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Relaxation of Short-Lived ^{57}Fe-Species in ^{57}Co-Labeled $Co(IO_3)_2$ Studied by Time-Resolved Emission Mössbauer Spectroscopy

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KX-Ray-gated and time resolved emission Mössbauer spectra of ^{57}Co-labeled $Co(IO_3)_2$ were measured at room temperature, using a coincidence technique. No remarkable difference was found on the relative intensity of Fe(II)/Fe(III) between the X-ray-gated and normal emission spectra. A lifetime for unstable ^{57}Fe(II)-species formed through EC-decay was estimated to be 43±5 ns and the initial distribution of Fe(II)/Fe(III) at 14.4 keV nuclear level to be 0.47±0.13 from the time-resolved emission Mössbauer spectrum. The results are discussed in terms of the chemical stability of the environments of the decayed ^{57}Fe-atoms.

Investigations on the lifetime and electronic state of short-lived chemical species provide very attractive fields for understanding chemical bond and reaction mechanism. Emission Mössbauer spectroscopy is useful for dynamic study of such short-lived chemical species in its nuclear lifetimes or the same order of magnitude; it has the advantage that it detects the chemical states of Mössbauer active atoms decayed from the parent nuclide in ultra-microquantities in the solid. The concentration of metastable or unstable species produced after EC-decay is usually too low to be detected by ordinary physicochemical techniques. By combining emission Mössbauer spectroscopy with a coincidence technique, more detailed and selected information can be provided. If a Mössbauer spectrum gated with a particular radiation among several ones associated with the de-excitation of nuclear or atomic states, we expect to extract information accompanied by the transition. In the present study, two simple coincidence systems were built to elucidate the relaxation processes of unstable chemical species formed through EC-decay. One of the systems involves an X,γ-coincidence and another a γ,γ-coincidence. In X,γ-ray coincidence, a Mössbauer spectrum gated with 6.4 keV KX-ray from decayed ^{57}Fe is observed, which reflects information relating the chemical effects of the KX-ray emission. Kobayashi and Friedt examined the effects of KX-ray emission on ^{57}Co-labeled $CoCl_2 \cdot nH_2O$ (n=2—6), finding a different chemical distribution of ^{57}Fe atoms between the normal and the X-ray-gated emission Mössbauer spectra.[1] In γ,γ-coincidence, the spectrum is taken at an appropriate time interval of the nuclear lifetime, which enables us to study dynamic chemical states of decayed ^{57}Fe atoms. Hoy et al. showed a filtering spectrum of a single resonance line,[2] and analyzed it based on Hamermesh's treatment.[3] Triftshäuser and Craig observed no time dependence of the intensity ratio of Fe(III)/Fe(II) on ^{57}Co-labeled CoO, $CoSO_4$, and $CoCl_2 \cdot 4H_2O$ on the time resolved Mössbauer spectra.[4] Gol′danskii's group estimated the intramolecular electron charge transfer rate from ^{57}Fe atoms to Fe(III) atoms in the system of $^{57}Co_3[Fe(III)(CN)_6]_2$.[5] Gütlich's group reported the lifetime of unstable high-spin Fe(II)-species formed in ^{57}Co-labeled $[Co(phen)_3](ClO_4)_2 \cdot 2H_2O$ at various temperatures.[6] In the present study, we examined the chemically unstable ^{57}Fe-species formed through EC-decay in ^{57}Co-labeled $Co(IO_3)_2$ using both coincidence systems. The labeled compound was selected because the iodate anion is highly oxidizable and its rather simple chemical structure is suitable for examining the stabilization mechamism of the decayed ^{57}Fe-species.

Experimental

Source Preparation. To prepare ^{57}Co-doped $Co(IO_3)_2 \cdot nH_2O$, the procedure described in the literature was modified for small scale synthesis.[7] $Co(NO_3)_2 \cdot 6H_2O$ was dissolved in dil. nitric acid containing ca. 3.0×10^6 Bq of ^{57}Co, and iodic acid was added dropwise to this solution. After heating the solution on a steam bath at 80 °C for ten minutes, the purple blue products were filtered, washed with distilled water and then dried under vacuum. The radioactivity of the sample was estimated to be ca. 2.2×10^6 Bq. Thermogravimetric analysis and X-ray diffraction of the product prepared without ^{57}Co by the same procedure proved it to be an anhydride.

