# Formation of Cadmium, Zinc-bearing Ferrites in Aqueous Suspension by Air Oxidation

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Slightly oxidized cadmium, zinc-bearing and cadmium-bearing ferrites have been prepared by air oxidation of iron(II) hydroxide suspensions at initial (Cd + Zn):$Fe_{tot}$ mol ratios ($r_{Cd+Zn}$) of 0.10:2.90–1.00:2.00 at pH 10.0 and 65 °C. The upper limit of Cd:$Fe_{tot}$ mol ratio in the ferrites was found to be about 0.1:1, and for each Zn:(Cd + Zn + $Fe_{tot}$) mol ratio in the suspensions upper limits were also found, respectively. The lattice constant $a_0$ and Mössbauer spectra at room temperature of the cadmium, zinc-bearing ferrites suggested that at $Cd^{2+}$:$Zn^{2+}$ mol ratios of $\leqslant$0.12:0.43 at the tetrahedral sites the crystal structure of the ferrites prepared at $r_{Cd+Zn}$ = 1.00:2.00 is that of zinc-bearing ferrites and approaches that of cadmium-bearing ferrites with increasing $Cd^{2+}$:$Zn^{2+}$ mol ratio. Also that at $r_{Cd+Zn}$ = 0.10:2.90–0.80:2.20, homogeneous mixtures of $CdFe_2O_4$–$Fe_3O_4$ and $ZnFe_2O_4$–$Fe_3O_4$ solid solutions are formed.

The formation of cadmium- and zinc-bearing ferrites by air oxidation of aqueous iron(II) hydroxide suspensions in the presence of cadmium and zinc ions respectively has been investigated previously.[1,2] The cadmium content in the cadmium-bearing ferrites formed at pH 9.0 and 65 °C increases with increase in the Cd:$Fe_{tot}$ mol ratio in the suspensions, but becomes constant above 0.1:1.0.[1] The stoichiometric zinc-bearing ferrites are formed in suspensions having Zn:$Fe_{tot}$ mol ratios ranging from 0.030:1.00 to 0.50:1.00 (except for 0.060:1.00) at pH 10.0 and 65 °C, but at 0.060:1.00 only α-FeO(OH) is formed.[2]

In this paper we report the formation of cadmium, zinc-bearing ferrites by air oxidation of aqueous iron(II) hydroxide suspensions containing both cadmium and zinc ions. The formation of cadmium-bearing ferrites in the suspensions in the presence of cadmium ion was also investigated.

## Experimental

*Reagents.*—Analytical grade reagents were used. Sodium hydroxide solutions were prepared by use of distilled water free from carbon dioxide and oxygen. A 0.863 mol $dm^{-3}$ cadmium sulfate solution was prepared from $CdSO_4{\cdot}7H_2O$.

*Procedure.*—A Dewar-type reaction vessel (capacity 2 $dm^3$) with a glass cover was used.[3] Distilled water, 0.5 mol $dm^{-3}$ sulfuric acid solution, cadmium sulfate solution, zinc sulfate heptahydrate, and sodium sulfate were transferred to the reaction vessel and nitrogen gas was bubbled into the rapidly stirred (600 revolutions $min^{-1}$) solution for 1 h to remove the dissolved $CO_2$ and oxygen. Then, iron(II) sulfate heptahydrate was added (total amount of iron, zinc and cadmium 0.4316 mol). The pH was adjusted to 10.0 by addition of solutions containing either 2 or 5 mol $dm^{-3}$ sodium hydroxide. The volume of the suspension was made up to 2.00 $dm^3$ and the total concentration of sulfate ion was fixed (0.375 mol $dm^{-3}$). The suspension was left to stand under nitrogen for 1 h at 65 °C with constant stirring. We call this suspension the 'initial suspension'. Air was passed through it at a rate of 0.2 $dm^3$ $min^{-1}$. During oxidation the pH was kept constant at 10.0 by the addition of a 0.2 mol $dm^{-3}$ solution of sodium hydroxide, and the oxidation potential was measured. The oxidation was stopped 10 min after the abrupt change in this parameter. The procedures were described in detail by Kaneko and Katsura.[3]

The product was obtained by lowering the pH of the suspension to 4.0 with 0.5 mol $dm^{-3}$ sulfuric acid after the air oxidation. At this pH, the hydroxides of cadmium, zinc and iron(II) dissolve completely.

