Mössbauer Study of ^{60}Co γ-Ray Irradiated $Fe_xMg_{1-x}(NH_4)_2(SO_4)_2 \cdot 6H_2O$

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The γ-ray radiolytic oxidation of Fe^{2+} ions in $Fe_xMg_{1-x}(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (x=1.0, 0.75, 0.56, 0.35, and 0.075) is studied by Mössbauer spectroscopy. For $x \leqq 0.75$, a part of Fe^{2+} ions remain unoxidized even after heavy irradiation of ^{60}Co γ-rays in contrast to the complete disappearance of Fe^{2+} ions for x=1.0. At least three kinds of Fe^{3+} ions are produced, and two of them order magnetically at liquid He temperature. Their saturated relative amount after heavy irradiation depends on the concentration of Fe, and is well explained by the random distribution probability of Fe and Mg ions among the six neighboring metallic sites around the Fe^{2+} ion.

Irradiation of ^{60}Co γ-rays induces oxidation of Fe^{2+} ions in hydrated salts. This phenomenon has been explained by the OH radical mechanism, *i.e.* energetic electrons created by the γ-ray Compton scattering or the photo-electron effect induce OH radicals along their paths from coordination H_2O molecules around Fe^{2+} ions, and these OH radicals oxidize the Fe^{2+} to Fe^{3+} ions.[1–3] A Mössbauer spectroscopic study of the oxidation of Fe^{2+} ions in $FeSO_4 \cdot nH_2O$[1] supported the OH radical mechanism. The oxidation occurs when n is not zero, and the chemical formula of the final radiolytic product was proposed to be $Fe_x(OH)_y(SO_4)_z \cdot nH_2O$,[1] and an accurate formula was later established in the case of $FeSO_4 \cdot 7H_2O$ to be $Fe(OH)(SO_4) \cdot 2H_2O$.[2] Electron and γ-ray irradiation experiments on $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ also indicate radiolysis of the water of crystallization.[4,5] The OH radical mechanism due to the electron capture process of ^{57}Co to ^{57}Fe was also suggested by a Mössbauer experiment on ^{57}Co-doped hydrated salts. However, except for the coordination water, little is known about the effect of the environment around a Fe atom on the oxidation of Fe^{2+} by γ-ray irradiation in a hydrated salt. Even though the water molecules around a Fe^{2+} are necessary to oxidize Fe^{2+} to Fe^{3+} at the primary step of the oxidation process, it is not clear whether their presence itself is sufficient or not for the final stabilization of Fe^{3+} ions in solids.

Besides the studies of the OH radical oxidation, aftereffects of Auger ionization following electron capture were studied[6] using several ^{57}Co-labelled Co(III) complexes having no H_2O molecules. In some cases, depending on the structure of neighboring molecules, Fe(II) states were observed in emission spectra, which led to the conclusion that fragmentation of the parent molecules occurred as a consequence of the Auger ionization. Furthermore, emission spectra of ^{57}Co-labelled Co(III) complexes, containing various anions in the second coordination sphere, revealed that the yield of Fe(II) state was strongly affected by the presence of oxalate anions in the second coordination sphere.[7]

In the present study, a mixed crystal system $Fe_xMg_{1-x}(NH_4)_2(SO_4)_2 \cdot 6H_2O$ was prepared to examine the effect of the environment around a Fe^{2+} ion on its oxidation induced by the γ-ray irradiation. Here, the environment around a Fe^{2+} ion is characterized by a local distribution of Mg^{2+} ions which is expected to be stable under γ-ray irradiation.