Measurement of X,γ-Ray Coincidence Mössbauer Spectra. The X,γ-ray coincidence system used in the present experiment is shown in Fig. 1. For detecting the 6.4 keV KX-rays two NaI(Tl) crystals of 0.8 mm in thickness and 1″ in diameter were used, and a crystal of 1 mm×1″ NaI(Tl) crystal for 14.4 keV γ-rays. These scintillators were coupled to photomultipliers; Hamamatsu R580, of which cathodes were set to operate at the photocathode potential of −1200 V with respect to the ground. The magnetic shield of Hamamatsu-E989 was used for the photomultiplier, which was effective for fast timing operation to eliminate the magnetic field of the Mössbauer transducer. The bleeder strings assemblies were built by us using low noise resistors, and the current was 0.4 mA. The anode signals from two photomultipliers for detection of KX-rays were fed into fast discriminators (ORTEC-473A) and then each logic signal was summed. The pulses from the third photomultiplier for measuring the Mössbauer spectra were amplified in pulse-height by a linear amplifier (CANBERRA-2011) and then 14.4 keV γ-rays were selected with a timing-SCA (ORTEC-551). These signals were gated by the logic pulses (0.5 μs in pulse width) of the summed 6.4 keV KX-rays.

Measurement of γ,γ-Coincidence Mössbauer Spectra. The γ,γ-coincidence system used in the present experiment

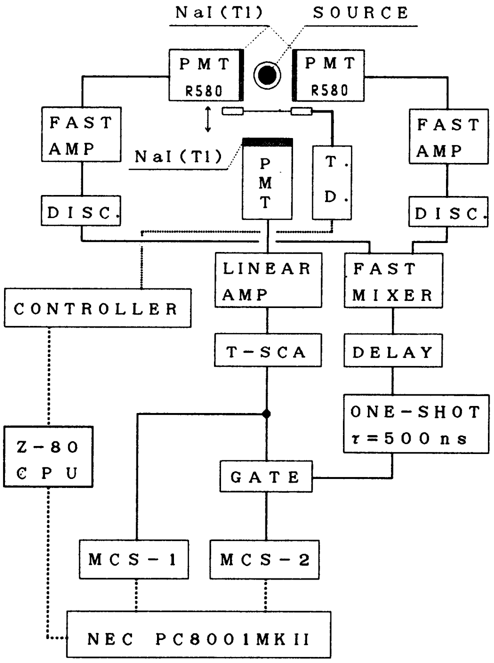

Fig. 1. Block diagram for the X,γ-ray coincidence Mössbauer system; memory units and a Mössbauer controller were governed by a Z-80 CPU. PMT=photomultiplier, AMP=amplifier, T.D.=transducer, T-SCA=timing single-channel analyzer, MIXER=sum circuit, DISC=fast discriminator, GATE=linear gate and stretcher, CONTROLLER=Austine S-600 Mössbauer controller, MCS-1,2=data acquisition system, CPU=central processing unit.

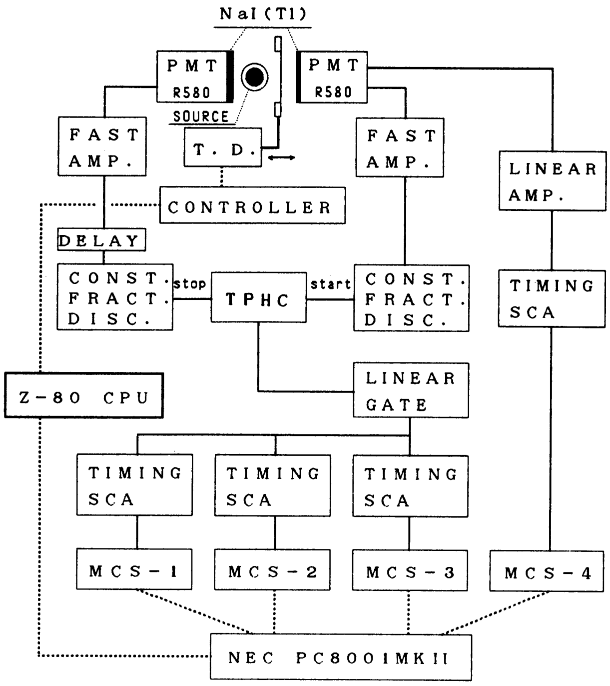

Fig. 2. Block diagram of the apparatus for the delayed coincidence Mössbauer experiments; a transducer controller and all memory units were supervised by a Z-80 CPU. PMT=photomultiplier, AMP=amplifier, T.D.=transducer, SCA=single-channel analyzer, TPHC=time-to-pulse height converter, CONST.FRACT.DISC=constant fraction discriminator, LINEAR GATE=linear gate and stretcher, CONTROLLER=Austine S-600 Mössbauer controller, MCS-1,2,3,4=data acquisition system, CPU=central processing unit.

