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Iron(III) Site Multiplicities in $Fe_2F_5\cdot 7H_2O$

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^{57}Fe Mössbauer spectra of $Fe_2F_5\cdot 7H_2O$ at 298 K are interpreted in terms of two Fe^{3+} species. The area fractions of 0.20 and 0.30 for the two sites are in agreement with the available structural data. The values of δ and ΔE_Q of the two Fe^{3+} patterns are 0.462 mm s^{-1} and 0.414 mm s^{-1}, respectively, for the more intense pattern and 0.459 mm s^{-1} and 0.817 mm s^{-1}, respectively, for the less intense pattern. The Fe^{3+} coordination polyhedra are either (1) isolated but have disordered ligand environments, (2) not isolated, or (3) not isolated and possess disordered ligand environments.

Introduction

In a recent communication concerning local structures in some selected iron fluorides, it was noted that the ^{57}Fe Mössbauer spectrum of $Fe_2F_5\cdot 7H_2O$ at 298 K could not be accounted for in terms of a single Fe^{3+} crystal chemical species.[1] The presence of more than one Fe^{3+} pattern in the 298 K spectrum had been suggested by one group of investigators,[2,3] but the parameters of the two spectral components were not reported. The ^{57}Fe spectrum of the magnetically ordered compound at 1.3 K clearly demonstrated the presence of two Fe^{3+} patterns.[4] Both the isomer shifts and magnetic hyperfine fields of the two Fe^{3+} patterns were significantly different, ruling out the possibility of a splitting of the spectrum of equivalent Fe^{3+} sites as a result of different relative orientations of the electric field gradient tensor and magnetic hyperfine field at otherwise equivalent positions. In our earlier report, the two Fe^{3+} patterns at 298 K were reported to have similar electric quadrupole splittings and rather different isomer shifts, contrary to the low-temperature[4] results. Further investigations of the spectra have shown another set of parameters to be equally consistent with the data and to be chemically and structurally more reasonable. One of our purposes here is to report these more acceptable results.

Furthermore, the initial X-ray diffraction characterization of $Fe_2Fe_2\cdot 7H_2O$, which indicated five $Fe_2Fe_5\cdot 7H_2O$ formula units per unit cell,[5] poses some difficulties for the 1.3 K spectrum.[1,4] The 1.3 K spectrum indicates the existence of two Fe^{3+} patterns with relative intensities of 2:2.6; if there are five $Fe_2F_5\cdot 7H_2O$ formula units per cell and one assumes no disorder, ratios of 2:3 and 1:4 are the expected ones for the relative areas of the two Fe^{3+} patterns. For temperatures as low as 1.3 K, it is not expected that the integrated intensities of the two Fe^{3+} patterns would deviate significantly from the site occupancy ratios, and the observed ratio of 2:2.6 deviates too far from 2:3 to be consistent with the available structural data. On the other hand, there is no a priori empirical basis for expecting substantial deviations at 298 K of the integrated intensities of the spectral components of $Fe_2F_5\cdot 7H_2O$ from the relative frequency of occurrence of the occupied Fe lattice sites, and information on the site occupancy can also be gained from the 298 K Mössbauer spectrum. For example, the previously reported ratios of the Fe^{3+} and Fe^{2+} patterns in the 298 K Mössbauer spectrum of $Fe_2F_5\cdot 2H_2O$ are in excellent agreement with the site occupancies.[6] While the relative frequency of occurrence of the two Fe^{3+} patterns of $Fe_2F_5\cdot 7H_2O$ of 2:3.12[1] was consistent with the earlier X-ray data, there are the above-mentioned concerns regarding the relative isomer shifts of the two patterns which warrant a confirmation of the area ratios for crystal chemically more acceptable hyperfine parameters. We have, therefore, repeated the synthesis and 298 K ^{57}Fe Mössbauer measurements on $Fe_2F_5\cdot 7H_2O$ in an attempt to resolve these ambiguities.

