Gamma-X Ray Coincidence Mössbauer Study with $FeSO_4 \cdot 7H_2O(^{57}Co)$

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(Received May 24, 1988)

Synopsis. The anomalous charge states formed after the EC decay of ^{57}Co in $FeSO_4 \cdot 7H_2O$ doped with ^{57}Co are investigated in detail using the gamma-X ray coincidence Mössbauer spectroscopy. The mechanism to form these states is explained in terms of the H_2O and SO_4^{2-} coordination shells around the decaying atom.

Anomalous states formed after a nuclear decay in insulating materials (aftereffects) have been usually investigated using the emission Mössbauer spectroscopy.[1-4] In hydrated divalent metallic compounds doped with ^{57}Co, anomalous Fe^{3+} states are usually formed and are considered to be due to the oxidation of Fe^{2+} by free OH radicals produced through radiolysis of the H_2O ligands.[5] This mechanism was examined in detail with cobalt chloride hydrates using the gamma-X ray coincidence Mössbauer spectroscopy,[6] and a determinant role of the nearest and the next nearest H_2O coordination shells according to the densities of H_2O molecules was noticed. In the recent study with metallic sulfate hydrates,[7] the influence of both H_2O and SO_4^{2-} ligands to the aftereffects has been suggested, but its detailed mechanism remains unknown. In the present work, a further investigation of the aftereffects in $FeSO_4 \cdot 7H_2O$ is therefore given using the gamma-X ray coincidence Mössbauer spectroscopy.

The principle of the experiment is based on the fact that the influence of low-energy electrons emitted during the Auger cascade after the EC decay of ^{57}Co on the surroundings of the decaying atom in the K-Auger process is approximately two times larger than that in the case of the K-X ray emission. A Mössbauer spectrum observed by using the coincidence technique only when K-X rays are emitted is, therefore, expected to give new information for the mechanism of the aftereffects on careful comparison with a conventional emission Mössbauer spectrum. More detailed explanations of the principle are described elsewhere.[6,8,9]

A sample of $FeSO_4 \cdot 7H_2O$ doped with ^{57}Co was prepared at room temperature from a very small amount of 0.25 $mol \cdot dm^{-3}$ H_2SO_4 solution of iron(II) sulfate including few μCi of ^{57}Co. The detectors used for 6.5 keV X-rays and 14.4 keV γ-rays were NaI(Tl) crystals with 1-inch diameter and 1-mm thickness. The coincidence spectrum was recorded by the conventional slow coincidence technique. The other experimental details including the block diagram of the measuring system has been given in our previous paper.[6]

The Mössbauer spectra observed and parameters obtained are shown in Fig. 1 and Table 1, respectively. The normal state in $FeSO_4 \cdot 7H_2O$ is represented by $Fe^{2+}(1)$ in Table 1, and the others are anomalous states. Figure 2 shows graphically the relative intensities of the components. The reason why the intensity of $Fe^{2+}(1)$ in the coincidence spectrum is large compared with that in the conventional spectrum can be explained obviously from the experimental principle.

The densities of the H_2O and SO_4^{2-} molecules in $FeSO_4 \cdot 7H_2O$ as a function of distance from the iron atom to the oxygen atom is shown in Fig. 3, which were calculated by considering the structure of the compound.[10] Two distinct coordination shells of H_2O and SO_4^{2-} are noticed at approximately 2 Å and 4 Å, respectively, from the iron atom. The component Fe^{3+} is considered to arise from a free OH radical pro-

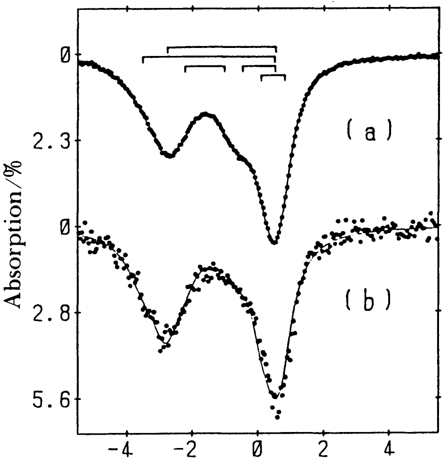

Fig. 1. Observed Mössbauer spectra; (a) conventional, (b) coincidence. The bar diagram represents the individual component peaks.