is shown in Fig. 2. A NaI(Tl) crystal of 1″ in thickness and 1″ in diameter was used to detect 122 keV γ-ray and another crystal of 0.8 mm in thickness and 1″ in diameter for 14.4 keV γ-ray. Anode signals from each multiplier were fed into a fast amplifier (ORTEC-574), the constant fraction discriminator (ORTEC-473A) and then to TPHC (ORTEC-467) as start and stop signals, respectively. In order to reduce the dead time of the time conversion to amplitude at TPHC, the busy start signals of 122 keV were delayed with a coaxial cable for about 2.0×10^{-7} s. Voltage signals from the 11th dynode of the multiplier with a thinner scintillator were used for energy selection of 14.4 keV. With the gated signals of transmitted γ-ray, a Mössbauer spectrum were measured. An Austine Mössbauer spectrometer (S-600) was used together with a data taking system. The latter built by us was a four-channel parallel-mode (4×512 channel) system which is essentially a microprocesser(Z80)-aided multichannel scaler and a memory unit. A microcomputer NEC PC-8001MKII was used for an auxiliary controller of this data acquisition system. The time resolution of γ,γ-coincidence was estimated to be (10.0±0.3) ns using annihilation radiations of ^{22}Na. The windows of the timing SCA were set at the same condition as were used in ^{57}Fe Mössbauer measurement. The time-resolved Mössbauer spectra were measured at the time windows of A(0-45 ns), B(45-88 ns), D(88-148)ns, and E(0-infinity), or A(0-45 ns), C(45-148 ns), and E(0-infinity) in a separate run, respectively. The oscillation due to the time filtering effects on the time resolved Mössbauer spectrum was hardly observed, because the preset time window was rather wide. By subtracting the randomly-coincided fraction from the observed spectrum, the truly-coincided spectra were tentatively analyzed with two sets of quadrupole doublets using a least square fitting of a Gaussian function. Gauss-Newton iteration method was used in the "SALS" least square fitting program developed by Nakagawa and Oyanagi.[9]

Results and Discussion

X,γ-Ray Coincidence Spectrum. An emission Mössbauer spectrum gated with KX-ray is shown in Fig. 3, together with the normal emission spectrum. The former was obtained by subtracting the randomly coincided spectrum from the observed spectrum. The contribution of the random coincidence was estimated to be 30% in the present experimental conditions. The resulting X-ray-gated spectrum does not show remarkable difference from the normal one in their parameters. It has been reported that in various kinds of chemical compounds, an Auger process plays an important role in determining the final chemical state of hot atoms produced through the de-excitation associated with the nuclear transformation. The low energy electrons and/or vacancies produced in Auger cascades dissipate their energies to neighbouring atoms. The Auger process is expected to emit a large

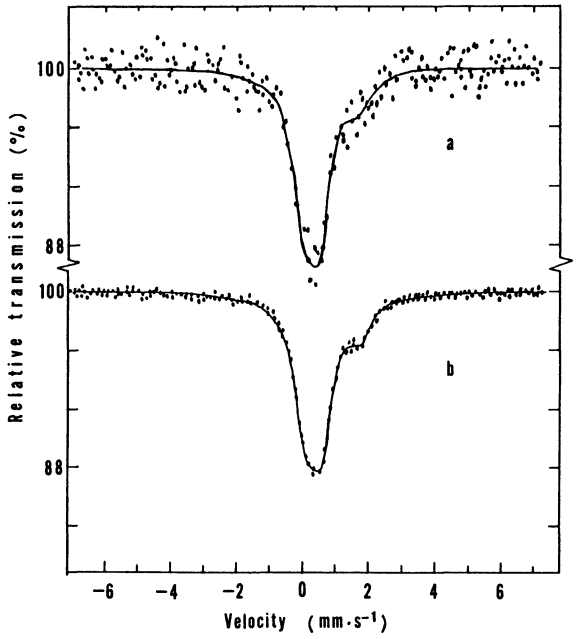

Fig. 3. (a) X,γ-Ray-gated and (b) normal emission Mössbauer spectra of ^{57}Co-labeled Co(IO$_3$)$_2$ at room temperature.

