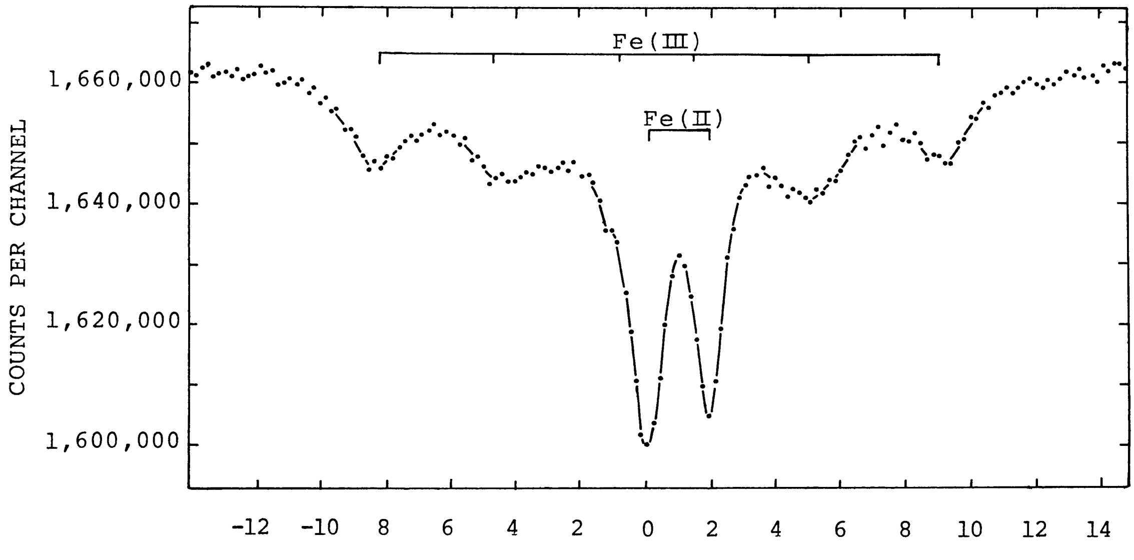

Fig. 4. The Mössbauer spectrum at 78°K for frozen ethereal phase extracted from aqueous solution of ^{57}Fe-iron thiocyanate. I. S.[Fe(II)]: 1.20 mm/sec, Q.S.[Fe(II)]: 1.80 mm/sec; I. S. [Fe(III)]: 0.30 mm/sec, I. F. [Fe(III)]: ~550 kOe.

support the results of Mitchell and Macdonald where most of iron were found in the divalent state based on the redox titration.

In order to improve the method of preparation of iron(III) thiocyanate, we used thiocyanic acid made by using a cation exchanger column by following the method described by Fujimoto,[3] instead of the distillation method. Iron(III) hydroxide was dissolved into the solution of thiocyanic acid, and ethereal extracts were evaporated in a vacuum desiccator in the dark. Fig. 2 shows a spectrum of the product. It may be found that the reduction of iron(III) is largely suppressed although there still remain small peaks of iron(II) species. Almost the same spectrum as that of Fig. 2 was observed for the crystals kept in a desiccator at room temperature for two months. This indicates that practically no reduction occurs after crystallization. Gravimetric determinations of total iron and titrimetric determinations of thiocyanate on the samples prepared in this method gave 0.33_8 as the ratio of Fe/SCN, which approach the theoretical value, 0.318.

To elucidate in which step of the preparation of this compound occurs the reduction, we measured Mössbauer spectra of aqueous solution and ethereal extracts prepared using thiocyanic acid made by ion exchange method and ^{57}Fe-enriched (ca. 90%) iron(III) hydroxide. The solutions were frozen at liquid nitrogen temperature in a thin (0.5 mm thick) liquid sample cell with Mylar windows. As seen in Fig. 3, aqueous solution shows the presence of iron(II) species. The ethereal extracts obtained from the aqueous solution shows the presence of only iron(III) species when measured soon after extraction. The ethereal extracts were further evaporated and used for the Mössbauer measurement in frozen solution. The spectrum shows an increasing peak component due to iron(II) species as seen in Fig. 4. The magnetic splitting due to an increased relaxation time caused by homogeneous dispersion is also clearly illustrated. The magnetic split lines are assigned to iron(III) species from internal field and isomer shift. The quadrupole split lines are ascribed to iron(II) species. The results indicate that some oxidation-reduction process was taking place both in aqueous and ethereal phases even in the dark.

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