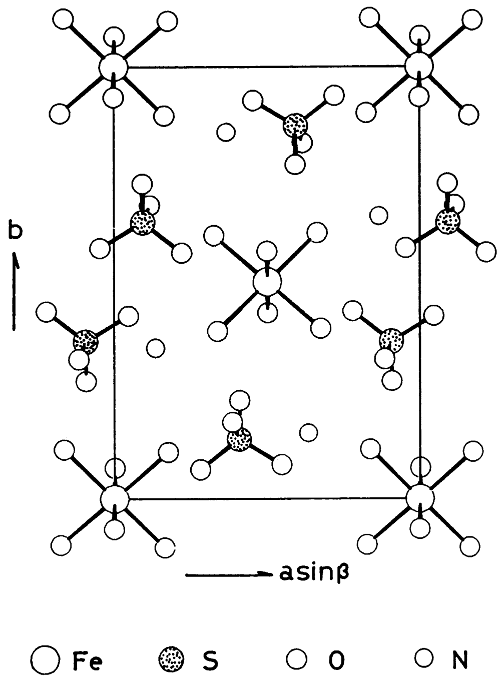

Fig. 1. Crystal structure of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$. The dimensions of the unit cell are a=9.324 Å, b=12.65 Å, c=6.24 Å, and β=106.8°.[8]

The crystal structure of ammonium magnesium sulfate hexahydrate, $Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$, is isomorphous to that of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, and a desired amount of Mg ions can be mixed without changing the monoclinic crystal structure of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$. A unit cell of this crystal is shown in Fig. 1. Each Fe ion in this crystal structure is surrounded by six H_2O, two NH_4, and two SO_4 molecules as first neighbors. Further apart, there are six Fe ions as second neighbors. If only the first neighbors around a Fe^{2+} ion contribute to the stabilization of a Fe^{3+} ion produced by irradiation, the ratio of Fe^{2+} to the induced Fe^{3+} ions should remain constant after the same irradiation dose, independent of a different Mg concentration. Therefore, if the ratio of Fe^{2+} to Fe^{3+} ions is found to change with the concentration of Mg ions, we can say that the stablization of the induced Fe^{3+}

ions are affected by the second neighboring Mg, Fe ions, or other molecules.

Experimental

Mixed crystals of $Fe_xMg_{1-x}(NH_4)_2(SO_4)_2 \cdot 6H_2O$ were prepared by dissolving commercially available reagents of x amount of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and $1-x$ amount of $Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$ into water for x=1.0, 0.8, 0.6, 0.4, and 0.1. Concentrations of Fe in the precipitated mixed crystals from saturated solution at room temperature were determined by chemical analysis to be 0.75, 0.56, 0.35, and 0.075 for x=0.8, 0.6, 0.4, and 0.1, respectively. The observed X-ray diffraction patterns of the mixed crystals were equivalent to that of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$. The mixed polycrystals were irradiated by ^{60}Co γ-rays at temperatures below 42 °C in loosely sealed glass tubes. The ^{60}Co γ-ray irradiation was accomplished up to 5.23×10^9 rad(H_2O). The dose rate was between 2.80 and 2.93×10^6 rad(H_2O)/h.

After being irradiated with the desired amount of dose, a part of each specimen was separated from the glass tube and mixed with vacuum grease for the Mössbauer spectroscopic analysis. After the heavy irradiation, the specimens were broken to fragile blocks, and the specimen with x=1.0 slightly moistened. Their colors were white or yellow-brown depending on the concentration of Fe ions. After an irradiation of 5.23×10^9 rad(H_2O), $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ crystals turned almost totally to blocks of transparent acicular crystals. The dimensions of each crystal were about 0.01 mm in diameter and 0.2 mm in length.

