Electronic States of Cobalt Iron Cyanides Studied by ^{57}Fe Mössbauer Spectroscopy

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The electronic states of cobalt iron cyanides were observed using ^{57}Fe Mössbauer. It was revealed that Prussian blue analogs $Co_{1.5}[Fe(CN)_6]6H_2O$ and $K_{0.5}Co_{1.25}[Fe(CN)_6]3.6H_2O$ have Fe^{III}(low spin) and Fe^{II}(low spin), respectively, at both room temperature and 4 K. In $Co_{1.5}[Fe(CN)_6]6H_2O$, a magnetic hyperfine interaction was observed at low temperature. Moreover, the Mössbauer spectra provided clear evidence for an internal electron transfer from Fe^{II} to Co^{III} in $K_{0.5}Co_{1.25}[Fe(CN)_6]3.6H_2O$ by red light illumination at low temperature.

The design of molecule-based compounds exhibiting spontaneous magnetization below a critical temperature (T_c) has been attracting increasing attention.[1-12] One of the challenging issues in this field is to synthesize a high T_c compound. Recently some spectacular results, including room temperature magnets, have been reported.[7,8] Our objective is the production of magnets with magnetic properties that can be controlled by external stimuli. One of the examples of such materials is a photochemically tunable cobalt iron cyanide.[4] The magnetic properties of this compound can be changed from paramagnetic to magnetic by visible light illumination. However, the magnetic properties vary depending on the preparation conditions. When the concentrations of both $K_3Fe(CN)_6$ and $CoCl_2$ are increased, the stoichiometric ratio K/Fe tends to increase and the ratio Co/Fe tends to decrease. This causes difficulties in clarifying the properties and mechanisms of the photoeffects.

Mössbauer spectroscopy is a powerful tool for diagnosing the electronic state, structure and reactions of a single type of atom or molecule.[13-17] In this work, the ^{57}Fe Mössbauer technique was applied to directly determine the oxidation state of Fe in the cobalt iron cyanide compounds. Moreover, we could obtain information about the spin state of iron and the magnetic properties before and after illumination and at various temperatures.

The reaction of $K_3Fe(CN)_6$ and $CoCl_2$ produces a precipitate of the cobalt iron cyanide. The stoichiometry depends on the preparation conditions. The compound obtained by mixing an aqueous solution of 1 mmol dm^{-3} $K_3Fe(CN)_6$ with an aqueous solution of 1 mmol dm^{-3} $CoCl_2$ has the formula $Co_{1.5}[Fe(CN)_6]6H_2O$, hereafter designated as compound 1. When the concentration of each aqueous solution was increased to 1 mol dm^{-3}, the stoichiometry of the precipitate was $K_{0.5}Co_{1.25}[Fe(CN)_6]3.6H_2O$, hereafter designated as compound 2. Magnetic properties were investigated with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-5S). An Hg-Xe lamp was used as the light source. The sample was illuminated at 5 K with the filtered red light (660 nm, 50 nm half width, 3.5 mW/cm^2). FT-IR spectra were measured with a Model 8900 h FT-IR (JASCO). The Mössbauer spectra were measured using a Wissel MVT-1000 Mössbauer spectrometer with a ^{57}Co/Rh source in the transmission mode. In order to enhance the Mössbauer spectra, some of the samples were enriched with ^{57}Fe. The measurements at low temperature were performed with a closed-cycle helium refrigerator (Iwatani Co.Ltd.) or liquid helium cryostat.

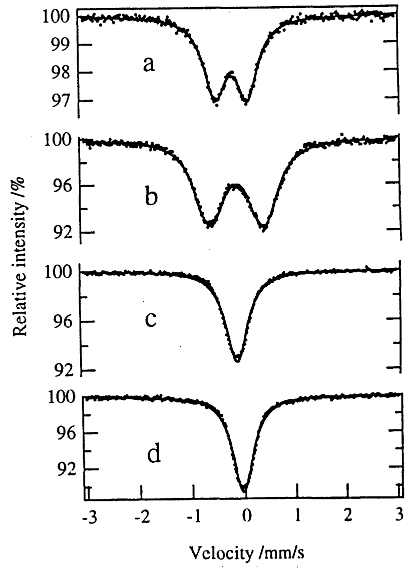

Figure 1. Mössbauer spectra of cobalt-iron cyanide.
a $Co_{1.5}[Fe(CN)_6]6H_2O$ at 293 K.
b $Co_{1.5}[Fe(CN)_6]6H_2O$ at 4 K.
c $K_{0.5}Co_{1.25}[Fe(CN)_6]3.6H_2O$ at 293 K.
d $K_{0.5}Co_{1.25}[Fe(CN)_6]3.6H_2O$ at 4 K.

The powder x-ray diffraction pattern was consistent with a face-centered cubic structure. The infrared (IR) spectra in the region from 2000 cm^{-1} to 2200 cm^{-1} for the two compounds differed from each other. Compound 1 has a strong peak around 2160 cm^{-1} and very weak peaks around 2115 cm^{-1} and 2095 cm^{-1}. On the other hand, compound 2 has a strong peak around 2115 cm^{-1} and a shoulder around 2160 cm^{-1}.