number of electrons than the competitive X-ray emission process; i.e., the former will give a large influence to the chemical species formed through the EC-decay. Multiple ionization will be larger in Auger electron emission than in X-ray emission. However, even if any unstable chemical species are formed by Auger processes and are different from those of the X-ray emission, such chemical species cannot be observed if their lifetimes are too short to be discriminated by the experimental set-up used. These considerations suggest that different chemical species to be discriminated by the present method are not formed in the labeled compound.

γ,γ-Coincidence. Line Width: Time-resolved Mössbauer spectra are shown in Fig. 4, together with a time integral spectrum for comparison. A gradual decrease was observed in the linewidth of both trivalent and divalent species with an increase in the delay time. This trend can be understood qualitatively from the uncertainty principle, as shown in Fig. 5. The line broadening has been observed in many source experiments. This effect arises from several factors. One is to use a thick absorber in order to increase the sensitivity of measurement. Secondly, it arises from superimposition of various kinds of hyperfine parameters corresponding to many electronically excited states formed through EC-decay in the insulator. Thirdly, it is caused by the slow relaxation time of spin-spin and spin-lattice interactions. The former effect is observed in some source experiments of a diamagnetic insulator host lattice where the decayed ^{57}Fe species are placed in a magnetically-diluted material. In the present work, a similar time-dependence of the line widths observed

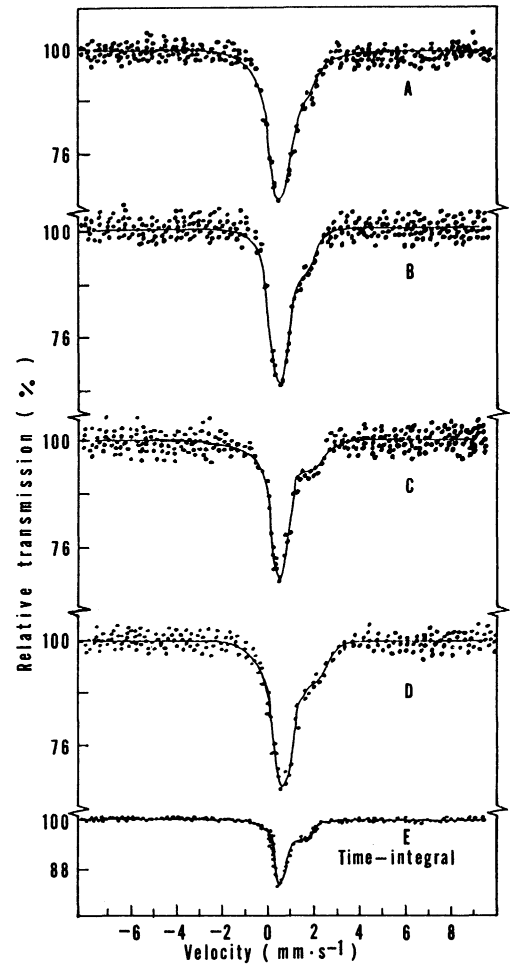

Fig. 4. Time-resolved Mössbauer spectra of ^{57}Co-labeled Co(IO$_3$)$_2$ at room temperature. The time windows were set to be A=0—45 ns, B=45—88 ns, C=45—148 ns, D=88—148 ns, E=0—infinity.