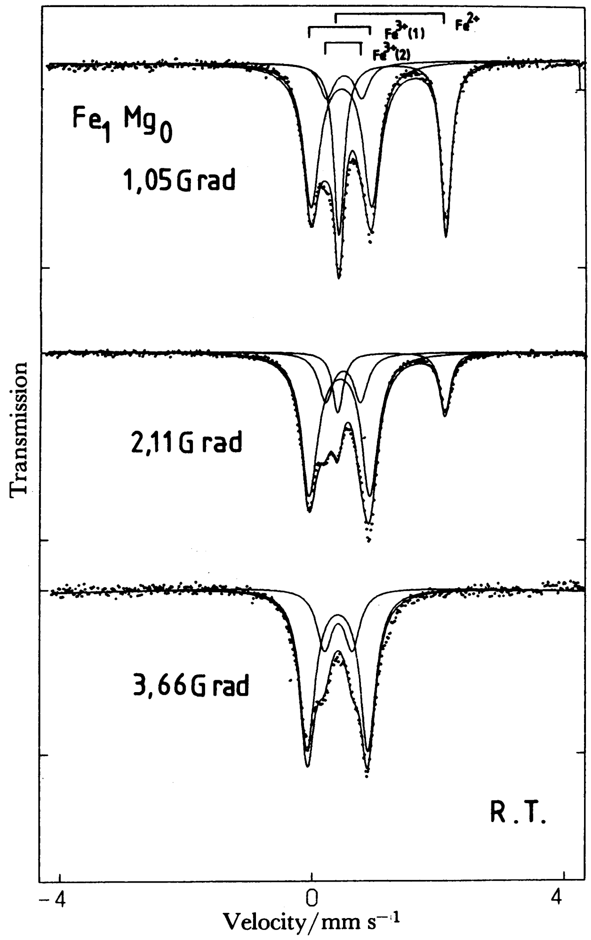

Fig. 2. Mössbauer spectra of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ irradiated by ^{60}Co γ-rays. The solid lines are the calculated absorption peaks.

Results

Measurements of the Mössbauer spectra of the irradiated samples were made mainly at room temperature, and partly at liquid N_2 and liquid He temperatures. The Mössbauer spectra were analyzed by a computer processing which includes least squares fitting of Lorentzian curves to the experimental absorption peaks, with a correction for the base-line sag. The same recoilless fraction was assumed for all the Fe ions. The assignments for Fe^{3+} in the following are based on the values of the isomer shifts of the corresponding absorption peaks.

$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$: The Mössbauer spectra of the irradiated $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ specimens measured at room temperature are shown in Fig. 2. The fitted absorption peaks are shown in the figure by the solid curves. Before irradiation, only the quadrupole-split peaks of Fe^{2+} were observed. The Fe^{3+} peaks are successfully analyzed under an assumption of two kinds of quadrupole-split peaks(Fe^{3+} (1) and Fe^{3+} (2)). The Fe^{2+} peaks disappeared completely on heavy irradiation above 3.66×10^9 rad(H_2O), and no changes were observed in the Mössbauer spectra by further irradiation up to 5.23×10^9 rad(H_2O). The Mössbauer spectrum of a sample irradiated to 5.23×10^9 rad(H_2O) was also measured at 4.2 K and shown in Fig. 3a. The peaks of Fe^{3+} radiolytic products in this specimen can be resolved at least into three components, and two of them are in magnetically ordered states. The major component denoted by Fe^{3+} (1a) evidently corresponds to the recognized acicular small crystals. The minor component denoted by Fe^{3+} (1b) in the figure was not resolved in the room-temperature spectrum, and is considered to be included in the Fe^{3+} (1) component. The values of the hyperfine magnetic fields and other Mössbauer parameters are tabulated in Table 1, together with those at room temperature.

The total amount of Fe^{3+} approaches nearly exponentially to a constant value in relation to the γ-ray dose. From the Fe^{3+}/Fe ratio determined by the computer fitting, the G value (the number of Fe^{3+} ions produced for each 100 eV of energy absorbed) is evaluated to be 2.65 ± 0.35 for the ^{60}Co γ-ray dose below 2.7×10^9 rad(H_2O); the ratio of the atomic number Z to the mass number A for the specimen and that for water were used to estimate the absorbed dose in the specimen.

The effect of humidity on the oxidation was examined in some cases. A specimen in a sealed tube with CaO as desiccant was irradiated. After an irradiation of 1.1×10^9 rad, the remaining Fe^{2+} peak became broad and the amount of Fe^{3+} was markedly higher, *i.e.* Fe^{2+}/Fe was lower in comparison with the irradiation

