

STUDIES ON THE CHEMICAL EFFECTS OF THE  ${}^6\text{Li}(n,\alpha)\text{T}$  REACTION IN  
TRIS(OXALATO)FERRATE(III) CRYSTALS

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Chemical effects of the neutron irradiation of  $\text{Li}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 4.5\text{H}_2\text{O}$  and  $(\text{NH}_4)_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$  were studied by means of Mössbauer spectroscopy. No significant change was found in the neutron-irradiated  $(\text{NH}_4)_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ , while Fe(II) species were observed to be produced by the  ${}^6\text{Li}(n,\alpha)\text{T}$  reaction in the neutron-irradiated  $\text{Li}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 4.5\text{H}_2\text{O}$ .

Although the radiation effects of the  ${}^6\text{Li}(n,\alpha)\text{T}$  reaction in several materials have been of great interest in connection with the nuclear fusion techniques,<sup>1)</sup> the chemical effects of the high energy alpha (2.05 MeV at maximum) and tritium (2.73 MeV at maximum) particles emitted in the nuclear reaction have not been fully elucidated. In the present work, we attempted to detect the chemical effects of the recoil alpha and tritium particles by using lithium tris(oxalato)ferrate,  $\text{Li}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 4.5\text{H}_2\text{O}$ , as a target material in thermal neutron irradiations, because tris(oxalato)ferrates are known to be sensitive to  $\gamma$ -ray radiolysis and to photolysis. For the sake of comparison, ammonium tris(oxalato)ferrate(III),  $(\text{NH}_4)_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ , was also irradiated by thermal neutrons in the same conditions as for the lithium salt. Both the salts were synthesized in the conventional way, and were recrystallized from water.

The purity was confirmed by elemental analyses. Each 100 or 200 mg portion of samples was sealed in a polyethylene envelope in air and in a polyethylene tube under nitrogen. These samples were irradiated by thermal neutrons at the flux of  $5 \times 10^{11}$  n.s<sup>-1</sup>.cm<sup>-2</sup> for four hours in a 100 kW Triga Mark II reactor at the Atomic Energy Institute of Rikkyo University. Mixtures of  $(\text{NH}_4)_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$  and  $\text{Li}_2\text{CO}_3$  were also subjected to neutron irradiation. After the irradiation, the samples were kept in a liquid nitrogen bath until the Mössbauer measurements were carried out. Mössbauer spectra were recorded with a constant acceleration-type spectrometer. All the velocity scales were normalized with respect to a metallic iron foil. Although a small difference has been reported for  $\gamma$ -ray radiolysis of  $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ , depending upon the atmosphere during the irradiation, little difference was observed in the present work between the samples sealed in polyethylene envelope in air and those sealed in polyethylene tubes filled with nitrogen gas. The results seem to imply that both the conditions are not effective in changing the oxidation state at least during the irradiation and storage. Therefore, no further attention was given to the atmospheric conditions of the samples in the discussion of the results.

Table 1 summarizes the Mössbauer parameters. The Mössbauer spectra of  $\text{Li}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 4.5\text{H}_2\text{O}$  at 80 K and at room temperature consist of a broad absorption line due to magnetic relaxation,<sup>2)</sup> as shown in Fig. 1.

Table 1. Mössbauer parameters of lithium and ammonium tris(oxalato)ferrate before and after neutron irradiation.

Compound	Component	T/K	I. S./mm·s <sup>-1</sup>	Q. S. <sup>*</sup> /mm·s <sup>-1</sup>
Unirradiated Li <sub>3</sub> [Fe(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ]·4.5H <sub>2</sub> O	Fe(III)	4	0.30±0.03	
		80	0.30±0.03	
		294	0.28±0.03	
Neutron-irradiated Li <sub>3</sub> [Fe(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ]·4.5H <sub>2</sub> O	Fe(III)	80	0.3±0.1	
		140	0.3±0.1	
		297	0.3±0.1	
	Fe(II)	80	1.32±0.03	1.97±0.05
		140	1.27±0.03	1.87±0.05
		297	1.18±0.03	1.70±0.05
Unirradiated (NH <sub>4</sub> ) <sub>3</sub> [Fe(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ]·3H <sub>2</sub> O	Fe(III)	80	0.30±0.03	
		299	0.35±0.03	
Neutron-irradiated (NH <sub>4</sub> ) <sub>3</sub> [Fe(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ]·3H <sub>2</sub> O	Fe(III)	80	0.33±0.03	
		298	0.40±0.03	

\* Q. S. values of Fe(III) species are not determined because of the broadening caused by magnetic relaxation in [Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>3-</sup> species.

