Mössbauer Spectroscopic Studies of the Oxidation State of ^{57}Fe produced in ^{57}Co-doped and γ-irradiated Trisacetylacetonatoiron(III)

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A number of cobalt compounds labelled with ^{57}Co used as Mössbauer sources have shown the presence of one or more "anomalous" charge states. The formation of iron-atom charge states less positive than the charge state of the cobalt atom in the parent compound has been interpreted in terms of the "internal pressure hypothesis" by Hazony and Herber,[1] based on the similarity between the Mössbauer spectra of Fe(acac)$_3$ under a high external pressure[2] and that of a ^{57}Co(acac)$_3$ source experiment.[3] This hypothesis has also been supported by the fact that such anomalous charge states were not observed in the IT(IC) decay of ^{119m}Sn in the various tin compounds.[1] We have, however, recently reported experimental evidence for the presence of an "anomalous" charge state in the IT(IC) decay of ^{119m}Sn in $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$.[4] It is debatable, therefore, whether or not the lattice can generate a high local internal pressure. Here we will describe the Mössbauer spectra of the first excited state of ^{57}Fe produced in a Fe(acac)$_3$ host crystal doped with ^{57}Co(acac)$_3$. The Mössbauer spectra of γ-irradiated Fe(acac)$_3$ are also shown for comparison.

An (Fe, ^{57}Co)(acac)$_3$ source was prepared from a solution containing 50 mg of ferric iron and 2 mCi of ^{57}Co by following the method described in Ref. 5. Another source was 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. 6. To the benzene phase were added 50 mg of Fe(acac)$_3$ or ^{56}Fe(acac)$_3$ prepared from natural iron or ^{56}Fe-enriched iron, and the benzene solution was filtered. After freezing the filtrate in liquid nitrogen, the frozen solution kept at −15°C was pumped out through a liquid nitrogen trap in order to remove the benzene and the excess acetylacetone. The source was then kept in a cryostat, and the Mössbauer spectra were measured against an ^{57}Fe-enriched stainless-steel absorber moving in a constant acceleration mode at room temperature. All the sources showed the same Mössbauer spectrum. The (Fe, ^{57}Co)(acac)$_3$ source prepared from natural iron was also used as an "absorber" against a 10 mCi ^{57}Co(Pt) source in order to confirm the absence of species other than Fe(acac)$_3$. X-ray diffraction data indicate that the doped sample has the same crystal structure as the host Fe(acac)$_3$ if the content of Co(acac)$_3$ incorporated in Fe(acac)$_3$ is less than 10%.

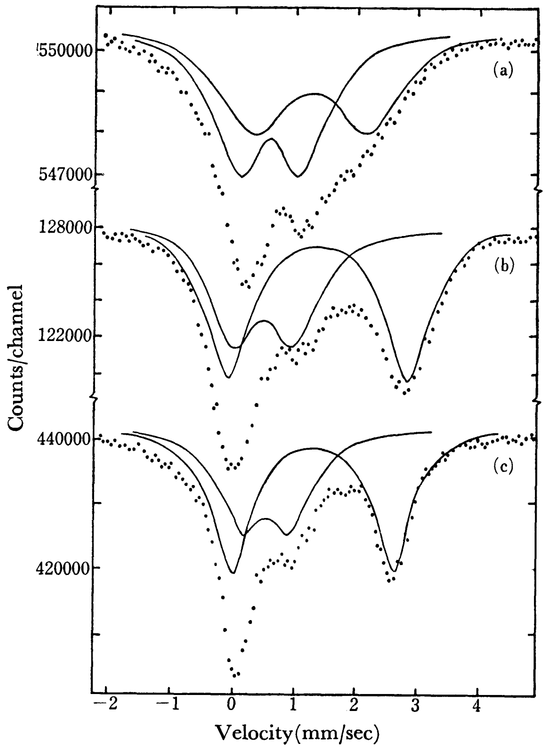

Fig. 1. Mössbauer spectra of (a) (Co, ^{57}Co)(acac)$_3$ source (kept at 78°K) *vs* ^{57}Fe-stainless steel absorber, (b) (^{56}Fe, ^{57}Co)(acac)$_3$ source (kept at 78°K) *vs* ^{57}Fe-stainless steel absorber, and (c) γ-irradiated (10^{10} r) Fe(acac)$_3$ absorber (kept at 78°K) *vs* ^{57}Co(Pt) source. All the velocity scales were normalized with respect to iron.

Typical Mössbauer spectra are shown in Fig. 1. The experiment involving the ^{57}Co(Pt) source and the (Fe, ^{57}Co)(acac)$_3$ "absorber" shows the absence of species other than Fe(acac)$_3$. The experiment using the (Fe, ^{57}Co)(acac)$_3$ source kept at 78°K and a stainless-steel absorber clearly shows the presence of divalent ^{57}Fe species. The experiment using the ^{57}Co(Pt) source and the γ-irradiated Fe(acac)$_3$ absorber kept at 78°K shows the same spectral pattern as that found in the (Fe, ^{57}Co)(acac)$_3$ source experiment.

The results indicate that the divalent ^{57}Fe species are still produced. As ^{57}Co was incorporated into a similar trisacetylacetonatoiron(III) matrix, the "internal-pressure effect" is supposed to be no longer working in the (Fe, ^{57}Co)(acac)$_3$ source. One possible mechanism is auto-radiolysis including an electronic excitation process initiated by the Auger effect. The latter would be followed by the decomposition of the acetylacetonate ligands to various fragments, such as carbon monoxide, carbon dioxide, methane, ethane, and hydrogen, which were detected in the gas chromatography of the γ-irradiated Fe(acac)$_3$.

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