Knowledge of the number of inequivalent Fe^{3+} sites in $Fe_2F_5\cdot 7H_2O$ is critical to understanding the dehydration reaction (eq 1) leading to $Fe_2F_5\cdot 2H_2O$ and the associated change in color from pale yellow to intense red.

$$\underset{\text{yellow}}{Fe_2F_5\cdot 7H_2O} \xrightarrow{\Delta} \underset{\text{red}}{Fe_2F_5\cdot 2H_2O} + 5H_2O(g) \qquad (1)$$

It had been supposed that the dehydration reaction corresponded to a simple clustering and condensation of coordination polyhedra, but there is only one Fe^{3+} site in $Fe_2F_5\cdot 2H_2O$, and associated with the dehydration is a reduction in the number of distinct Fe^{3+} species. Dehydration occasions some changes in the long-range crystal/chemical interactions in $Fe_2Fe_5\cdot 7H_2O$ which would have important implications in understanding the crystal chemical basis for the color changes.

Experimental Section

$Fe_2Fe_5\cdot 7H_2O$ was synthesized according to the method of Brauer and Eichner.[5] A portion of the initial batch of crystals was dissolved in and recrystallized from a dilute HF aqueous solution. Both were verified to be single phase by means of powder X-ray diffraction.

The Mössbauer spectra were obtained with a constant acceleration, electromechanical velocity drive employing a sawtooth velocity waveform. The spectrum was stored in 512 channels of a 1024 channel multichannel analyzer operated in the multiscaling mode. Disodium pentacyanonitrosylferrate(III) dihydrate, $Na_2Fe(CN)_5NO\cdot 2H_2O$, and Fe metal foil were used as calibrants. The source was a 25-mCi ^{57}Co/Pd foil, and both the source and absorber were at a temperature of 298 K. The absorber consisted of 15 mg of finely ground powder which was held under compression in a 12 mm diameter Lucite cup by means of a tightly fitting Lucite cover. The parameters reported were obtained from a least-squares fitting process assuming Lorentzian line shapes; the isomer shifts are reported relative to Fe metal.

Results

The spectra for the initial crystallization product and the recrystallized sample of $Fe_2F_5\cdot 7H_2O$ are shown in Figures 1 and 2. Two fits to the spectra are presented: one for a fit of two quadrupole (Figures 1A and 2A), e.g., one Fe^{3+} and one Fe^{2+} pattern and one for a fit of three quadrupole doublets (Figures 1B and 2B), e.g., two Fe^{3+} and one Fe^{2+} patterns. The superiority of the fit of three patterns is evident both qualitatively and quantitatively (cf. Table I). It is to be noted that the deviations of the two quadrupole doublets fits from the experimental data are located in the region of maximum absorption amplitude and changes in line shape from Lorentzian to Gaussian are not capable of accounting for the inadequacy of the two quadrupole doublet fits.

The fit of the three quadrupole doublets is, however, highly degenerate. Two interpretations of the line positions are consistent with the data. One assignment is reported in Table

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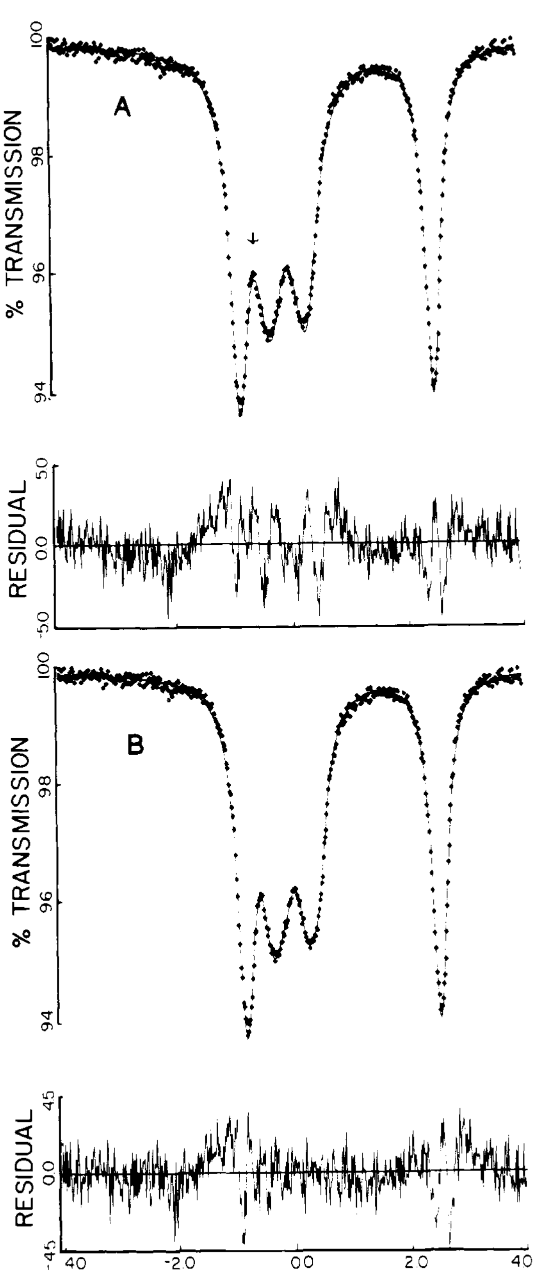