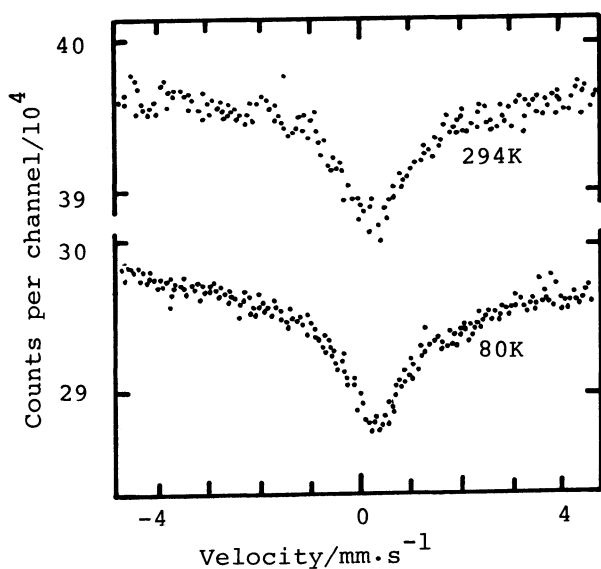


Fig. 1. Mössbauer spectra at 294 and 80 K of the unirradiated Li<sub>3</sub>[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]·4.5H<sub>2</sub>O.

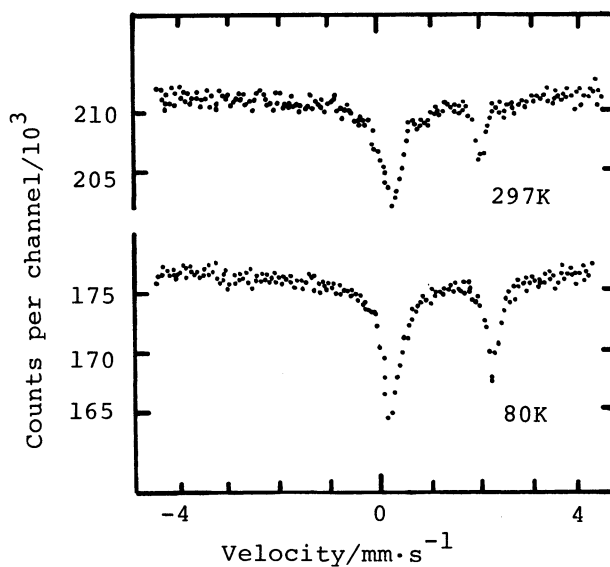


Fig. 2. Mössbauer spectra at 297 and 80 K of the neutron-irradiated Li<sub>3</sub>[Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]·4.5H<sub>2</sub>O.

Figure 2 shows the Mössbauer spectra of the neutron-irradiated  $\text{Li}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 4.5\text{H}_2\text{O}$  sealed under nitrogen. In the spectra, a new doublet is found and the Mössbauer parameters (I. S. =  $1.32 \text{ mm} \cdot \text{s}^{-1}$ , Q. S. =  $1.97 \text{ mm} \cdot \text{s}^{-1}$ , both at 80 K) are characteristic of the high-spin Fe(II) species. Although the broad line component of the original Fe(III) species still remains in the spectra, more than 2/3 of the total spectral area in each spectrum is contributed by this new species.

