NOTE

A Mössbauer Study of Mixed Valence Iron Fluorides†

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Mössbauer spectroscopy is a useful technique to obtain discrete information about different oxidation states in mixed valence compounds. We have applied this technique to study the change in structural environment of ferric and ferrous iron in the course of the dehydration process in mixed valence iron fluorides. In the present article are reported our preliminary results on the Mössbauer spectra of two hydrates of the mixed valence iron fluoride, $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$. Mössbauer parameters were reported only on the former compound¹⁾, whereas no Mössbauer study has been made on the latter compound.

$\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$ was prepared by modifying the Brauer's method²⁾. After iron powder was heated in (1:1) HF for several hours at 80°C, the yellowish brown supernatant solution was separated from the mixture and oxidized by bubbling air for about 2 days at room temperature. Yellowish brown crystals of $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$ were then separated from the solution^{*1)}. Found: Fe^{2+} , 16.8; Fe^{3+} , 16.8; F, 28.3%. Calcd. for $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$: Fe^{2+} , 16.8; Fe^{3+} , 16.8; F, 28.6%. Dark reddish brown crystals of $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$ ^{*2)} were obtained by heating ground crystals of the heptahydrate for about 2 hours at 100°C in a dry nitrogen stream. Found: Fe^{2+} , 23.0; Fe^{3+} , 23.2; F, 37.8%. Calcd. for $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$: Fe^{2+} , 23.0; Fe^{3+} , 23.0; F, 39.1%.

The Mössbauer absorption spectra of these compounds were measured by using a Hitachi AA-40 Mössbauer spectrometer with a ^{57}Co source diffused into Cu foil. Typical spectra are shown in Fig. 1 and Mössbauer parameters are summarized in Table 1.

Fig. 1 Mössbauer spectra of (a) $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$ at room temperature; (b) $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$ at room temperature; and (c) $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$ at 80K.

The Mössbauer spectrum of $\text{Fe}_2\text{F}_5 \cdot 7\text{H}_2\text{O}$ (Fig. 1a) is composed of two sets of quadrupole doublets corresponding to Fe^{2+} and Fe^{3+} ions, respectively. Their Mössbauer parameters at room temperature are in agreement with the values reported¹⁾. Since the Fe^{3+} peaks appear to be fairly broad, there could be different Fe^{3+} sites as sug-

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*1) On prolonged bubbling of air, these crystals were further oxidized and dissolved again as FeF_3 .

*2) Based on our chemical analyses and TGA data, these crystals were assumed to be $\text{Fe}_2\text{F}_5 \cdot 2\text{H}_2\text{O}$, rather than the trihydrate reported in the literature²⁾.

Table 1 Mössbauer parameters of mixed valence iron fluorides

Temperature (K)	Isomer shift* (mm/sec)	Quadrupole splitting (mm/sec)
(a) $\text{Fe}_2\text{F}_3 \cdot 7\text{H}_2\text{O}$	(± 0.02)	(± 0.02)
80 { Fe^{2+} Fe^{3+}	1.41 0.55	3.55 0.62
295 { Fe^{2+} Fe^{3+}	1.24 0.41	3.31 0.61
(b) $\text{Fe}_2\text{F}_3 \cdot 2\text{H}_2\text{O}$		
80 { Fe^{2+} Fe^{3+}	1.45 0.56	3.31 0.59
195 { Fe^{2+} Fe^{3+}	1.37 0.50	2.93 0.59
295 { Fe^{2+} Fe^{3+}	1.32 0.47	2.57 0.56
380 { Fe^{2+} Fe^{3+}	1.20 0.44	2.28 0.49

* With respect to the centroid of the spectrum of iron foil at room temperature.

gested in the literature¹⁾.

The Mössbauer spectra of $\text{Fe}_2\text{F}_3 \cdot 2\text{H}_2\text{O}$ (Fig. 1b and 1c) also consists of two sets of doublets corresponding to Fe^{2+} and Fe^{3+} ,

respectively. Since discrete spectra were found for Fe^{2+} and Fe^{3+} , rapid electron exchange is unlikely to take place between Fe^{2+} and Fe^{3+} in this compound. As seen in Table 1, Mössbauer parameters of $\text{Fe}_2\text{F}_3 \cdot 2\text{H}_2\text{O}$ differ from those of $\text{Fe}_2\text{F}_3 \cdot 7\text{H}_2\text{O}$ as the result of the structural change in the vicinity of iron caused by removal of water. The quadrupole splitting for Fe^{2+} in $\text{Fe}_2\text{F}_3 \cdot 2\text{H}_2\text{O}$ showed greater dependence on temperature over the range from 80 to 380 K. Moreover, it is worth mentioning that the widths of Fe^{3+} peaks in $\text{Fe}_2\text{F}_3 \cdot 2\text{H}_2\text{O}$ are narrower than in $\text{Fe}_2\text{F}_3 \cdot 7\text{H}_2\text{O}$.

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