A Mössbauer Study of Graphite Intercalated with Iron(III) Chloride and Aluminum Chloride

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The Mössbauer spectra of graphite–$FeCl_3$ and graphite–$FeCl_3$–$AlCl_3$ compounds with varying $FeCl_3/AlCl_3$ ratios were measured. At 298 K, the isomer shift of the Fe^{3+} peak of $FeCl_3$ intercalated in the graphite–$FeCl_3$ compounds was larger than that of pure anhydrous $FeCl_3$, and two sets of Fe^{2+} quadrupole doublets appeared in the spectra of the graphite–$FeCl_3$–$AlCl_3$ compounds with $FeCl_3/AlCl_3$ ratios of approximately one or less. These results may be accounted for in terms of the transfer of graphite π-electrons to intercalated $FeCl_3$.

In 1967 one of the present authors (T.T.) investigated the Mössbauer spectra of the graphite–$FeCl_3$ intercalation compounds with a view to obtaining a clue as to the nature of the bonding in such systems.[1] The isomer shift of the intercalated iron(III) chloride was found to be larger than that of pure anhydrous iron(III) chloride, indicating the possibility of the transfer of graphite π-electrons to the intercalated molecules. Similar results have been reported thereafter from several groups of workers for the Mössbauer spectra of graphite intercalated with iron chloride, or iron chloride and aluminum chloride.[2–9] In contrast to the previous report[3] that the spectra of the graphite–$FeCl_3$–$AlCl_3$ compounds were essentially the same as those of the graphite–$FeCl_3$ compound, we have recently observed the presence of quadrupole doublets of Fe^{2+} in the Mössbauer spectra of the graphite–$FeCl_3$–$AlCl_3$ compounds with $FeCl_3/AlCl_3$ ratios of about one or less.[9]

The object of the present article is to report the detailed results of the Mössbauer spectroscopic study on the graphite–$FeCl_3$–$AlCl_3$ compounds with varying $FeCl_3/AlCl_3$ ratio so as to elucidate the chemical states of iron chloride intercalated in such systems.

Experimental

Materials. A pulverized natural graphite (Spectroscopic Powder) purchased from Union Carbide Corp. was used for preparation of the intercalation compounds. The graphite-$FeCl_3$ compounds were obtained by procedures similar to those described in the literature.[10] Mixtures of weighed quantities of graphite and anhydrous iron(III) chloride were heated in sealed glass tubes between 230 and 350 °C. The products were freed from unreacted iron chloride by washing with hot 2 M HCl and then dried at 110 °C. The products were analyzed for their metal content by decomposition to oxides. The chlorine content was determined by neutron activation analysis. The analytical results of the intercalation compounds obtained under various heating conditions are summarized in Table 1.

The graphite–$FeCl_3$–$AlCl_3$ compounds were prepared by methods essentially similar to those reported in the literature.[11,12] Mixtures of graphite with anhydrous iron(III) chloride and aluminum chloride were heated in sealed glass tubes at temperatures between 210 and 300 °C, and excess metal chlorides were removed by washing with hot 2 M HCl. The analytical results of the products prepared under various conditions are also summarized in Table 1.

Mössbauer Spectroscopy. The Mössbauer spectra of the intercalation compounds were measured at 298 and 80 K by using a Hitachi AA-40 or a Shimadzu MEG-1A Mössbauer spectrometer with a ^{57}Co source diffused into copper foil. The isomer shifts are given as related to the centroid of the spectrum of iron foil at 298 K. The errors in isomer shifts and quadrupole splittings are generally of the order of 0.02—0.03 mm/s, except for the spectra subjected to larger uncertainties because of weak absorption intensities or the complexity of overlapping peaks.