The spectra of neutron-irradiated  $(\text{NH}_4)_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$  at 80 K and at room temperature are shown in Fig. 3. Although the irradiation condition for this sample was the same as for lithium salt, no remarkable change was found in the Mössbauer spectra compared with in the spectra of the unirradiated one. Therefore, the effects of  $\gamma$ -rays in the reactor (estimated to be  $1.4 \times 10^6 \text{ rad} \cdot \text{h}^{-1}$ ) and the effects of nuclear events such as  $^{54}\text{Fe}(n, \gamma)^{55}\text{Fe}$  may be concluded to be negligible in the present irradiation condition. The remarkable effect of neutron irradiation on  $\text{Li}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 4.5\text{H}_2\text{O}$  is attributed to radiolytic effects caused by the alpha and tritium particles emitted through the  $^6\text{Li}(n, \alpha)\text{T}$  reaction. In order to confirm this explanation, a mixed sample of  $(\text{NH}_4)_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$  and  $\text{Li}_2\text{CO}_3$  (2:1 in mass ratio) was also irradiated with thermal neutrons in the same condition as in the previous experiments. Typical Mössbauer spectra were shown in Fig. 4. The Mössbauer parameters agree with those of the Fe(II) species observed in the spectra of the neutron-irradiated  $\text{Li}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 4.5\text{H}_2\text{O}$ . The results indicate that the reduction of iron atoms was caused when lithium atoms exist in the target materials.

Infrared absorption spectra of neutron-irradiated and unirradiated  $\text{Li}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 4.5\text{H}_2\text{O}$  are shown in Fig. 5. The unirradiated salt shows a band at  $1280 \text{ cm}^{-1}$ , and the intensity of this band decreases in the spectrum of the neutron-irradiated salt; while the intensity of the band at  $1330 \text{ cm}^{-1}$  becomes larger after the neutron irradiation.

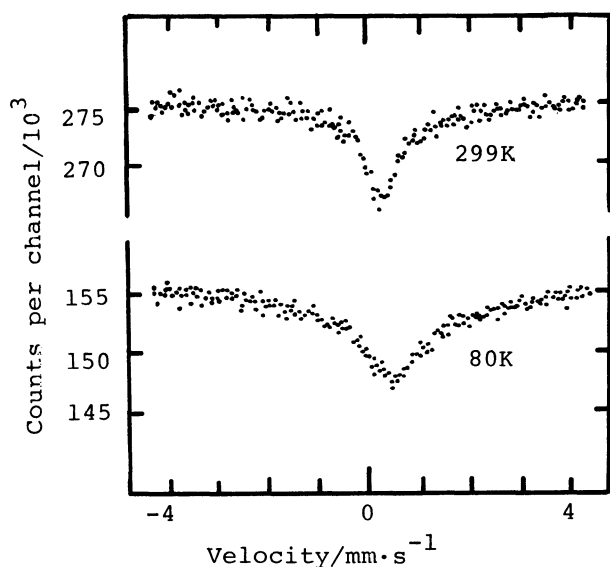


Fig. 3. Mössbauer spectra at 299 and 80 K of the neutron-irradiated  $(\text{NH}_4)_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ .

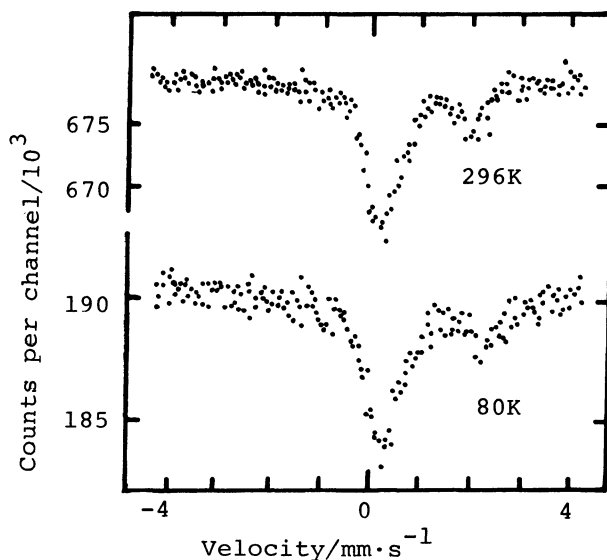


Fig. 4. Mössbauer spectra at 296 and 80 K of the neutron-irradiated mixture of  $(\text{NH}_4)_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$  and  $\text{Li}_2\text{CO}_3$  (2:1 in mass ratio).

ation. The same changes in infrared spectra were observed by Bancroft *et al.* in the  $\gamma$ -ray irradiated  $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ .<sup>3)</sup> The species were assigned to  $[Fe(C_2O_4)_2(H_2O)_2]^{2-}$  species by them.