*X-Ray Powder Diffraction Measurements.*—X-Ray powder diffraction patterns were obtained using manganese-filtered Fe-Kα radiation. The 2θ angles of the diffraction peaks were calibrated against standard silicon powder by using the Fe-$K\alpha_1$ radiation.

*Mössbauer Spectroscopic Measurements.*—Iron-57 Mössbauer spectra were obtained at room temperature using cobalt-57 radiation with an electromechanical transducer operating in constant-acceleration mode in conjunction with a 512-channel analyser. The velocity scale was calibrated using the hyperfine spectra of a natural α-iron foil at room temperature, which also served as the isomer shift reference.

*Chemical Analysis.*—The solid samples (200 mg) of the products were dissolved in 9 mol $dm^{-3}$ sulfuric acid. By this procedure the $Fe^{II}$:$Fe^{III}$ mol ratio was maintained.[4] The amounts of cadmium and zinc were determined within 1% by atomic absorption spectrometry. The amounts of iron-(II) and -(III) were determined by titration[4] with a 0.005 mol $dm^{-3}$ standard solution of potassium permanganate (determination limit 7 × $10^{-6}$ mol; corresponding to an estimation limit of 0.01 for $Fe^{2+}$ or $Fe^{3+}$ in the composition of the ferrites). The oxygen content was estimated by subtracting the weights of cadmium, zinc and/or iron from the total weight of the solid sample.

## Results and Discussion

*Formation of* Cd,Zn-*Bearing Ferrites in Iron*(II) *Hydroxide Suspensions at Initial* (Cd + Zn):$Fe_{tot}$ *Mol Ratios* ($r_{Cd+Zn}$) *of* 0.10:2.90–1.00:2.00.—The electron micrographs of the products obtained from the suspension at initial Zn:$Fe_{tot}$ mol ratios of 0.80:2.00 and above showed the formation of spherical or cubic particles of a spinel-type compound, and at ratios below 0.80:2.00 showed in addition a small amount of needle-like crystals of α-FeO(OH). In the X-ray powder diffraction

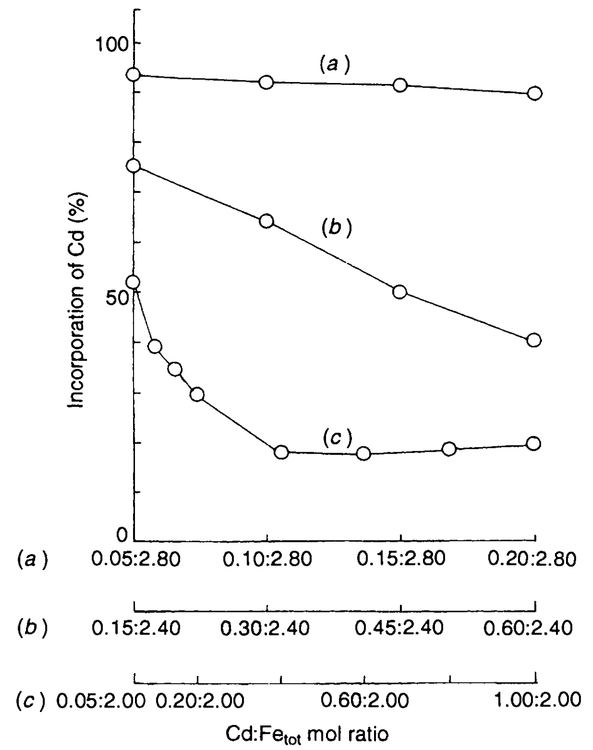

**Fig. 1** Variation of the percentage incorporation of cadmium into cadmium,zinc-bearing ferrites with Cd:Fe$_{tot}$ mol ratio in the initial suspension. Curves (*a*), (*b*) and (*c*) represent the oxidation reactions at initial (Cd + Zn):Fe$_{tot}$ mol ratios ($r_{Cd+Zn}$) of 0.20:2.80, 0.40:2.60 and 1.00:2.00 respectively