Results and Discussion

Graphite–$FeCl_3$ Compounds. As a typical example of the graphite–$FeCl_3$ compounds, Mössbauer spectra of $C_{10}FeCl_3$ (compound II with 55.8 % $FeCl_3$) at 298 and 80 K are illustrated in Figs. 1a and 2a respectively. The spectrum at 298 K consists of a single absorption peak of Fe^{3+} with an isomer shift of 0.50 mm/s, which is obviously larger than that of pure anhydrous iron(III) chloride, $FeCl_3$ ($\delta = 0.42$ mm/s). This observation is in agreement with the results obtained previously,[1–8] and may indicate that the graphite π-electrons are transferred to the d-orbitals of iron in all iron(III) chloride molecules rather than in one quarter of the intercalated molecules as postulated by Dzurus and Hennig.[12,13] Such an electron transfer mechanism may be further confirmed by the reverse effect observed in boron nitride–$FeCl_3$ compounds:[14] the isomer shift of $FeCl_3$ intercalated in boron nitride was lower than that of pure anhydrous $FeCl_3$, revealing that an electron transfer from $FeCl_3$ to boron nitride layers probably takes place in the system. However, the isomer shift of $C_{10}FeCl_3$ at 80 K (0.54 mm/s) is very close to that of pure anhydrous $FeCl_3$ (0.52 mm/s). Hence, it is probable that the electron transfer from graphite to $FeCl_3$ is considerably attenuated at low temperatures.

The Mössbauer spectra of all the graphite–$FeCl_3$ preparations appear to be essentially similar; the isomer shift does not change significantly with the $FeCl_3$ content or with the heating temperature (Table 2). It is worth mentioning that only a very weak component of an Fe^{2+} doublet was observed in the spectrum of C_9FeCl_3 prepared by heating at 350 °C (compound III), whereas no iron(II) state was detected in the spectrum of $C_{10}FeCl_3$ reheated at 300 °C *in vacuo* (compound IV). On heating $C_{10}FeCl_3$ at 400 °C in vacuum or air, two sets of Fe^{2+} doublets arose in the spectrum, indicating the formation of $FeCl_2$ by decomposition.

Graphite–$FeCl_3$–$AlCl_3$ Compounds. The Mössbauer spectra of typical graphite–$FeCl_3$–$AlCl_3$ compounds at 298 and 80 K are represented in Figs. 1 and 2 respective-

TABLE 1. ANALYSES OF THE INTERCALATION COMPOUNDS PREPARED IN THIS WORK

Compound	Heating conditions	Analytical (%)			$FeCl_3/AlCl_3$ [a]	$Cl/(Fe+Al)$ [a]
		C	$FeCl_3$	$AlCl_3$		
Graphite-$FeCl_3$ compounds:						
I	230 °C, 4 h	56.6	43.4	—	—	3.01±0.05
II	250 °C, 4 h	44.2	55.8	—	—	3.05±0.07
III	350 °C, 4 h	39.6	60.4	—	—	
IV	II reheated 300 °C, 4 h	50.8	49.2	—	—	
Graphite-$FeCl_3$-$AlCl_3$ compounds:						
V	270 °C, 4 h	40.9	48.5	10.6	4	
VI	210 °C, 4 h	41.9	38.0	20.1	1.5	
VII	210 °C, 4 h	42.1	34.4	23.5	1.2	
VIII	220 °C, 4 h	64.2	20.1	15.7	1.0	
IX	300 °C, 6 h	61.7	14.3	24.0	0.5	
X	300 °C, 24 h	73.1	6.8	20.1	0.3	2.93±0.07
XI	230 °C, 4 h	82.6	4.9	12.5	0.3	2.99±0.02

a) Molar or atomic ratio.

TABLE 2. MÖSSBAUER PARAMETERS OF THE INTERCALATION COMPOUNDS PREPARED IN THIS WORK[a]

Compound	Temperature (K)	Fe^{2+}				Fe^{3+}
		Inner doublet		Outer doublet		
		δ	ΔE_Q	δ	ΔE_Q	δ
				(mm/s)		
Graphite-$FeCl_3$ compounds:						
I	298	—	—	—	—	0.49
II	298 80	— —	— —	— —	— —	0.50 0.54
III	298	—	—	—	—	0.50
IV	298	—	—	—	—	0.49
Graphite-$FeCl_3$-$AlCl_3$ compounds:						
V	298	—	—	—	—	0.50
VI	298	—	—	—	—	0.46
VII	298	—	—	—	—	0.47
VIII	298 80	1.11 1.23	0.86 1.05	(1.09) (1.24)	(1.76) (2.10)	0.45 0.52
IX	298 80	1.08 1.25	0.72 0.97	1.06 1.23	1.61 2.09	(0.45) (0.50)
X	298 80	1.05 1.20	0.78 1.03	1.12 1.21	1.49 2.05	(0.45) (0.50)
XI	80	1.18	0.96	1.19	1.91	(0.52)

a) Parameters given in parentheses involve rather large uncertainties (±0.05 mm/s) due to the weak absorption intensities of overlapping peaks.