Figure 6 shows the powder X-ray patterns taken for the neutron-irradiated and unirradiated  $Li_3[Fe(C_2O_4)_3] \cdot 4.5H_2O$ . The new peak clearly found at  $27.2^\circ$  in the pattern is assigned to the Fe(II) species, suggesting that the Fe(II) species do not sit in the interstitial sites.

Since the fast-neutron flux in these experiments is estimated about 1/10 of the thermal neutron flux, the effects of the fast neutron may not play an important role in the radiolytic processes involved in the present experimental condition. If the effects of the fast neutron are neglected, we can evaluate the number of the nuclear event of the  ${}^6Li(n,\alpha)T$  reaction during the irradiation as  $2.2 \times 10^{14}$  for 100 mg of  $Li_3[Fe(C_2O_4)_3] \cdot 4.5H_2O$ , which contains  $1.43 \times 10^{20}$  iron atoms. Supposing that 2/3 of the iron atoms are converted to the divalent iron, it can be concluded that each  ${}^6Li(n,\alpha)T$  reaction affects  $4 \times 10^5$  iron atoms. Since the reaction energy provided by the  ${}^6Li(n,\alpha)T$  reaction is known to be 4.78 MeV, the G-value for the reduction of iron-(III) species is estimated to be about 9.1. This value seems to be reasonable for the reduction of tris(oxalato)ferrate(III) complex species, because the close values have been reported for the  $\gamma$ -ray radiolysis of  $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ <sup>4)</sup> and of  $K_3[Co(C_2O_4)_3] \cdot 3H_2O$ .<sup>5)</sup> The results suggest that the radiolysis induced by alpha and tritium particles reduces iron atoms in a similar manner to the  $\gamma$ -ray radiolysis during the neutron irradiation of  $Li_3[Fe(C_2O_4)_3] \cdot 4.5H_2O$ .

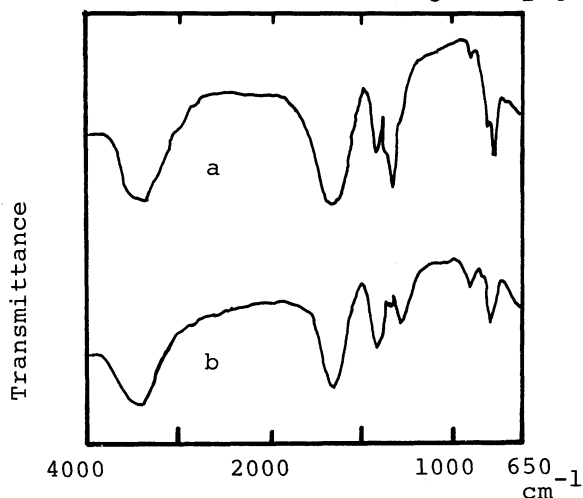


Fig. 5. Infrared absorption spectra of (a) the neutron-irradiated and (b) unirradiated  $Li_3[Fe(C_2O_4)_3] \cdot 4.5H_2O$  both at room temperature.

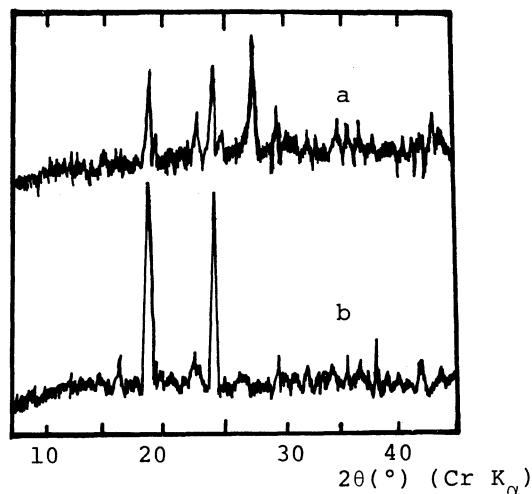


Fig. 6. X-Ray diffraction patterns of (a) the neutron-irradiated and (b) unirradiated  $Li_3[Fe(C_2O_4)_3] \cdot 4.5H_2O$  both at room temperature.

#### References

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