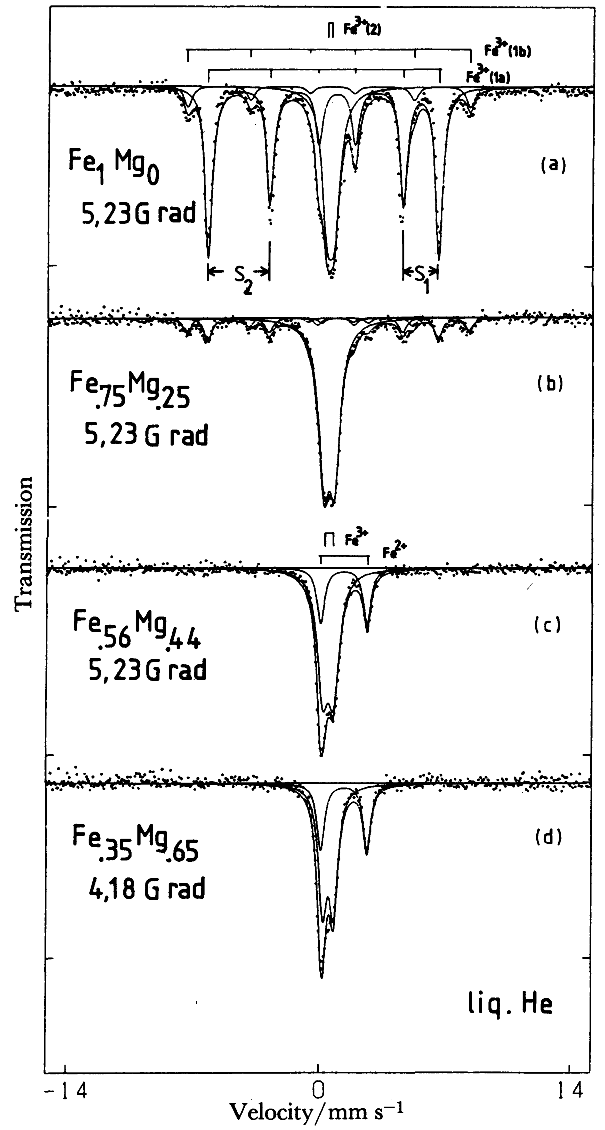

Fig. 3. Mössbauer spectra of γ-ray irradiated $Fe_xMg_{1-x}(NH_4)_2(SO_4)\cdot 6H_2O$ measured at 4.2 K.

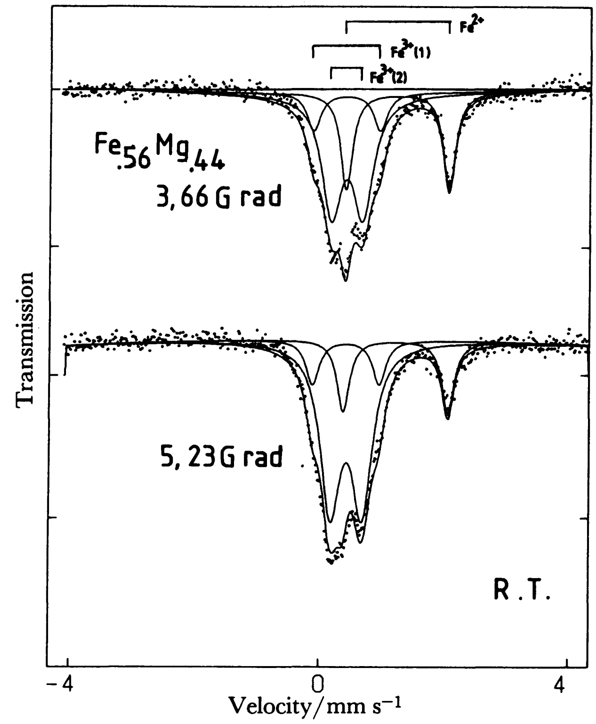

Fig. 4. Mössbauer spectra of γ-ray irradiated $Fe_{0.56}Mg_{0.44}(NH_4)_2(SO_4)_2\cdot 6H_2O$ measured at room temperature.

in air (see Fig. 6). On the contrary, the Fe^{2+}/Fe ratio was higher when a specimen was irradiated together with a small amount of water.

