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A MÖSSBAUER SPECTROSCOPIC STUDY OF INTERCALATION COMPOUNDS OF GRAPHITE WITH FERRIC CHLORIDE AND ALUMINUM CHLORIDE

Takeshi TOMINAGA, Takuhiko SAKAI, and Tomohiko KIMURA

Department of Chemistry, Faculty of Science,
The University of Tokyo, Hongo, Tokyo

The Mössbauer spectra of graphite-$FeCl_3$ and graphite-$FeCl_3$-$AlCl_3$ compounds with varying $FeCl_3/AlCl_3$ ratio were measured at 80°K and 298°K. In the spectra of the latter compounds with $FeCl_3/AlCl_3$ ratio of approximately one and less were observed two quadrupole doublets indicating the presence of high-spin Fe(II).

There have been arguments as to the nature of bonding of graphite-ferric chloride intercalation compounds since the presence of species of the type $C_n{}^+Cl^-FeCl_2 \cdot 3FeCl_3$ was postulated on the basis of electrical measurements.1) In 1967, one of the present authors (T.T.) applied the Mössbauer technique to gain some clue as to this problem and found that the isomer shift of the intercalated ferric chloride was slightly larger than that of pure anhydrous ferric chloride.2) This fact is indicative of the transfer of graphite π-electrons into the intercalated ferric chloride molecules. Similar results were reported by several groups of workers on the Mössbauer spectra of the graphite-$FeCl_3$ and graphite-$FeCl_3$-$AlCl_3$ intercalation compounds.3-6) According to previous work,4) the Mössbauer spectra of graphite-$FeCl_3$-$AlCl_3$ compounds (with $FeCl_3/AlCl_3$ ratio between 0.2 and 0.5) were essentially the same as those of the graphite-$FeCl_3$ compounds. However, we have recently found that the Mössbauer spectra of graphite-$FeCl_3$-$AlCl_3$ compounds change with the decrease in $FeCl_3/AlCl_3$ ratio and that quadrupole doublets corresponding to high-spin Fe(II) appear in the spectra of the compounds with $FeCl_3/AlCl_3$ ratio of approximately one and less.

The object of the present article is to report our preliminary data concerning the chemical states of iron chloride intercalated in the graphite-$FeCl_3$-$AlCl_3$ compounds on the basis of the Mössbauer spectra of the graphite-$FeCl_3$-$AlCl_3$ compounds with varying $FeCl_3/AlCl_3$ ratio.

The graphite-$FeCl_3$ compounds were prepared by procedures similar to those described in the literature.7) Mixtures of graphite and anhydrous ferric chloride were heated in sealed glass tubes between 250° and 350°C. The products were freed from excess iron chloride by washing with hot 2 M HCl and dried at 110°C. The products were analyzed by decomposition to oxide. The $FeCl_3$ content of the products ranged from about 49 to 60 % by weight, corresponding to the formula C_nFeCl_3 with n ranging from 9 to 14. The graphite-$FeCl_3$-$AlCl_3$ compounds were prepared by essentially similar methods.[1,8)] Mixtures of graphite with anhydrous ferric chloride and aluminum chloride were heated in sealed glass tubes between 210° and 300°C to give the intercalation compounds with $FeCl_3/AlCl_3$ ratio ranging from 0.3 to 4 (the $FeCl_3$ content ranged from about 7 to 49 % by weight).[9)] The Mössbauer absorption spectra of the intercalation compounds were measured at 298° and 80°K by using either a Hitachi AA-40, or a Shimadzu MEG-1A Mössbauer spectrometer with a ^{57}Co source diffused into copper foil (the source was kept at 298°K). Typical Mössbauer spectra are illustrated in Figs.1 and 2.