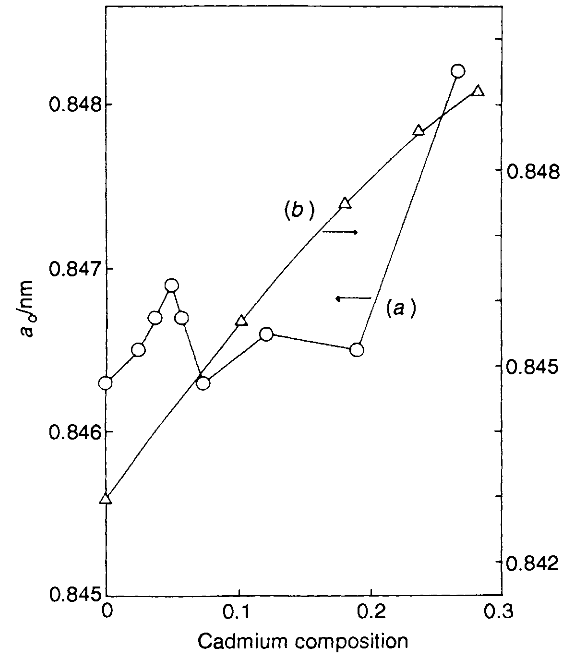

**Fig. 2** Variation of the lattice constant of cadmium, zinc-bearing ferrites with cadmium composition. Curves (*a*) and (*b*) represent the variations for the ferrites obtained at initial (Cd + Zn):Fe$_{tot}$ mol ratios ($r_{Cd+Zn}$) of 1.00:2.00 and 0.60:2.40, respectively. Error for the lattice constant ±0.0001 nm

**Table 1** Chemical composition of the Cd,Zn-bearing ferrites

| Initial suspension | | Chemical composition* | | | |
|---|---|---|---|---|---|
| (Cd + Zn):Fe$_{tot}$ mol ratio, $r_{Cd+Zn}$ | Cd:Zn mol ratio | Cd | Zn | Fe$^{2+}$ | Fe$^{3+}$ |
| 0.10:2.90 | 0.00:0.10 | | 0.09 | 0.73 | 2.12 |
| | 0.025:0.075 | 0.02 | 0.07 | 0.72 | 2.17 |
| | 0.05:0.05 | 0.05 | 0.05 | 0.69 | 2.07 |
| | 0.075:0.025 | 0.06 | 0.03 | 0.71 | 2.05 |
| | 0.10:0.00 | 0.08 | | 0.66 | 2.00 |
| 0.20:2.80 | 0.00:0.20 | | 0.18 | 0.68 | 2.06 |
| | 0.05:0.15 | 0.04 | 0.13 | 0.64 | 2.00 |
| | 0.10:0.10 | 0.09 | 0.09 | 0.65 | 2.01 |
| | 0.15:0.05 | 0.13 | 0.05 | 0.64 | 2.00 |
| | 0.20:0.00 | 0.17 | | 0.65 | 2.01 |
| 0.40:2.60 | 0.00:0.40 | | 0.37 | 0.52 | 2.04 |
| | 0.10:0.30 | 0.09 | 0.27 | 0.51 | 1.99 |
| | 0.20:0.20 | 0.17 | 0.18 | 0.51 | 1.98 |
| | 0.30:0.10 | 0.23 | 0.09 | 0.51 | 1.93 |
| | 0.40:0.00 | 0.27 | | 0.56 | 2.03 |
| 0.60:2.40 | 0.00:0.60 | | 0.53 | 0.35 | 1.91 |
| | 0.15:0.45 | 0.10 | 0.39 | 0.35 | 1.85 |
| | 0.30:0.30 | 0.18 | 0.26 | 0.36 | 1.89 |
| | 0.45:0.15 | 0.24 | 0.15 | 0.49 | 2.02 |
| | 0.60:0.00 | 0.28 | | 0.62 | 2.18 |
| 0.80:2.20 | 0.00:0.80 | | 0.72 | 0.18 | 1.83 |
| | 0.40:0.40 | 0.17 | 0.40 | 0.34 | 2.01 |
| | 0.80:0.00 | 0.30 | | 0.61 | 2.18 |
| 1.00:2.00 | 0.00:1.00 | | 0.90 | 0.13 | 1.84 |
| | 0.05:0.95 | 0.03 | 0.83 | 0.11 | 1.80 |
| | 0.10:0.90 | 0.04 | 0.83 | 0.13 | 1.80 |
| | 0.15:0.85 | 0.05 | 0.75 | 0.14 | 1.79 |
| | 0.20:0.80 | 0.06 | 0.73 | 0.17 | 1.79 |
| | 0.40:0.60 | 0.07 | 0.58 | 0.24 | 1.84 |
| | 0.60:0.40 | 0.12 | 0.43 | 0.35 | 1.93 |
| | 0.80:0.20 | 0.19 | 0.24 | 0.49 | 2.02 |
| | 1.00:0.00 | 0.27 | | 0.63 | 2.06 |