Table 1. Obtained Mössbauer Parameters of the Conventional and Coincidence Spectra

State	I.S.[a]	Q.S.	[Conventional] Width	[Conventional] Intensity	[Coincidence] Width	[Coincidence] Intensity
	$mm\,s^{-1}$	$mm\,s^{-1}$	$mm\,s^{-1}$	%	$mm\,s^{-1}$	%
$Fe^{2+}(1)$	−1.15±0.01	3.31±0.03	1.01±0.03	32.9	1.10±0.08	51.7
$Fe^{2+}(2)$	−1.52±0.04	3.97±0.06	1.24±0.06	18.4	1.22±0.15	23.7
$Fe^{2+}(3)$	−1.64±0.01	1.22±0.03	1.09±0.02	19.7	0.87±0.16	9.5
Fe^{3+}	−0.02±0.03	0.99±0.06	0.72±0.02	14.9	0.62±0.10	4.0
Fe*	0.43±0.02	0.69±0.02	0.72±0.02	14.1	0.62±0.10	11.1

a) Relative to α-iron at room temperature.

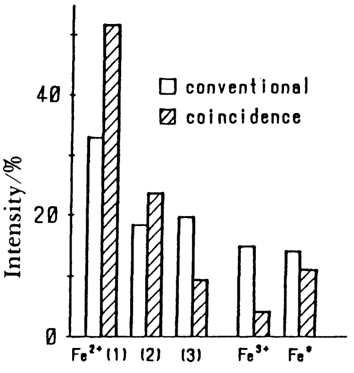

Fig. 2. Relative intensities of the component peaks in the spectra.

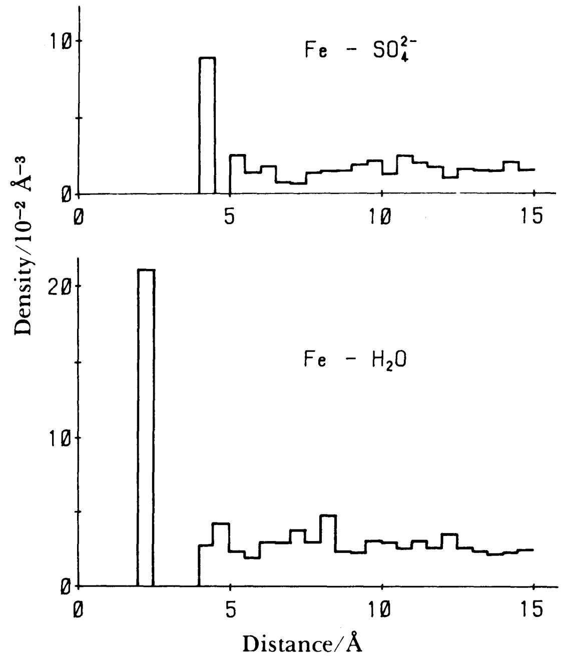

Fig. 3. Densities of H_2O or SO_4^{2-} molecules as a function of distance from a Fe atom in $FeSO_4 \cdot 7H_2O$.

duced through radiolysis of a H_2O ligand in the shell being nearest to the decaying atom, because its intensity in the coincidence spectrum is much smaller than that in the conventional spectrum. The species of Fe* having the unusual value of its isomer shift (I.S.) is unknown, but is probably a high-charged state.

The formation of the Fe^{2+}(2) state can be attributed to the effect of radiolysis of SO_4^{2-} lingands. Owing to a relatively long distance between the decaying atom and a SO_3^- radical produced through radiolysis of a SO_4^{2-} ligand, this radical can hardly oxidize the iron ion which is produced after the decay of ^{57}Co. When this radical recombines with O^-, which is also produced through radiolysis, or remains in its state for a while, the local symmetry around the iron ion becomes lower and this results in a large Q.S. value. It is not easy to show the mechanism of the formation of the Fe^{2+}(3) state, which has a smaller Q.S. value than the other divalent states and a similar I.S. value to the Fe^{2+}(2) component. As in the case of $CoCl_2 \cdot 2H_2O$, where an equivalent component appears,[6] the ligands being further than those in the two H_2O and SO_4^{2-} shells may be involved in the formation of the Fe^{2+}(3) state. The decreased Fe^{2+}(3) intensity in the coincidence spectrum in comparison with that in the conventional spectrum supports this explanation. Owing to the reduction of the flux of low-energy electrons under the coincidence conditions, the number of electrons passing through the H_2O and SO_4^{2-} shells then decreases, which results in a low intensity of the component. The cause of the small Q.S. value of Fe^{2+}(3) compared with that of the other divalent components is unknown.

The results obtained in the present work matches collectively with those of $CoCl_2 \cdot nH_2O$ (n=2,6).[6]

Miss Kazuko Fukumura should be acknowledged for her cooperation in preparing the sample material and in measuring the spectra.

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