Graphite-$FeCl_3$ compounds

As seen in Fig.1a, the Mössbauer spectrum of $C_{10}FeCl_3$ ($FeCl_3$ content: 56 %) at 298°K consists of a single absorption peak with an isomer shift of 0.48 mm/sec, which is slightly larger than that of anhydrous $FeCl_3$ (i.e., 0.42 mm/sec).[10)] This fact is in agreement with the results reported previously,[2-6)] and may be taken as evidence for the transfer of graphite π-electrons into the d-orbitals of iron[11)] in all ferric chloride molecules rather than in only one fourth of the intercalated molecules as postulated previously from electrical measurements.[1)] The isomer shift of $C_{10}FeCl_3$ at 80°K (Fig.2a), however, was found to be 0.52 mm/sec, identical with that of anhydrous $FeCl_3$ (i.e., 0.52 mm/sec). Hence, the electron transfer appears to be ambiguous at low temperatures. The Mössbauer spectra of the graphite-$FeCl_3$ compounds prepared in the present work were all the same, irrespective of the $FeCl_3$ content and conditions of preparation such as heating temperature (250°—350°C).[12)] Moreover, the spectrum of $C_{10}FeCl_3$ was not changed significantly even after the original compound had been reheated in vacuo for 4 hr at 300°C.

Graphite-$FeCl_3$-$AlCl_3$ compounds

The Mössbauer spectra of graphite-$FeCl_3$-$AlCl_3$ compounds change with the decrease in $FeCl_3/AlCl_3$ ratio and new quadrupole doublets appear in the compounds with $FeCl_3/AlCl_3$ ratio of approximately one and less.

1) $FeCl_3/AlCl_3$ ratio = 4. The spectrum of this compound at 298°K is essentially similar to those of the graphite-$FeCl_3$ compounds (Fig.1b).

2) $FeCl_3/AlCl_3$ ratio = 1. At 298°K the spectrum of this compound (prepared by heating for 4 hr at 220°C) consists of a single absorption peak of $FeCl_3$ and a quadrupole doublet with an isomer shift of 1.09 mm/sec and a quadrupole splitting of 0.61 mm/sec (Fig.1c). The presence of a second outer doublet which can be observed in Figs.1d and 1e is somewhat ambiguous. In the spectrum at 80°K (Fig.2b) the intensity of the $FeCl_3$ single peak is enhanced relative to the intensity of the inner doublet (δ=1.31 mm/sec and ΔE_Q = 0.84 mm/sec).

3) $FeCl_3/AlCl_3$ ratio = 0.5. The spectrum at 298°K (Fig.1d) is composed of an inner doublet (δ= 1.10 mm/sec and ΔE_Q = 0.69 mm/sec) and an outer doublet of weaker intensity (δ=1.10 mm/sec and ΔE_Q = 1.67 mm/sec), whereas the single peak of $FeCl_3$