$Fe_xMg_{1-x}(NH_4)_2(SO_4)_2\cdot 6H_2O$: The Mössbauer spectra of the irradiated mixed crystals with x= 0.56 and x=0.075 measured at room temperature are shown in Figs. 4 and 5, respectively. The Fe^{2+} quadrupole splitting of x=0.075 is 2% smaller than that of x=1.0. All spectra were analyzed by assuming two Fe^{3+} components (Fe^{3+}(1) and Fe^{3+}(2)). The best fitted values of the quadrupole splitting and the isomer shift of Fe^{3+}(2) were not the same for all the spectra and distributed to some extent as tabulated in Table 1. In the case of the specimen with x=0.56, some of the Fe ions retain the Fe^{2+} state even after the irradiation of 5.32×10^9 rad(H_2O) which was sufficient in the case of $Fe(NH_4)_2(SO_4)_2\cdot 6H_2O$ to change all Fe^{2+} ions to Fe^{3+}. The suppression of the radiolytic oxidation of Fe^{2+} ions is more significant for x=0.075 as can be seen in Fig. 5. Almost 85% of Fe ions still remain in the Fe^{2+} state after an irradiation of 2.8×10^9 rad(H_2O). The ratio of the remaining Fe^{2+} to the total Fe *versus* the γ-ray dose is plotted in Fig. 6. It should be noted that the Fe^{2+}/Fe ratios measured at liquid N_2 temperature agreed with those at room temperature within 5%. Then, the assumption that Fe^{2+} and Fe^{3+} ions have the same recoilless fraction is fairly good. It is characteristic that all the curves for the Fe^{2+}/Fe ratios are saturated. The

TABLE 1. MÖSSBAUER PARAMATERS OF γ-IRRADIATED $Fe_xMg_{1-x}(NH_4)_2(SO_4)_2\cdot 6H_2O$

Component	T / K	ΔE_Q / mm s⁻¹	δ(Fe)[a] / mm s⁻¹	H_{hf} / kOe	4ε[b] / mm s⁻¹
Fe^{2+}	300	1.71±0.03(x=1.0) 1.67±0.03(x=0.1)	+1.25±0.02		
Fe^{3+}(1)	300	0.96±0.03	+0.42±0.03		
(1a)	4.2		+0.24±0.02	396.3	−1.41
(1b)	4.2		+0.24±0.02	485.8	−0.36
Fe^{3+}(2)	300	0.35—0.45	+0.40—+0.45		
Fe^{3+}(3)	300	0.19±0.03	+0.36±0.03		

a) Relative to metallic iron. b) $4\varepsilon = S_1 - S_2$; for the definitions of S_1 and S_2, see Fig. 3a.

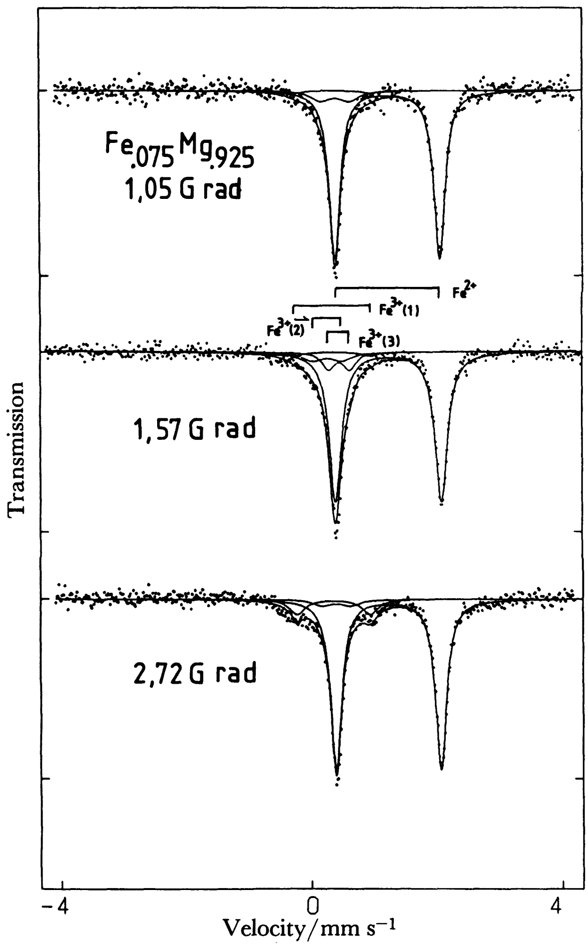

Fig. 5. Mössbauer spectra of γ-ray irradiated mixed crystal $Fe_{0.075}Mg_{0.925}(NH_4)_2(SO_4)_2\cdot 6H_2O$ measured at room temperature.

saturated final value of the Fe^{2+}/Fe ratio is lower for higher concentration of Fe ions.