* For all ferrites value for oxygen is 4.00.

patterns of the products only the peaks for the spinel-type structures were seen. These facts indicate that almost all the products (>95%) are spinel-type compounds. Chemical analysis of the products showed that almost all the zinc in the initial suspension (>91%) was incorporated in the spinel-type compounds; 18–98% of the cadmium was also taken up. This indicates that the spinel-type compounds are Cd,Zn-bearing ferrites. The percentage incorporation of cadmium decreased with increasing Cd:Fe$_{tot}$ (except for 0.40–1.00:2.00, $r_{Cd+Zn}$ = 1.00:2.00) or Zn:Fe$_{tot}$ mol ratio in the initial suspension (Fig. 1), and the upper limit of Cd:Fe$_{tot}$ mol ratio in the ferrites was about 0.1:1. At Cd:Fe$_{tot}$ mol ratios ranging from 0.40 to 1.00:2.00 ($r_{Cd+Zn}$ = 1.00:2.00) in the initial suspension the percentage incorporations are approximately constant. On the other hand, the oxidation reactions in the suspensions at constant Zn:(Cd + Zn + Fe$_{tot}$) mol ratios indicated the upper limits of Cd:Fe$_{tot}$ mol ratio, *i.e.* for Zn:(Cd + Zn + Fe$_{tot}$) mol ratios of 0.40, 0.80 and 0.90:3.00 the upper limits of Cd:Fe$_{tot}$ mol ratios are 0.053, 0.030 and 0.020:1.00, respectively.

The chemical compositions of the Cd,Zn-bearing ferrites (Table 1) show that the total compositions of the divalent cations, $Cd^{2+} + Zn^{2+} + Fe^{2+}$, are in the range 0.74–0.97 (except for 1.00 at an initial Cd:Zn mol ratio of 0.10:0.90). This suggests that slightly oxidized Cd,Zn-bearing ferrites are formed by air oxidation of iron(II) hydroxide suspensions in the presence of cadmium and zinc ions.

*Lattice Constants of the* Cd,Zn-*Bearing Ferrites*.—The lattice constants, $a_0$, of the Cd,Zn-bearing ferrites prepared from the iron(II) hydroxide suspensions at $r_{Cd+Zn}$ = 1.00:2.00 are plotted against the cadmium compositions of the ferrites in Fig. 2 (*a*). They increase with increasing cadmium compositions in the range 0–0.05, followed by a decrease and an abrupt increase above 0.19. Yagnik and Mathur[5] reported that the lattice constants of Cd,Zn-bearing ferrites $Cd_xZn_yFe_{3-(x+y)}O_4$ ($x + y = 1$) prepared by a solid-state reaction increased gradually with increasing cadmium composition in the range 0–0.5, followed by an abrupt increase. For cadmium compositions of 0–0.05, the sum of the cadmium and zinc compositions of the Cd,Zn-bearing ferrites is in the range 0.90–0.80. The increase in the lattice constants with increase in the cadmium compositions ranging from 0 to 0.05 is explained by the results of Yagnik and Mathur.[5] The variation of the lattice constants with cadmium compositions ranging from 0.06 to 0.19 is caused by both the limit in incorporation of $Cd^{2+}$ ions into the lattice sites of the ferrites and the decrease in $Zn^{2+}$ ions at the lattice sites. The abrupt increase in the lattice constant above a cadmium composition of 0.19 is explained by an increase in $Cd^{2+}$ ions at the lattice sites as described later.