The Mössbauer spectrum at 293 K of compound 1 has a doublet absorption peak (I.S. = -0.17 ± 0.01 mm/s, Q.S. = 0.61

± 0.01 mm/s), which can be assigned to Fe^{III} (low spin)(Figure 1a). This Mössbauer spectrum and charge analysis shows the oxidation states to be $Co^{II}_{1.5}[Fe^{III}(CN)_6]6H_2O$. The IR peak observed about 2160 cm^{-1} is, therefore, due to CN stretching in the Fe^{III}-CN-Co^{II} structure.

Compound 2 at 293 K, on the other hand, has a singlet absorption peak (I.S. = -0.08 ± 0.01 mm/s), which is ascribable to Fe^{II} (low spin)(Figure 1c). This indicates that the oxidation state of compound 2 can be expressed by $K_{0.5}Co^{II}_{0.25}Co^{III}[Fe^{II}(CN)_6]3.6H_2O$. The IR peak observed at about 2115 cm^{-1} is due to CN stretching in the Fe^{II}-CN-Co^{III} structure.

The Mössbauer spectrum at 4 K of compound 2 exhibited almost the same absorption peak as that at room temperature (Figure 1d). On the other hand, the spectrum at 4 K of compound 1 has a signal with wider half-width and greater asymmetry compared with the room temperature one (Figure 1b), suggesting that it can be attributed to the overlapping of at least two slightly differing spectra.[17] Although the new species has not been assigned yet, it seems that the wider half-width peak contains a magnetically relaxed species.

The field-cooled magnetization (FCM) versus temperature plots at H = 5 G of compound 1 displayed an abrupt break at T_c = 16 K. The magnetization value was about 1000 $cm^3mol^{-1}G$ at 5K. Although compound 2 also has a magnetic phase transition at around 15 K, the magnetization value is smaller (ca. 500 $cm^3mol^{-1}G$), because it contains a large number of Fe^{II}(low spin) and Co^{III} (low spin), which are diamagnetic components.

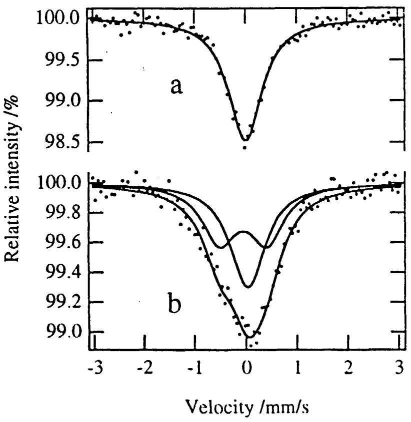

Figure 2 . Mössbauer spectra of $K_{0.5}Co_{1.25}[Fe(CN)_6]3.6H_2O$.
a Before illumination at 25 K.
b Under illumination at 25 K.

The illumination was performed at 5 K in the SQUID magnetometer. Compound 1 did not respond to the filtered red light. On the other hand, the magnetization of compound 2 was substantially enhanced, as was reported previously.[4] The magnetization value was changed from 500 $cm^3mol^{-1}G$ to 1100 $cm^3mol^{-1}G$ at 5 K.[4] Furthermore, T_c after the illumination increased to about 19 K, which is higher than the T_c of the material before illumination (15K).[4] Mössbauer spectra were measured before and during illumination at 25 K. Figure 2a shows the Mössbauer spectra of compound 2 before illumination at 25 K. The spectra show a singlet absorption peak (I.S.=0.00 ± 0.01 mm/s), indicating the presence of only Fe^{II} (low spin). In contrast, a doublet absorption peak (I.S. = -0.06 ± 0.01 mm/s, Q.S. = 0.93 ± 0.01 mm/s) appeared in the Mössbauer spectra measured under illumination (0.1 W/cm^2, 20 h) (Figure 2b). The spectra indicate that Fe^{II} (low spin) is oxidized to Fe^{III} (low spin) during illumination. This Mössbauer parameter for Fe^{III} (low spin) is consistent with the result in the case of compound 1 at room temperature, which was described before. A similar spectrum could be measuered after illumination, since the Fe^{III}-CN-Co^{II} species thus formed is stable at 25 K for at least 2 days. That is, the electronic states of Fe and Co changed from Fe^{II}-CN-Co^{III} to Fe^{III}-CN-Co^{II}. This is consistent with IR results reported in our previous papers.[4,12]

In summary, we could observe the electronic states of the Prussian blue analog, cobalt iron cyanide, directly by means of Mössbauer. It was found that $Co_{1.5}[Fe(CN)_6]6H_2O$ and $K_{0.5}Co_{1.25}[Fe(CN)_6]3.6H_2O$ consist of Fe^{III}-CN-Co^{II} and Fe^{II}-CN-Co^{III}, respectively, and that the electron in $K_{0.5}Co_{1.25}[Fe(CN)_6]3.6H_2O$ is transfered from Fe^{II} to Co^{III} to produce Fe^{III}-CN-Co^{II} during illumination with red light.

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