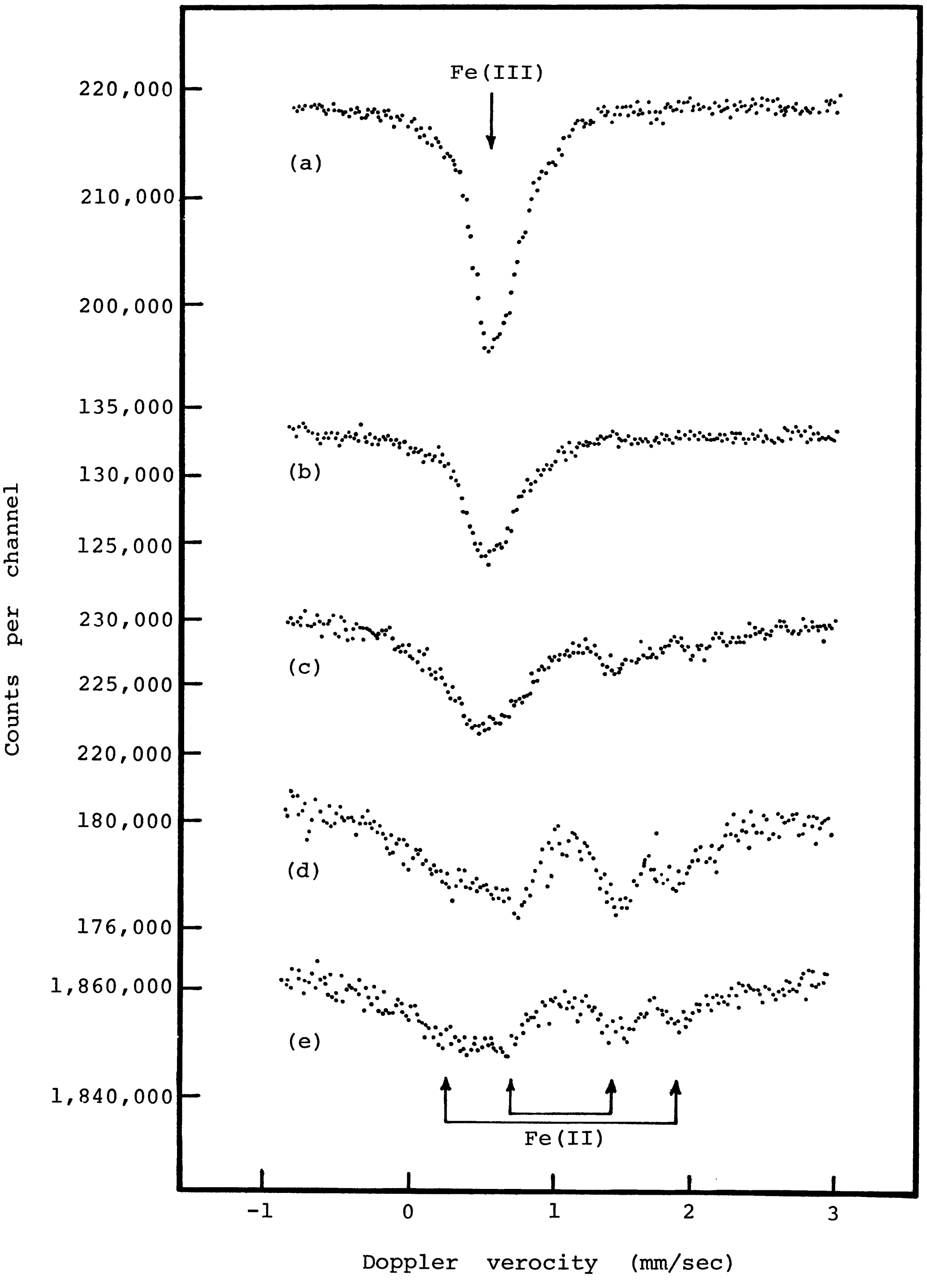

Fig.1. Mössbauer spectra at 298°K of (a) graphite-$FeCl_3$ intercalation compound, and (b)〜(e) graphite-$FeCl_3$-$AlCl_3$ intercalation compounds.