On the other hand, the lattice constants $a_0$ of the Cd,Zn-bearing ferrites prepared from iron(II) hydroxide suspensions at $r_{Cd+Zn} = 0.10{:}2.90–0.80{:}2.20$ increased with increasing cadmium compositions of the ferrites [Fig. 2(*b*) shows the variation for ferrites obtained at $r_{Cd+Zn} = 0.40{:}2.60$]. Similar variation of the lattice constants with cadmium composition for Cd-bearing ferrites is described later and was also reported by Bhaduri.[6]

*Room-temperature Mössbauer Spectra of the* Cd,Zn-*Bearing Ferrites*.—Room-temperature Mössbauer spectra of the Cd,Zn-bearing ferrites prepared from iron(II) hydroxide suspensions at $r_{Cd+Zn} = 1.00{:}2.00$ are shown in Fig. 3. The spectra were analysed by a least-squares fit computer program.[7] The results are shown in the Figure by solid lines and Mössbauer parameters are listed in Table 2. Area fractions were calculated from the peak areas estimated using the least-squares fit by assuming that the non-recoilless fractions for the different spectra are equal. The spectra of the ferrites having cadmium compositions in the range 0–0.5 show a paramagnetic pattern B′ arising from $Fe^{3+}$ ions on the octahedral sites.[8–10] This fact suggests that almost all $Fe^{3+}$ ions on the tetrahedral sites are replaced by $Cd^{2+}$ and $Zn^{2+}$ ions, and is in good agreement with the variation of the lattice constants with the cadmium composition described above.

The Mössbauer spectra for the ferrites having cadmium compositions of $\geqslant 0.06$ in addition show a hyperfine splitting pattern. Such patterns for ferrites of cadmium compositions $\geqslant 0.12$ were analysed as patterns A and B arising from $Fe^{3+}$ ions on the tetrahedral sites, and the sum of the $Fe^{2+}$ and $Fe^{3+}$ ions on the octahedral sites.[8] The area fractions of the hyperfine splitting pattern A increase with increasing cadmium compositions of the ferrite. This suggests a decrease in incorporation of $Cd^{2+}$ and $Zn^{2+}$ ions into the tetrahedral sites, and supports the limit of incorporation of Cd into the ferrites.

The values of the quadrupole splitting, Δ, for the paramagnetic pattern B′ are constant for cadmium compositions of $\leqslant 0.12$. For compositions of $\geqslant 0.19$ the values increase with increasing composition and approach that of cadmium ferrite, $CdFe_2O_4$, prepared by a solid-state reaction (0.080 cm $s^{-1}$).[6] This suggests that the crystals of the Cd,Zn-bearing ferrites having $Cd^{2+}{:}Zn^{2+}$ mol ratios of $0{:}0.90–0.12{:}0.43$ at the tetrahedral sites possess a similar structure to that of Zn-bearing ferrites, and that the crystals approach the structure of Cd-bearing ferrites with increasing $Cd^{2+}{:}Zn^{2+}$ mol ratio. It would also explain the variation of the lattice constants of the Cd,Zn-bearing ferrites with cadmium compositions.