ly. The Mössbauer spectra at 298 K of the graphite–$FeCl_3$–$AlCl_3$ compounds with $FeCl_3/AlCl_3$ ratios of 4—1.2 (compounds V to VII) were essentially similar to those of the graphite–$FeCl_3$ compounds composed of an Fe^{3+} singlet alone (Figs. 1b and 1c.) As the $FeCl_3/AlCl_3$ ratio was decreased to one, however, a weak Fe^{2+} quadrupole doublet appeared in addition to the Fe^{3+} peak (compound VIII, Fig. 1d). In the spectra of the compounds with $FeCl_3/AlCl_3$ ratios of 0.5 and 0.3 (compounds IX and X), a second Fe^{2+} doublet arose outside of the initial doublet, and the intensities of both doublets exceeded that of the Fe^{3+} peak (Figs. 1e and 1f). Hence we may presume that iron chloride molecules intercalated in the graphite–$FeCl_3$–$AlCl_3$ compounds with $FeCl_3/AlCl_3$ ratios of 0.3—0.5 exist predominantly in high-spin iron(II) states.

The Mössbauer spectra at 80 K of the intercalation compounds with $FeCl_3/AlCl_3$ ratios of 1—0.3 (compounds VIII to XI) similarly show the presence of the Fe^{2+} doublets. However, the Fe^{2+}/Fe^{3+} area ratio at 80 K becomes considerably smaller than that at 298 K; thus the percentage of the Fe^{2+} fraction tends to decrease with the decrease in temperature. Although the origin of such temperature dependence of the Fe^{2+}/Fe^{3+} area ratio cannot yet be explained without ambiguities, it is likely that the transfer of graphite π-electrons to

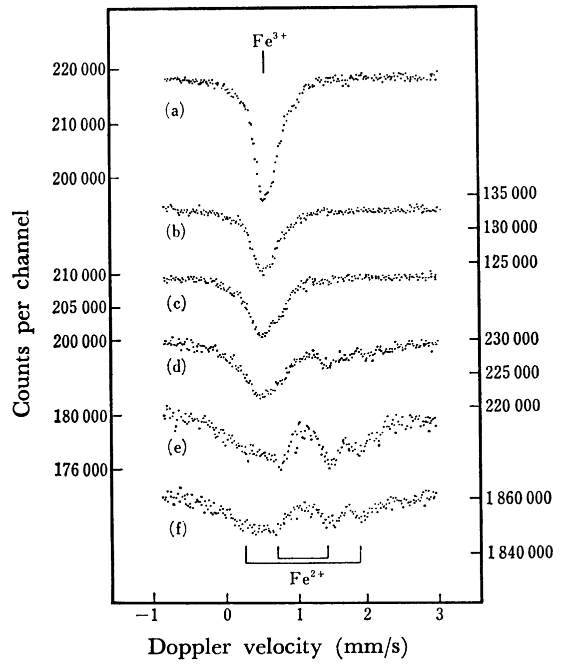

Fig. 1. Mössbauer spectra at 298 K of (a) graphite–$FeCl_3$ intercalation compound, and (b)—(f) graphite–$FeCl_3$–$AlCl_3$ intercalation compounds: (a) compound II, (b) compound V, (c) compound VI, (d) compound VIII, (e) compound IX, (f) compound X.