Figure 1. (A) Fit of two quadrupole doublets (solid line), one Fe^{2+} and one Fe^{3+} doublet, to the 298 K ^{57}Fe Mössbauer spectrum (points) of the initial crystallization product of $Fe_2F_5 \cdot 7H_2O$. (B) Fit of three quadrupole doublets (solid line), one Fe^{2+} and two Fe^{3+} doublets to the 298 K ^{57}Fe Mössbauer spectrum (points) of the initial crystallization product. The overestimate of the intensities of the Fe^{3+} pattern indicated by the arrows and the appreciable structure in the residual of (A) are noteworthy. The residual is plotted in units of $[(N_{\text{exptl}} - N_{\text{calcd}})/N_{\text{exptl}}^{1/2}]_i$, where N_{exptl} is the number of experimental counts at velocity i and N_{calcd} is the calculated number of counts at velocity i for the model used in the fitting.

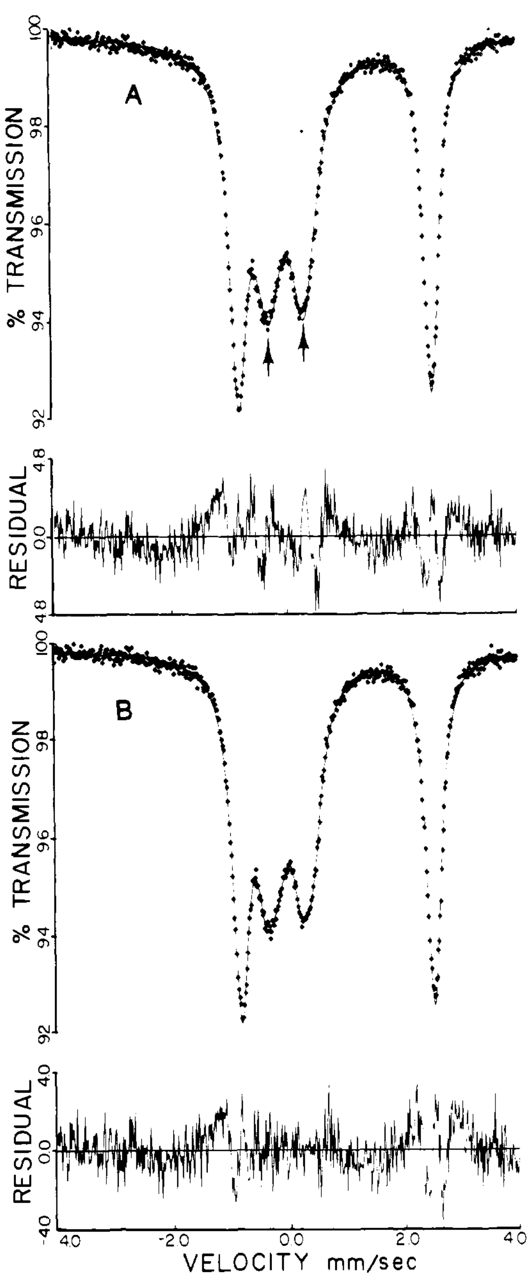

Figure 2. Same as in Figure 1 except that the spectrum is for the recrystallized sample. The lack of any qualitative differences between the appearance of the two spectra in Figures 1 and 2 is obvious, and the parameters corresponding to the envelope (solid line) are within the experimental error, virtually identical (cf. Table I).