Figure 3b shows a spectrum of the specimen with x=0.75 measured at 4.2 K after an irradiation of 5.23× 10^9 rad(H_2O). The Fe^{3+}(1) component having a large quadrupole splitting at room temperature orders magnetically, but the rest of the Fe^{3+}(2) having a smaller splitting does not. The room-temperature Mössbauer spectrum of x=0.56 contains a small amount of the Fe^{3+}(1) component. However, no magnetically split peaks were observed at 4.2 K for this specimen (see Fig. 3c). This can be ascribed to the weak intensities of these absorption peaks.

Discussion

The Mössbauer spectra of the mixed crystals Fe_x-$Mg_{1-x}(NH_4)_2(SO_4)_2\cdot 6H_2O$ show that the relative amount of the Fe^{3+} radiolytic products to the total Fe varies remarkably with the concentration of Mg ions. The evaluated absorbed dose in each mixed crystal from the Z/A ratio different slightly from one another, but their mutual deviations are only within 2%. Thus the large differences in the saturated ratios of the remaining Fe^{2+} to the total Fe (Fig. 6) can not be explained by these slight differences between the absorbed doses in the mixed crystals.

We notice that there are two kinds of Fe^{3+} (Fe^{3+}(1) and Fe^{3+}(2)) in the spectra shown in Figs. 2—4; one of them orders magnetically at 4.2 K and another does not. There is a possibility of another Fe^{3+} component (Fe^{3+}(3)) to exist, which has a much smaller quadrupole splitting, in the spectra of x=0.075 and 0.35, because its addition is effective in obtaining a better fitted spectrum as shown in Fig. 5; this component does not order magnetically at 4.2 K.

In Fig. 7, the summed saturated ratio of the magnetically ordered components (Fe^{3+}(1)=Fe^{3+}(1a)+Fe^{3+}(1b)) to the total Fe, and that of the rest Fe^{3+} (Fe^{3+}(2,3)) are plotted separately. We can analyze the behavior of these ratios as follows. Since the ratios depend on the Fe concentration, the spacial statistical average for the distribution of Fe in the mixed crystal seems to be related to these ratios. Assuming a random distribution of Fe and Mg atoms among the simple cubic lattice, we can estimate the probability that we find N or more than N Fe atoms within a sphere with radius

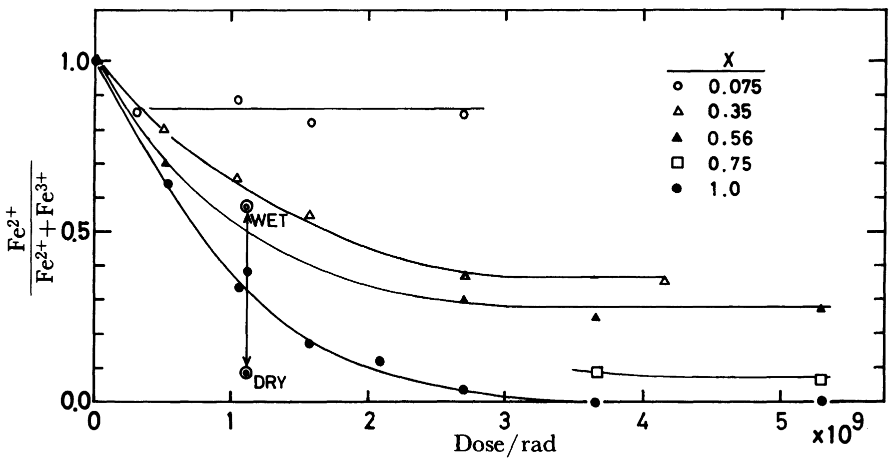

Fig. 6. Fe^{2+}/Fe ratios determined by the calculated Mössbauer absorption intensities. The notations WET and DRY for x=1.0 denote the specimens irradiated with water and CaO, respectively.