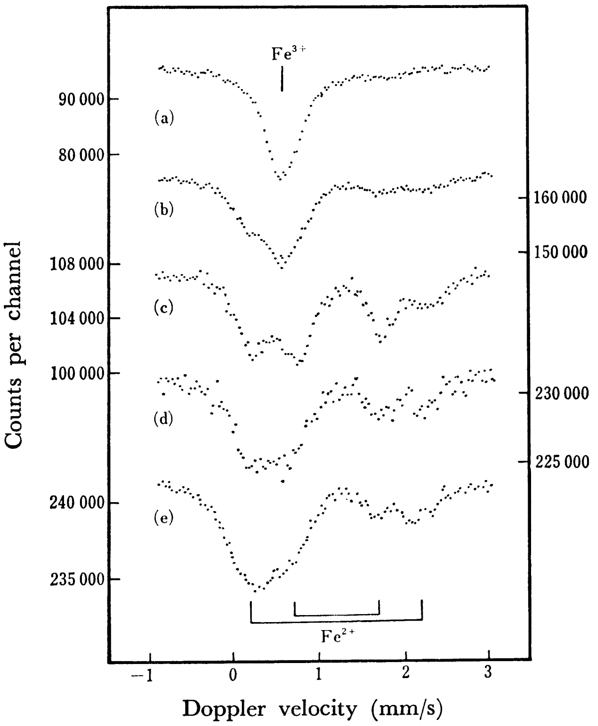

Fig. 2. Mössbauer spectra at 80 K of (a) graphite–$FeCl_3$ intercalation compound, and (b)—(e) graphite–$FeCl_3$–$AlCl_3$ intercalation compounds: (a) compound II, (b) compound VIII, (c) compound IX, (d) compound X, (e) compound XI.

$FeCl_3$ may be attenuated at low temperatures, as has been observed with the graphite–$FeCl_3$ compounds; the other possibilities, such as an effect due to the difference in temperature dependence of the recoilless fractions of Fe^{2+} and Fe^{3+} species,[15)] or any irreversible change in structure over the above temperature range,[16)] may be ruled out.

As shown in Table 2, two sets of quadrupole doublets with nearly equal isomer shifts arise in the Mössbauer spectra of the graphite–$FeCl_3$–$AlCl_3$ compounds with $FeCl_3/AlCl_3$ ratios of 1—0.3. This is indicative of the presence of two kinds of Fe^{2+} ion sites, one of which (corresponding to the inner doublet) may not differ appreciably from the Fe^{2+} site in pure anhydrous $FeCl_2$ because their Mössbauer parameters are alike. Moreover, it is worthwhile mentioning that the Mössbauer parameters of the Fe^{2+} doublets of the graphite–$FeCl_3$–$AlCl_3$ compounds are generally similar to those of the Fe^{2+} peaks of the graphite–$FeCl_2$ compounds obtainable by reduction of the graphite–$FeCl_3$ compounds.[4,6–8)] The origin of the two Fe^{2+} sites in the graphite–$FeCl_2$ compounds has been ascribed to dissimilar distortions from a regular octahedron of chlorine in the $FeCl_2$ structure.[8)]

The appearance of the Fe^{2+} doublets in the graphite–$FeCl_3$–$AlCl_3$ compounds with small $FeCl_3/AlCl_3$ ratios may be tentatively accounted for as follows.[17)] If the $AlCl_3$ concentration in the metal halide layer is small, a graphite π-electron donated to an Fe^{3+} ion may be shared among several neighboring Fe^{3+} ions through a rapid exchange process, and eventually will increase the isomer shift of the Fe^{3+} single peak. As the $AlCl_3$ concentration exceeds the $FeCl_3$ concentration ($FeCl_3/AlCl_3 \leq 1$), the donated electron may be localized on one Fe^{3+} ion to produce Fe^{2+}, since the iron ion is surrounded with Al^{3+} ions which are not electron acceptors, and no direct exchange of an electron between Fe^{3+} ions is probable. Accordingly, this may give evidence that a species of the type $C_n^+Cl^-$-$FeCl_2 \cdot 3AlCl_3$ is formed by the transfer of graphite π-electrons in the compounds with $FeCl_3/AlCl_3$ ratios of about 0.3, as postulated by Dzurus and Hennig.[12)]

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15) The Fe^{2+}/Fe^{3+} area ratios measured at 298 and 80 K for a mixture of pure anhydrous $FeCl_2$ and $FeCl_3$ were nearly equal, within about 10% uncertainty. The layer structures of pure anhydrous iron chlorides may be essentially retained in the intercalation compounds where they are sandwiched between graphite layers.

16) The spectrum at 298 K was reproducible even after the compound had been cooled to 80 K and then warmed up to room temperature again.

17) We may exclude the possibility of the formation of $FeCl_2$ by decomposition under the conditions employed in this work. In fact, the observed Cl/(Fe+Al) ratios (Table 1) were close to 3, while the ratio should be as low as 2.76 if $FeCl_3$ was completely decomposed to $FeCl_2$ in the compounds with $FeCl_3/AlCl_3$ ratio of about 0.3.