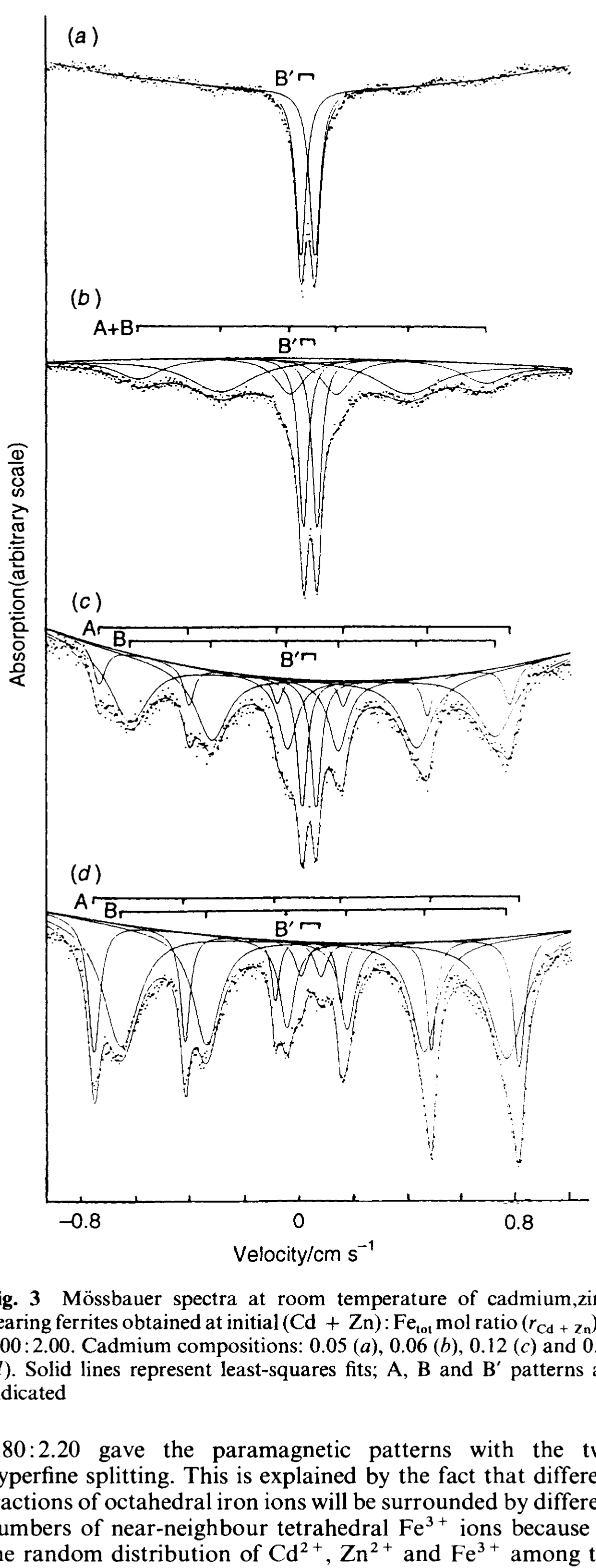

**Fig. 3** Mössbauer spectra at room temperature of cadmium,zinc-bearing ferrites obtained at initial (Cd + Zn) : $Fe_{tot}$ mol ratio ($r_{Cd+Zn}$) of 1.00:2.00. Cadmium compositions: 0.05 (*a*), 0.06 (*b*), 0.12 (*c*) and 0.27 (*d*). Solid lines represent least-squares fits; A, B and B′ patterns are indicated

Mössbauer spectra at room temperature of the Cd,Zn-bearing ferrites prepared from iron(II) hydroxide suspensions at $r_{Cd+Zn} = 0.10{:}2.90$ showed two hyperfine splitting patterns arising from $Fe^{3+}$ ions on the tetrahedral sites, and from the sum of $Fe^{2+}$ and $Fe^{3+}$ ions on the octahedral sites. For $r_{Cd+Zn} = 0.20{:}2.80$, paramagnetic patterns arising from $Fe^{3+}$ ions on the octahedral sites with the two hyperfine splitting patterns were seen in the Mössbauer spectra of ferrites having cadmium compositions of 0.04–0.09, and only the two hyperfine splitting patterns were seen at compositions of 0.13–0.17. Ferrites prepared from the suspensions at $r_{Cd+Zn} = 0.40{:}2.60–0.80{:}2.20$ gave the paramagnetic patterns with the two hyperfine splitting. This is explained by the fact that different fractions of octahedral iron ions will be surrounded by different numbers of near-neighbour tetrahedral $Fe^{3+}$ ions because of the random distribution of $Cd^{2+}$, $Zn^{2+}$ and $Fe^{3+}$ among the tetrahedral sites.[9] The Mössbauer parameters obtained from the spectra for the ferrites prepared from suspensions at $r_{Cd+Zn} = 0.40{:}2.60$ are listed in Table 3. The Δ values for the paramagnetic patterns increase with increasing $Cd^{2+}{:}Zn^{2+}$ mol ratio on the tetrahedral sites and approach the value of $CdFe_2O_4$.[6] A similar increase was seen for the Cd,Zn-bearing ferrites prepared from suspensions at $r_{Cd+Zn} = 0.20{:}2.80$, 0.60:2.40 and 0.80:2.20. This suggests that in the iron(II) hydroxide suspensions having $r_{Cd+Zn} = 0.10{:}2.90–0.80{:}2.20$ homogeneous mixtures of $CdFe_2O_4–Fe_3O_4$ and $ZnFe_2O_4–Fe_3O_4$ solid solutions are formed. Considering the variation of