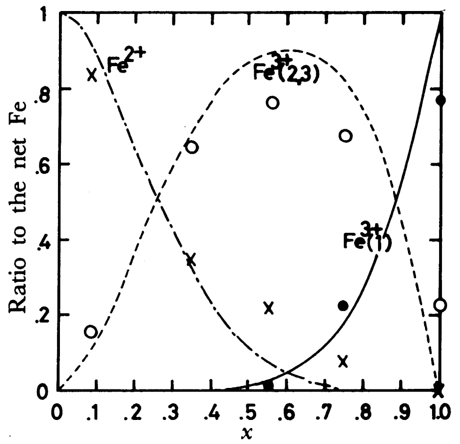

Fig. 7. The ratios of the saturated amount of Fe^{3+} ions induced by γ-ray irradiation and the remaining Fe^{2+} ions. The notations $Fe^{3+}(1)$ and $Fe^{3+}(2,3)$ denote the magnetically ordered component and the rest one, respectively.

R around an Fe atom. Figure 8 shows the concentration dependence of this probability. The unit of the radius is the lattice constant of the simple cubic lattice. The change of the probability becomes steep as the radius increases, that is, as the number of the sites in the sphere increases. The observed ratios shown in Fig. 7 change rather gradually against the Fe concentration. Then the effective local environment, which is considered to be related to the formation of stable Fe^{3+} ions, is best characterized by the probability for $R=1.0$. This means that only the neighboring six metallic-ion sites are strongly related to the radiolysis of a Fe atom.

Using the probability for $R=1.0$, we can interpret the saturated ratios of the remaining Fe^{2+}, $Fe^{3+}(1)$, and $Fe^{3+}(2,3)$. When a Fe^{2+} is initially surrounded by six or five Mg ions ($N<2$), this Fe^{2+} ion cannot be oxidized into a stable Fe^{3+} ion by the ^{60}Co γ-ray irradiation (dot-dashed curve: $N=2$ curve of Fig. 8(a) being inverted), even though water molecules exist as the nearest neighbors. The ratio of the $Fe^{3+}(2,3)$ components can be explained by the total probability that any number of Fe ions from 2 to 5 initially occupies the neighboring six metallic-ion sites (dashed curve: the vertical distance from the curve 2 to 6 of Fig. 8a). The distributed values of the quadrupole splitting of $Fe^{3+}(2,3)$ component as mentioned in Table 1 reflect the occurrence of the different sites of this component. Furthermore, if the neighboring six metallic ion sites around a Fe^{2+} ion are initially all occupied by Fe ions, this Fe^{2+} ion is oxidized and has a possibility to recrystallize into the new compounds denoted by $Fe^{3+}(1)$. The calculated probability is shown in the figure by a solid curve.

The above proposed interpretation implies that the Fe^{3+} ions are stabilized only when more than one Fe^{3+} states are produced among the neighboring six sites at the same time or within the relaxation time of Fe^{3+} states, and these Fe^{3+} states are probably stabilized by constituting a Fe^{3+} ion cluster. In a low Fe concentration region, these clusters are considered to be created isolatedly, and Fe^{3+} ions ($Fe^{3+}(2,3)$) in the clusters cannot be in a magnetically ordered state, at least above 4.2 K. In a high Fe concentration region, $x>0.5$, a part of the created clusters can segregate new Fe^{3+} compounds (Fe^{3+}(1a,1b)), because the original mixed crystal possesses many paths which connect Fe ions without interruption by Mg ions. According to the percolation theory, the percolation probability of the simple cubic lattice is 0.254 for the site property.[9]

This simple model, however, does not completely explain the observed ratios; fairly large Fe^{2+} ratios above $x=0.5$, and the existence of the nonmagnetic component at $x=1.0$. It should be emphasized that the proposed model describes only the initial circumstance around a Fe^{2+} ion, and does not specify the process of recrystallization of the material, which will occur