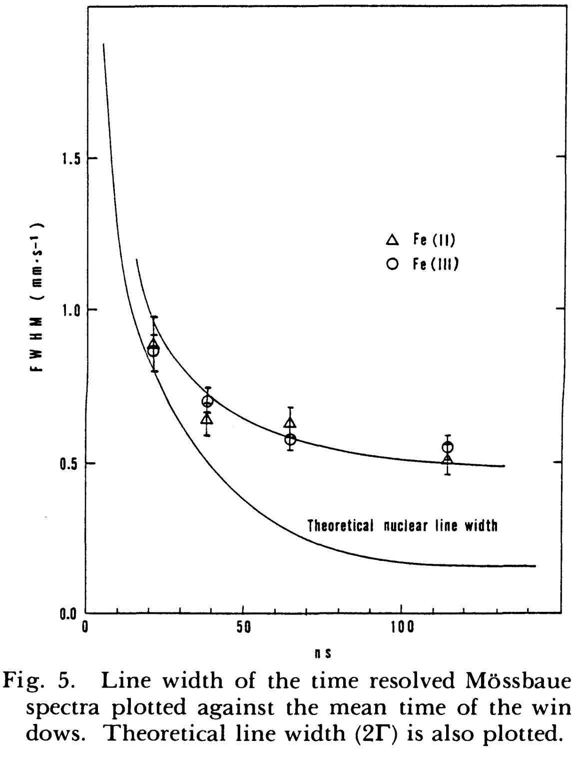

Fig. 5. Line width of the time resolved Mössbauer spectra plotted against the mean time of the windows. Theoretical line width (2Γ) is also plotted.

for the two species shows that the line broadening due to the uncertainty principal predominates over other factors such as the time-dependent population of given species in the present compound.

Evaluation of Relative Intensity on Time-Resolved Spectra: The ratio of the absorption peak area of ^{57}Fe(II) to ^{57}Fe(III) is plotted against the mean time, t, of the time windows in Fig. 6. The mean time for the time window was evaluated by the equation as

$$\frac{t}{\tau_N} = \int_{T_A}^{T_B} Te^{-T}\,dT \Big/ \int_{T_A}^{T_B} e^{-T}\,dT \tag{1}$$

where t is the mean time in the interval $T_A \leqq t \leqq T_B$, and τ_N the mean nuclear lifetime of the first excited state of ^{57}Fe. The chemical decay constant of the unstable ^{57}Fe(II)-species is estimated in the following manner. Several factors are assumed to facilitate the discussion; Debye-Waller factors of ^{57}Fe(II)- and ^{57}Fe(III)-species are the same at every time window. Fe(II)-species decay with a pseudo-first order kinetics of a chemical decay constant, λ_c, and Fe(III) once formed are stable during the time in question, since the anion concentration in the vicinity of the decayed ^{57}Fe-atoms may be regarded as constant. The chemical reaction of ^{57}Fe(II)-species can be assumed to be the electron transfer from the species to the highly oxidizable iodate anion. Let the distributions of ^{57}Fe(II) and ^{57}Fe(III) be $P_2(t)$ and $P_3(t)$ at t after the emission of 122 keV γ-ray and their ratio at t=0 be R.

Then, $P_2(t)+P_3(t)=1$ and

$$R = P_2(0)/P_3(0). \tag{2}$$

With the decay constant, λ_c, of the Fe(II)-species, the populations found at time t after the emission 122 keV gamma-ray can be written as

$$P_2(t) = P_2(0)e^{-\lambda_c t}, \tag{3}$$

$$P_3(t) = P_2(0)(1 - e^{-\lambda_c t}) + P_3(0). \tag{4}$$

Since emission Mössbauer spectroscopy gives us information on the electronic states of "nucleogenic" probe atoms, the observable quantities with this probe at time t should be those of Eqs. 3 and 4 multiplied by $\exp(-\lambda_N t)$, where λ_N is the nuclear decay constant of ^{57}Fe at the 14.4 keV level.

Actually, time-resolved Mössbauer spectroscopy offers a spectrum integrated with respect to the preset time window between T_A and T_B. Then, Eqs. 3 and 4 should be written as

$$\int_{T_A}^{T_B} P_2(t)\,dt = \int_{T_A}^{T_B} P_2(0)e^{-\lambda_c t}dt, \tag{5}$$

$$\int_{T_A}^{T_B} P_3(t)\,dt = \int_{T_A}^{T_B} [P_3(0) + P_2(0)(1 - e^{-\lambda_c t})]dt. \tag{6}$$

Due to the finite resolution of the equipment, the observed spectrum involves a time distribution of Gaussian type, $G(t-t', 2\tau_0)$, where $2\tau_0$ is a full width at half maximum of the time resolution and estimated to be 10.0±0.3 ns by the measurement of annihilation radiations of ^{22}Na in Al metal. Taking the resolution function into consideration, the observed intensity ratio of Fe(II) to Fe(III), at time interval between T_A and T_B, can be described as follows using Eqs. 2, 5, and 6.