I; this is the preferred interpretation. The other set of parameters is similar to those published previously[1] in which the two patterns have nearly equal ΔE_Q values of 0.590 and 0.594 mm s^{-1} but very different isomer shifts of 0.553 and 0.349 mm s^{-1}, respectively. This latter set of parameters can be eliminated on empirical grounds: no Fe^{3+} halides have been observed to have isomer shifts as small as 0.35 mm s^{-1} at 298 K.[7] The relative isomer shifts for the two Fe^{3+} patterns according to the parameters presented in Table I are in good agreement with those obtained at 1.3 K. The relative areas of the three patterns are also presented in Table I.

Discussion

There can be little question as to the existence of at least two Fe^{3+} crystal chemical species in $Fe_2F_5 \cdot 7H_2O$. The question of the large difference in the isomer shifts for the two Fe^{3+} patterns has been resolved satisfactorily and found to result from alternative assignments of the line positions to the two patterns. The similarity of the isomer shifts suggests that both Fe^{3+} environments are similar and perhaps octahedral. The substantially different quadrupole splittings are indicative either of different ligand configurations, different distortions of the octahedra, or a combination of these two factors at the two Fe^{3+} sites.

The relative intensities of the two patterns are in good agreement with the gross structural data currently available.

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Table I. ^{57}Fe Mössbauer Parameters of $Fe_2F_5 \cdot 7H_2O$ at 298 K

sample		ΔE_Q, mm s^{-1}	δ,[a] mm s^{-1}	Γ, mm s^{-1}	rel integrated intens
initial[b] crystallization product (χ^2 = 539, MISFIT = 0.06%)	Fe^{2+}	3.322 ± 0.001	1.228 ± 0.001	0.340 ± 0.002	5 ± 0.2
	$Fe^{3+}{}_I$	0.414 ± 0.004	0.462 ± 0.003	0.473 ± 0.003	3.05 ± 0.5
	$Fe^{3+}{}_{II}$	0.817 ± 0.003	0.459 ± 0.002	0.37 ± 0.01	2.24 ± 0.5
recrystallized[c] sample (χ^2 = 703, MISFIT = 0.05%)	Fe^{2+}	3.319 ± 0.001	1.291 ± 0.001	0.340 ± 0.001	5 ± 0.1
	$Fe^{3+}{}_I$	0.431 ± 0.030	0.462 ± 0.002	0.50 ± 0.02	3.15 ± 0.2
	$Fe^{3+}{}_{II}$	0.83 ± 0.02	0.465 ± 0.003	0.37 ± 0.03	2.05 ± 0.2

[a] Relative to iron metal. [b] The off-resonant count = 2.4 × 10^6. For a two quadrupole doublet fit χ^2 = 1249 and MISFIT = 0.1%. [c] The off-resonant count = 1.2 × 10^6. For a two quadrupole doublet fit χ^2 = 953 and MISFIT = 0.1%.