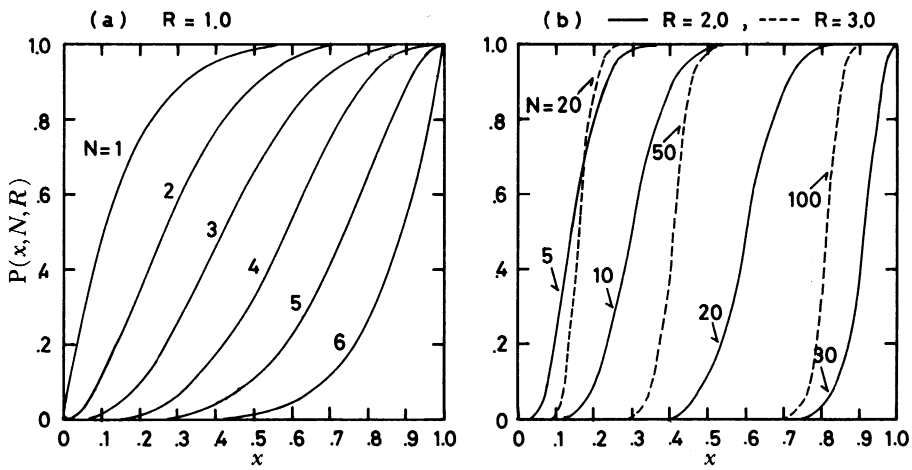

Fig. 8. The probabilities that N or more than N Fe atoms are found in a sphere of radius R. Fe atoms with a concentration of x are assumed to be dispersed at random on the simple cubic lattice sites. (a) $R=1.0$, and the number of the lattice sites in the sphere, N_s, is 6. (b) solid curves; $R=2.0$ and $N_s=32$, dashed curves; $R=3.0$ and $N_s=122$.

during irradiation for several months. Therefore, during recrystallization, the model-calculated ratios of Fe^{3+} ions will be modified. As mentioned above, humidity evidently affected the formation of the Fe^{3+} compound. Particularly, when the initial amount of water of crystallization is not the same as the final one, as it probably is in the present case, excess water molecules will play an important role in the recrystallization process, which act to suppress the formation of Fe^{3+} ions. The amount of the remaining Fe^{2+} ions above x=0.5, which is larger than the model-calculated value, seems to be due to this excess water. Thus, the final amount of Fe^{3+} ions is the result of at least two competitive processes; the OH radical process which is considered to be an important mechanism at the primary step of the radiolysis, and the following recrystallization process.

The radiolytic chemical reaction which produces Fe^{3+}(1a) component from $Fe(NH_4)_2(SO_4)_2\cdot 6H_2O$ is considered to be

$$Fe(NH_4)_2(SO_4)_2\cdot 6H_2O \rightsquigarrow$$

$$Fe(NH_4)_2(OH)(SO_4)_2\cdot nH_2O + 1/2H_2 + (5-n)H_2O, \quad (n < 5),$$

because i) the radiolytic product did not have an odour of ammonia, and ii) SO_4 molecules are not separated by the γ-ray irradiation in the case of $FeSO_4\cdot 7H_2O$. The measured X-ray diffraction pattern of the radiolytic product from $Fe(NH_4)_2(SO_4)_2\cdot 6H_2O$ could not be found in the X-ray powder diffraction file.[10] To the authors' knowledge, a material having the chemical formula $Fe(NH_4)_2(OH)(SO_4)_2\cdot nH_2O$ is not known.

Conclusion

The ^{60}Co γ-ray irradiation induced the oxidation of Fe^{2+} ions in a mixed salt $Fe_xMg_{1-x}(NH_4)_2(SO_4)_2\cdot 6H_2O$ (x=1.0, 0.75, 0.56, 0.35, and 0.075). At least three kinds of Fe^{3+} states were clearly observed, and the relative saturated amount of the induced Fe^{3+} ions to the total Fe ions in each mixed salt varied remarkably with the concentration of Mg ions. This phenomenon can not be explained only by the presence of the coordination water. The simple six-neighbor metallic site model, which represents the effective initial environment around a Fe^{2+} ion, well explains the characteristic concentration dependence of the saturated amounts of these Fe^{3+} radiolytic products. This result suggests that the initial environment, which includes only the neighboring six metallic ion sites around a Fe^{2+} ion, strongly affects the formation of the final Fe^{3+} products from this mixed hydrated salt. It is interpreted that the induced Fe^{3+} states are only stabilized when more than one Fe^{3+} ions are produced among the neighboring six sites at the same time or within the relaxation time of Fe^{3+} states, and these Fe^{3+} states are probably stabilized by constituting a Fe^{3+} cluster. In a high Fe concentration region, these clusters can segregate new Fe^{3+} compounds. However, to clarify the discrepancy between the model-calculated ratios and the experimental ones, more detailed consideration on the recrystallization process is required.

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