(b) $FeCl_3/AlCl_3 = 4$ (c) $FeCl_3/AlCl_3 = 1$

(d) $FeCl_3/AlCl_3 = 0.5$ (e) $FeCl_3/AlCl_3 = 0.3$

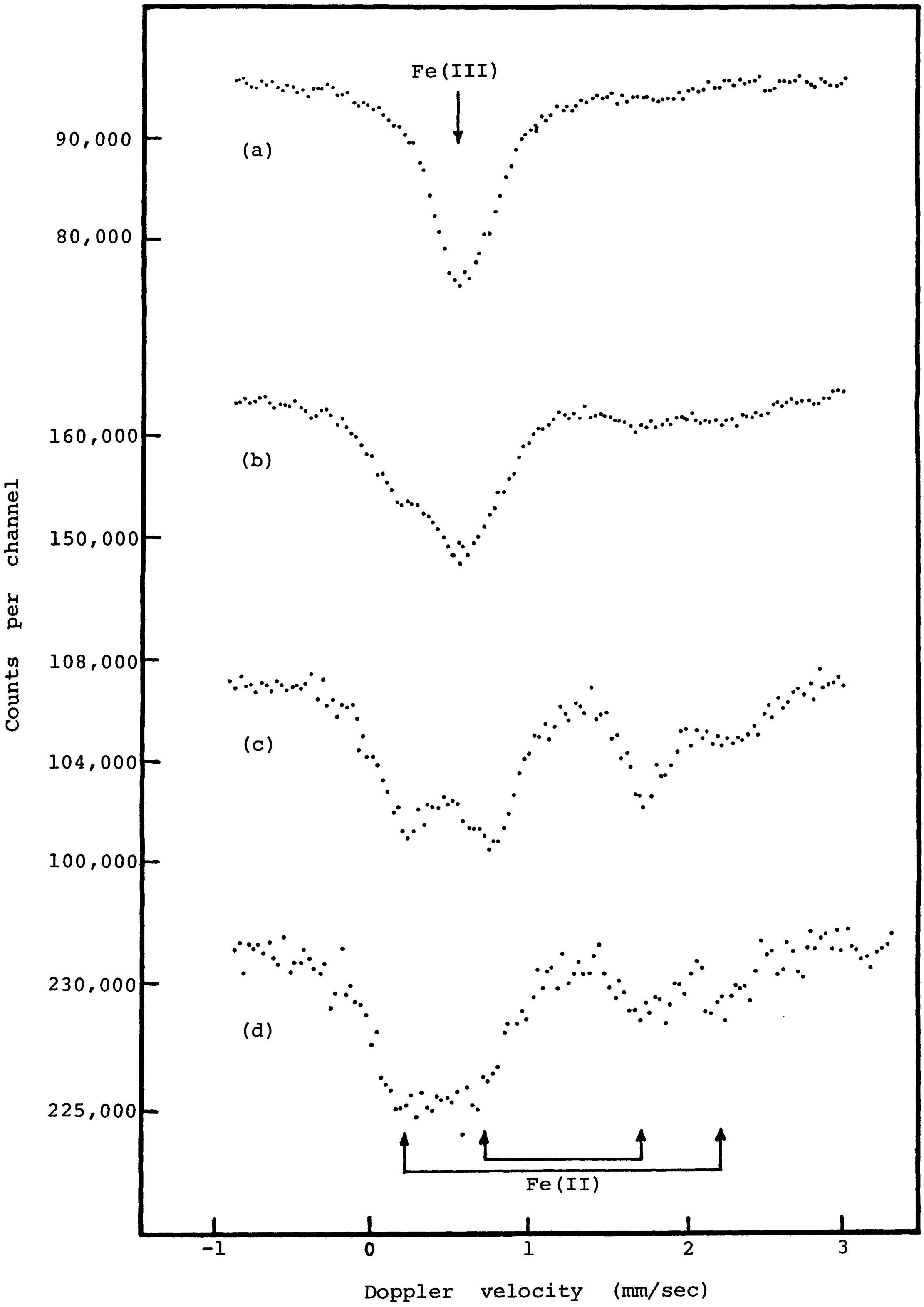

Fig.2. Mössbauer spectra at 80°K of (a) graphite-$FeCl_3$ intercalation compound, and (b)～(d) graphite-$FeCl_3$-$AlCl_3$ intercalation compounds.

(b) $FeCl_3/AlCl_3 = 1$ (c) $FeCl_3/AlCl_3 = 0.5$

(d) $FeCl_3/AlCl_3 = 0.3$

almost disappears. Although the spectrum at 80°K (Fig.2c) mainly consists of the inner doublet (δ = 1.27 mm/sec and ΔE_Q = 0.90 mm/sec) and outer doublet (δ = 1.28 mm/sec and ΔE_Q = 2.17 mm/sec), the intensity of the superposed $FeCl_3$ peak appears to be increased relative to intensities of the doublets.