**Table 2** Parameters and area fractions estimated from the room-temperature Mössbauer spectra of Cd,Zn-bearing ferrites prepared from aqueous suspensions at $r_{Cd+Zn}$ = 1.00:2.00

| Chemical composition | Mössbauer pattern | $\delta^a$/cm s$^{-1}$ | $\Delta^a$/cm s$^{-1}$ | Internal field$^b$ (kOe) | Area fraction: Mössbauer spectra | Area fraction: Chemical composition$^c$ |
|---|---|---|---|---|---|---|
| $Zn_{0.90}Fe_{1.97}O_{4.00}$ | B′ | 0.039 | 0.048 | — | — | — |
| $Cd_{0.05}Zn_{0.75}Fe_{1.92}O_{4.00}$ | B′ | 0.039 | 0.051 | — | — | — |
| $Cd_{0.06}Zn_{0.73}Fe_{1.96}O_{4.00}$ | A + B | 0.051 | 0.007 | 394 | 0.728 | — |
|  | B′ | 0.039 | 0.049 | — | 0.272 | — |
| $Cd_{0.12}Zn_{0.43}Fe_{2.29}O_{4,00}$ | A | 0.035 | 0.010 | 469 | 0.129 | 0.194 |
|  | B | 0.050 | 0.003 | 410 | 0.722 | 0.806 |
|  | B′ | 0.035 | 0.050 | — | 0.149 |  |
| $Cd_{0.19}Zn_{0.24}Fe_{2.51}O_{4.00}$ | A | 0.033 | 0.004 | 469 | 0.197 | 0.227 |
|  | B | 0.049 | −0.003 | 414 | 0.760 | 0.773 |
|  | B′ | 0.032 | 0.060 | — | 0.043 |  |
| $Cd_{0.27}Fe_{2.70}O_{4.00}$ | A | 0.028 | 0.002 | 484 | 0.254 | 0.272 |
|  | B | 0.057 | 0.002 | 433 | 0.712 | 0.728 |
|  | B′ | 0.037 | 0.071 | — | 0.034 |  |

[a] Values with respect to natural α-iron foil; error ±0.004 cm s$^{-1}$. [b] Oe = 1000/4π A m$^{-1}$. [c] Estimated with assumption that the sum of the cations in the tetrahedral sites is equal to 1.00.

**Table 3** Parameters and area fractions estimated from the room-temperature Mössbauer spectra of Cd,Zn-bearing ferrites prepared from aqueous suspensions at $r_{Cd+Zn}$ = 0.40:2.60. See footnotes to Table 2