$$\{I_2(t)/I_3(t)\}_{ob} \equiv$$

$$\frac{R\int_{T_A}^{T_B}\left[\int_0^{\infty} e^{-\lambda_c t'} e^{-\lambda_N t'} G(t-t'; 2\tau_0)\,dt'\right]dt}{\int_{T_A}^{T_B}\left\{\int_0^{\infty}\left[1+R(1-e^{-\lambda_c t'})\right] e^{-\lambda_N t'} G(t-t', 2\tau_0)\,dt'\right\}dt} \tag{7}$$

$$\text{where}\quad G(t-t'; 2\tau_0) = \frac{1}{\sqrt{2\pi(2\tau_0)^2}} \exp\left\{\frac{-(t-t')^2}{(2\tau_0)^2}\right\}$$

Numerical calculation of Eq. 7 was carried out with a computer. The initial distribution ratio of Fe(II)- to Fe(III)-species, R=0.46±0.13, and the chemical decay constant of Fe(II)-species, $\lambda_c=2.33\times10^{-2}$ ns^{-1} (or τ_c= 43±5 ns), were obtained. In Fig. 6, the obtained and calculated relative intensities of spectral area are plotted vs. mean time t. The integral value, shown as oblique lines, is obtained by the normal emission Mössbauer spectrum without gate. The relative intensities of ^{57}Fe(II) and ^{57}Fe(III) against time calculated by using the values of R, λ_c, and Eqs. 3, 4 are shown in Fig. 7. The intensity of ^{57}Fe(III)-species just after the 122 keV γ-ray emission is taken as an unity. Although the present method for analyzing the relative intensity on the time resolved spectrum is similar to that used by Gütlich's group,[6] the initial distribution ratio of Fe(II)- to Fe(III)-species at 14.4 keV nuclear level was taken as an arbitrary parameter, R, in the present work.

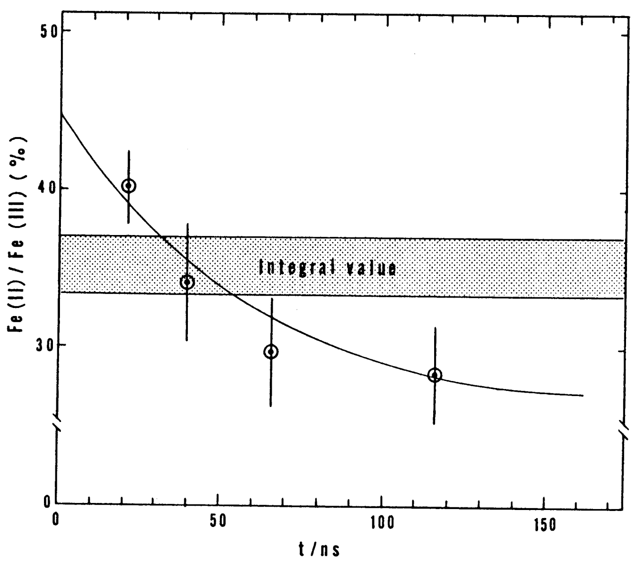

Fig. 6. The ratio of the absorption peak area of ^{57}Fe(II) to ^{57}Fe(III) plotted against the mean time, t, of the time windows. The line is the best-fitted values calculated using Eq. 7.

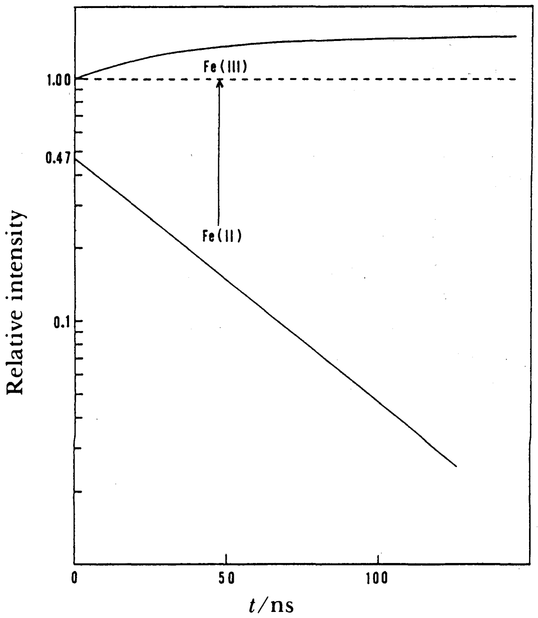

Fig. 7. Growth curve of ^{57}Fe(III)-species and decay curve of ^{57}Fe(II)-species are depicted based on Eqs. 3 and 4. The intensity of ^{57}Fe(III)-species just after the 122 keV γ-ray emission is taken as an unity.

