Mössbauer Studies of the Oxidation State of ^{57}Fe produced in EC-decay of ^{57}Co-doped and in γ-Irradiation of ^{57}Fe-doped Mn(acac)$_3$, Fe(acac)$_3$, and Co(acac)$_3$

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Summary It has been demonstrated that the surrounding matrix of an EC-decayed ^{57}Co(acac)$_3$ moiety is involved in the localized radiolytic process initiated by the Auger effect.

THE formation of bivalent iron-atom charge state in ^{57}Co-labelled tris(acetylacetonato)cobalt(III) has been interpreted in terms of the "internal pressure hypothesis".[1] However, the hypothesis has been challenged by others on the grounds that such anomalous charge states were observed in the IT(IC)-decay of ^{119m}Sn in $K_6Sn_2(C_2O_4)_7$,-$4H_2O$[2] and $SnSO_4$[3] and that the bivalent charge state was still observed in K_3(Fe,^{57}Co)$(C_2O_4)_3$,$3H_2O$[4] and (Fe,^{57}Co)-(acac)$_3$.[5] We have previously suggested that one possible mechanism is the radiolytic process initiated by the Auger effect.[2,5,6] Recently, it has been reported that the emission Mössbauer spectra after EC-decay in ^{57}Co-labelled Co(acac)$_3$ are similar to the absorption spectra of electron-irradiated Fe(acac)$_3$.[7] The comparison of those spectra has, however, been made on the ^{57}Fe species produced in the two different environmental matrices, Co(acac)$_3$ and Fe(acac)$_3$. In order to prove the radiolytic process and to check whether the host material was involved in the process, we studied the effects of the γ-irradiation of ^{57}Fe-doped Mn(acac)$_3$, Fe(acac)$_3$, and Co(acac)$_3$, and the effects of the ^{57}Co EC-decay in the ^{57}Co-doped Mn(acac)$_3$, Fe(acac)$_3$, and Co(acac)$_3$.

(Mn,^{57}Co)(acac)$_3$ and (Fe,^{57}Co)(acac)$_3$ sources were prepared by the extraction method. Carrier-free 2 mCi ^{57}Co(acac)$_3$ was extracted from the aqueous solution into the benzene phase by following the method described in ref. 8. To the benzene phase was added about 100 mg of the host metal acetylacetonate prepared from manganese and iron, and the benzene solution was filtered. After freezing the filtrate in liquid nitrogen, the frozen solution kept at −15° was pumped out through a liquid nitrogen trap in order to remove the benzene and the excess of acetylacetone. Mn(acac)$_3$ and Co(acac)$_3$ targets for the γ-irradiation, which

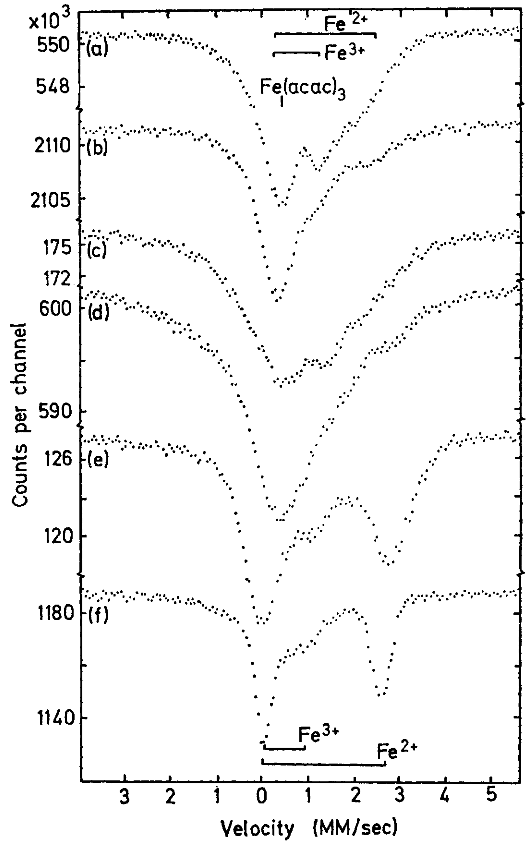

FIGURE. *Mössbauer spectra at* 78 K *of* (a) ^{57}Co-*labelled* Co(acac)$_3$ *source,* (b) *γ-irradiated* (3·0 × 10^9 r) (Co,^{57}Fe)(acac)$_3$ *absorber,* (c) (Mn,^{57}Co)(acac)$_3$ *source,* (d) *γ-irradiated* (3·0 × 10^9 r (Mn,) ^{57}Fe)(acac)$_3$ *absorber,* (e) (Fe^{57},Co)(acac)$_3$ *source, and* (f) *γ-irradiated* (3·0 × 10^9 r) Fe(acac)$_3$ *absorber. All the velocity scales were normalized with respect to iron.*

contain *ca.* 3% ^{57}Fe(acac)$_3$ by weight, were also prepared by freeze-drying the benzene solution containing the host acetylacetonate and the ^{57}Fe(acac)$_3$ synthesized from ^{57}Fe-enriched (90%) iron. Fe(acac)$_3$ and ^{57}Co-labelled Co(acac)$_3$ were prepared by standard methods.[9] *X*-Ray diffraction data indicate that the ^{57}Fe-doped sample has the same crystal structure as the host acetylacetonate if the content of ^{57}Fe(acac)$_3$ incorporated in the host acetylacetonate is less than 10%. The powdered (Mn,^{57}Fe)(acac)$_3$, Fe(acac)$_3$, and (Co,^{57}Fe)(acac)$_3$ were irradiated in a 10^4 Ci ^{60}Co unit at JAERI under 1 Torr helium. Total doses of $4{\cdot}0 \times 10^8$, $1{\cdot}0 \times 10^9$, $3{\cdot}0 \times 10^9$, and $7{\cdot}0 \times 10^9$ r were given to these samples. A constant-acceleration spectrometer was used with a moving source of ^{57}Co(Pt) for irradiated absorber studies and a moving stainless-steel absorber for source studies.

The absorption spectrum after γ-irradiation changes in shape depending upon the total dose. The most significant result concerns the comparison of the spectra of (M,^{57}Fe)(acac)$_3$ obtained after γ-irradiation with the emission spectra of the corresponding (M,^{57}Co)(acac)$_3$. The spectra are decomposed into two quadrupole doublets ascribed to ^{57}Fe^{2+} and ^{57}Fe^{3+} species and one broad singlet of the original ^{57}Fe(acac)$_3$. As shown in the Figure, the shapes of the two spectra are quite similar when the host material, M(acac)$_3$, is the same, whereas they are not always similar when the host material is different. The similarities indicate that the radiolytic process initiated by the Auger effect determines the final oxidation state of the ^{57}Fe in a time of 10^{-7} s. The increased peak intensity and quadrupole splitting of ferrous ^{57}Fe species observed in the spectra of (Fe,^{57}Co)(acac)$_3$ source and the γ-irradiated Fe(acac)$_3$ absorber suggest that the surrounding neighbours of an EC-decayed ^{57}Co(acac)$_3$ or a γ-ray absorbed ^{57}Fe(acac)$_3$ moiety are involved in the local radiolytic processes, and that Fe(acac)$_3$ matrix is more radiosensitive than Mn(acac)$_3$ or Co(acac)$_3$.

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