4) $FeCl_3/AlCl_3$ ratio = 0.3. The spectrum at 298°K (Fig.1e) similarly consists of two doublets of nearly equal intensity (δ = 1.10 mm/sec and ΔE_Q = 0.70 mm/sec; δ = 1.10 mm/sec and ΔE_Q = 1.68 mm/sec). At 80°K (Fig.2d), the intensity of the remaining $FeCl_3$ peak appears to be enhanced relative to those of the doublets.

These two doublets with an equal isomer shift of 1.10 mm/sec (298°K) in the spectra of the graphite-$FeCl_3$-$AlCl_3$ compounds with $FeCl_3/AlCl_3$ ratio ranging from 0.3 to 1 obviously correspond to high-spin Fe(II). The parameters of the inner doublet are in agreement with those of pure anhydrous ferrous chloride, while the outer doublet implies the presence of a different Fe(II) site.13) Accordingly, we may presume that iron chloride molecules intercalated in the graphite-$FeCl_3$-$AlCl_3$ compounds with $FeCl_3/AlCl_3$ ratio of 0.3—0.5 exist predominantly in high-spin Fe(II) states. It is worth mentioning that at 80°K intensities of the Fe(II) doublets appear to be decreased relative to the intensity of the Fe(III) peak.

Further work should be necessary before we can unequivocally settle the question: whether the presence of high-spin Fe(II) states in the graphite-$FeCl_3$-$AlCl_3$ compounds can be taken as evidence for the species of the type $C_n^+Cl^-FeCl_2\cdot 3AlCl_3$ formed by the transfer of graphite π-electrons,1) or can be explained by assuming the possible formation of $FeCl_2$ from the equilibrium $FeCl_3 \rightleftharpoons FeCl_2 + 1/2\ Cl_2$ between the graphite layers.5)

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REFERENCES

1) M. L. Dzurus and G. R. Hennig, J. Amer. Chem. Soc., 79, 1051 (1957).
2) N. Saito, T. Tominaga, M. Takeda, Y. Ohe, F. Ambe, and H. Sano, Proc. 7th Japan Conf. Radioisotopes, 231 (1967).
3) B. V. Liengme, M. W. Bartlett, J. G. Hooley, and J. R. Sams, Phys. Lett., A25, 127 (1967).
4) A. G. Freeman, Chem. Comm., 1968, 193.
5) J. G. Hooley, M. W. Bartlett, B. V. Liengme, and J. R. Sams, Carbon, 6, 681 (1968).
6) F. D. Grigutsch, D. Hohlwein, and A. Knappwost, Z. Phys. Chem. (Frankfurt am Mein), 65, 322 (1969).
7) W. Rüdorff and H. Schulz, Z. anorg. allgem. Chem., 245, 121 (1940).
8) R. C. Croft, J. Appl. Chem., 2, 557 (1952).

9) The $FeCl_3/AlCl_3$ ratio is given by molar ratio. The metal/chlorine ratio in the compounds was checked by neutron activation analysis.

10) Isomer shifts are relative to the centroid of the spectrum of iron foil at 298°K. Errors: ± 0.02 mm/sec.

11) This may be confirmed by the opposite effect observed in boron nitride-$FeCl_3$ compounds (A. G. Freeman, J. Chem. Soc. A, 1969, 1307). The isomer shift value of $FeCl_3$ intercalated in boron nitride was slightly lower than that observed for pure $FeCl_3$. It was suggested that there was the electron transfer from the iron chloride molecule to the boron nitride layers.

12) In the spectrum of C_9FeCl_3 prepared by heating at 350°C can be observed very slight contribution of a high-spin Fe(II) doublet, one component of which is superposed on the $FeCl_3$ peak.

13) The structure corresponding to the outer doublet has not been clarified yet.

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