Charge State of ^{57}Fe: The observed lifetime of the short-lived ^{57}Fe-species is 43±5 ns and the initial distribution of Fe(II)/Fe(III) at 14.4 keV level is obtained to be 0.46±0.13 by assuming the divalent ^{57}Fe-species are oxidized monotonically to trivalent species. Although the evaluation of the data for the time-resolved Mössbauer spectra is not the same as that used in the present work, Gol'danskii and his coworkers obtained the electron transfer rate of 1×10^8 or 5.5×10^7 s^{-1} in ^{57}Co-labeled Co$_3$[Fe(CN)$_6$]$_2$, and reporting the value of the mean lifetime of the order 10—20 ns.[5] They attributed such fast decay rate to the transition from an electronically excited level in a narrow well of Fe(II) to various kinds of levels in a deep well of [Fe(II)(CN)$_6$]$^{3-}$. Gütlich's group reported that the lifetime of anomalous high-spin species is of the order of 23.0±5.0 ns at 223 K in ^{57}Co-labeled [Co(phen)$_3$](ClO$_4$)$_2\cdot$2H$_2$O, assuming the initial distribution of high-spin Fe(II) equal to that of low-spin Fe(II). On the other hand, no time dependence has been observed on CoO, and CoCl$_2\cdot$4H$_2$O as mentioned in the introduction. It seems likely from the results on many systems reported so far the normal emission spectroscopy that the stabilization of the ^{57}Fe charge state does not depend on the charge state of the parent cobalt atoms in their compounds but on the radiation stability of the neighboring atoms, ligands, and/or anions.[10—15] The present results may suggest that the chemical stability may affect the lifetime of the unstable Fe-species observed by time-resolved Mössbauer spectroscopy. In fact, Fe(II) iodate is very sensitive for oxidation even under nitrogen atmosphere.

In the decay of radioactive nuclide or nuclear transformations, the recoiled atoms are often found in aliovalent states. In the case of ^{57}Co EC-decay, the recoil energy associated with the 122 keV γ-ray emission and neutrino emission (600 keV maximum) are 0.14 and 3.5 eV, respectively, which is smaller than the displacement energy of ^{57}Co atoms in the solid. Then, the initial chemical effects in the EC-decay of ^{57}Co will be the electronic excitation of ^{57}Fe atoms. This excitation is caused by Anger cascade following the EC-decay. The Auger ionization processes have been calculated by Pollak, using Watson wave functions.[16] His result predicts a distribution of charge states ranging from Fe^{2+} to Fe^{7+} with most probability for a Fe^{5+} configuration for free ^{57}Co^{2+} and from Fe^{1+} to Fe^{6+} with a most probability for Fe^{4+} for free neutral ^{57}Co atoms. Highly-charged states other than Fe^{4+}, however, relax rapidly in the solid, even in insulators, and have not been observed with Mössbauer spectroscopy. It seems likely that the neutralization of such highly-charged states is much faster than the Mössbauer time scale. In addition, the initial distribution ratio of ^{57}Fe(II)/^{57}Fe(III)-species at 14.4 keV nuclear level indicated the short-lived ^{57}Fe(II)-species formed through EC-decay exhibits a relatively small distribution even immediately after the emission of 122 keV gamma-rays; i.e., since the second excited state of ^{57}Fe has a lifetime of 12.4 ns, the chemical species once formed and relaxed after the EC-decay can be observed by time-resolved Mössbauer spectrum.

Conclusion

No remarkable differences between X-ray gated and normal spectra were observed, although when a KX-ray is emitted, the total numbers of low energy electrons and vacancies generated by the Auger cascade are about a half compared with those generated when a K-Auger electron is emitted. In the present system, gate signals of 0.5 μs both for X-ray and 14.4 keV γ-ray were used in order to avoid the time filtering effect on the spectrum. It may be reasonable to conclude from the lifetime obtained that the unstable Fe(II)-species will fully relax or decay into the stable Fe(III)-species within the resolving time on X-ray-gated spectrum and that the chemical effects on X-ray emission will produce no remarkable difference in Co(IO$_3$)$_2$. It is also noted that the chemical lifetime and the distribution ratio of ^{57}Fe(II)/^{57}Fe(III) at 14.4 keV nuclear level are closely related to the chemical instability of the corresponding iron compound.

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