That is to say, if there are 5 formula units per unit cell, then the two Fe^{3+} patterns are expected to occur with relative intensities of 3:2 or 1:4. It is clear from the data that the relative frequencies of the two sites are 3:2. The broad line widths of the more intense Fe^{3+} component could be indicative of local crystallographic disorder. This possibility makes an attempt to arrive at some tentative conclusion as to the nature of the coordination of the two Fe^{3+} sites less straightforward. The average Fe^{3+} coordination is $[FeF_5(H_2O)]^2$ which must therefore be divided into two crystal chemical species with a relative frequency of occurrence of 3:2. Of course, there could be just one combination of ligands for both species, i.e., five F^- and one H_2O. It is noteworthy that at 77 K the Mössbauer parameters of $K_2[FeF_5(H_2O)]$,[8] (ΔE_Q = 0.60 mm s^{-1} and δ_{IS} = 0.43 mm s^{-1}) in which there are isolated $[Fe(H_2O)F_5]^{2-}$ octahedra are intermediate to those of the two Fe^{3+} patterns in $Fe_2F_5 \cdot 7H_2O$; the difference in the temperatures at which the measurements have been made preclude a more critical comparison. The Mössbauer parameters of the Fe^{3+} patterns in $Fe_2F_5 \cdot 7H_2O$ and β-$FeF_3 \cdot 3H_2O$ are quite similar. It is significant, then, that the structure of β-$FeF_3 \cdot 3H_2O$ consists of infinite chains of vertex sharing (via a fluoride bridge) *trans*-$[Fe(H_2O)_2F_4]^-$ octahedra for which the equatorial positions are occupied in a disordered fashion by two water molecules and two fluoride ions.[9] Such a structure cannot be transferred simply to the Fe^{3+} environments in $Fe_2F_5 \cdot 7H_2O$ if the $[Fe(H_2O)F_5]^{2-}$ stoichiometry is correct. The line widths of the Fe^{3+} patterns in $Fe_2F_5 \cdot 7H_2O$ are also significantly larger than those in β-$FeF_3 \cdot 3H_2O$. Under any circumstance, it is not possible to arrive at two unique ligand groupings for isolated octahedra in the required 3:2 ratio which would give an average $[Fe(H_2O)F_5]^{2-}$ coordination. The Fe^{3+} octahedra are either disordered, share-polyhedral elements or are both disordered and share-polyhedral elements. Even though $K_2FeF_5(H_2O)$ contains isolated $[FeF_5(H_2O)]^{2-}$ octahedra, other pentafluoride hydrates, e.g., $K_2AlF_5(H_2O)$ and $K_2MnF_5(H_2O)$ contain infinite chains of vertex sharing MnF_6 octahedra. Therefore, the tentative conclusion arrived at in this investigation regarding the probable qualitative structural features of the Fe^{3+} coordination is not without precedence and the postulation of completely isolated and well-defined coordination polyhedra for all iron species in $Fe_2F_5 \cdot 7H_2O$ warrants further investigation by direct structural methods.

The complexity of the dehydration processes in $Fe_2F_5 \cdot 7H_2O$ and $Fe_2F_5 \cdot 2H_2O$ and the variable behavior of $Fe_2F_5 \cdot 2H_2O$ produced by different means[12] might be better understood not only in terms of differences in the changes of the ligation at structurally and chemically inequivalent Fe^{2+} and Fe^{3+} ions but also in terms of different processes at the structurally inequivalent Fe^{3+} sites, which must have available appropriate kinetic routes for the removal of the site inequivalence during the dehydration process.

Registry No. Fe_2F_5, 12061-94-8.

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Kinetics and Mechanism of the Chromium(III)–Periodate Reaction

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The kinetics of oxidation of chromium(III) by periodate showed an unusual second-order dependence on chromium(III). Over the pH range 1.88–3.03 the kinetics obeyed the rate law $d[Cr(VI)]/2dt = a[Cr(III)]_T^2[I(VII)]_T/(b[H^+]^2 + [H^+])$. The values of a and b were determined as 12.8 ± 2.2 M^{-1} s^{-1} and 770 ± 26 M^{-1}, respectively, at I = 0.25 M and T = 25 °C. An inner-sphere mechanism in which two chromium(III) ions are bridged to I(VII) is proposed. The routes that may lead to the formation of dichromium(III)–iodine(VII) species are outlined. A single-step two one-electron transfer is suggested within the bridged species. An alternative mechanism may operate by inner- and outer-sphere mechanisms in which concurrent electron transfer occurs within $[Cr–(OH)–I(VII)]^+$ and from the Cr^{3+} ion.

Introduction

Chromium(III) is reported to catalyze oxidation by periodate.[1,2] Catalysis is believed to be caused by chromium(VI) produced by a relatively rapid oxidation process of chromium(III) by periodate.[2] This observation seems to contradict previous reports that an inner-sphere mechanism is the preferred, if not the only, path for periodate oxidation of metal complexes.[3-7] This conclusion is based on the observations

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