| Chemical composition | Mössbauer pattern | δ/cm s$^{-1}$ | Δ/cm s$^{-1}$ | Internal field (kOe) | Area fraction: Mössbauer spectra | Area fraction: Chemical composition |
|---|---|---|---|---|---|---|
| $Zn_{0.37}Fe_{2.56}O_{4.00}$ | A | 0.029 | 0.002 | 488 | 0.238 | 0.248 |
|  | B | 0.056 | 0.002 | 438 | 0.667 | 0.752 |
|  | B′ | 0.035 | 0.046 | — | 0.095 |  |
| $Cd_{0.09}Zn_{0.27}Fe_{2.49}O_{4.00}$ | A | 0.027 | 0.002 | 476 | 0.202 | 0.259 |
|  | B | 0.056 | 0.003 | 419 | 0.767 | 0.741 |
|  | B′ | 0.034 | 0.051 | — | 0.031 |  |
| $Cd_{0.17}Zn_{0.18}Fe_{2.49}O_{4.00}$ | A | 0.028 | 0.003 | 478 | 0.197 | 0.260 |
|  | B | 0.054 | 0.002 | 425 | 0.774 | 0.740 |
|  | B′ | 0.035 | 0.057 | — | 0.029 |  |
| $Cd_{0.23}Zn_{0.09}Fe_{2.44}O_{4.00}$ | A | 0.029 | 0.003 | 483 | 0.226 | 0.281 |
|  | B | 0.056 | 0.002 | 429 | 0.742 | 0.719 |
|  | B′ | 0.037 | 0.067 | — | 0.032 |  |
| $Cd_{0.27}Fe_{2.59}O_{4.00}$ | A | 0.028 | 0.002 | 483 | 0.240 | 0.282 |
|  | B | 0.056 | 0.003 | 432 | 0.747 | 0.718 |
|  | B′ | 0.035 | 0.077 | — | 0.013 |  |

the lattice constants with cadmium or zinc composition of Cd- or Zn-bearing ferrites,[2,6,10] this would explain the variation of the lattice constants with cadmium composition of the Cd,Zn-bearing ferrites described in the preceding section.

On the other hand, the area fractions of the hyperfine splitting pattern A in the Mössbauer spectra of the Cd,Zn-bearing ferrites obtained at $r_{Cd+Zn}$ = 0.10:2.90–1.00:2.00 are also lower than the values calculated from the chemical compositions by assuming that the sum of the cations (sum of the compositions of $Cd^{2+}$, $Zn^{2+}$ and $Fe^{3+}$ ions) on the tetrahedral sites are equal to 1.00. This suggests that vacancies are present in the tetrahedral sites of the Cd,Zn-bearing ferrites.

*Chemical Compositions, Lattice Constants and Mössbauer Spectra of* Cd-*Bearing Ferrites prepared from Iron*(II) *Hydroxide Suspensions at Initial* Cd:Fe$_{tot}$ *Mol Ratios of* 0.10:2.90–1.00:2.00.—Fig. 4 shows the chemical compositions of the Cd-bearing ferrites for the ternary system FeO, $Fe_2O_3$ and CdO. They are located on the oxygen reaction lines and slightly lower in FeO than those of stoichiometric Cd-bearing ferrites. This suggests that oxidized Cd-bearing ferrites are formed by air oxidation of iron(II) hydroxide suspensions in the presence of cadmium ions. Fig. 4 also shows that ferrites prepared from the suspensions at initial Cd:Fe$_{tot}$ mol ratios of 0.40:2.60, 0.60:2.40 and 1.00:2.00 have the same composition. As described in the preceding section, this indicates that a

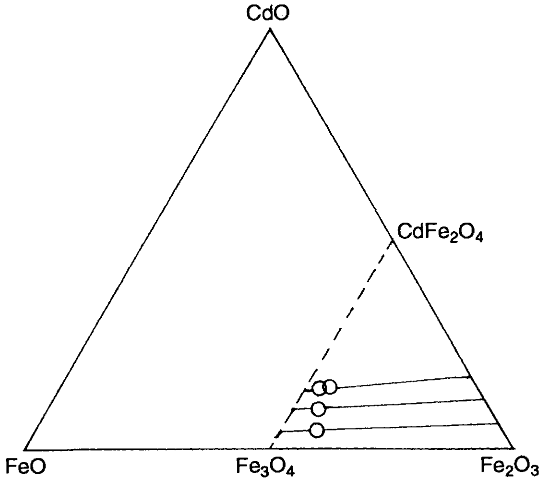

**Fig. 4** Chemical composition of cadmium-bearing ferrites for the ternary system FeO, $Fe_2O_3$ and CdO: – – –, value for a solid solution of $Fe_3O_4$–$CdFe_2O_4$; ——, oxygen reaction lines

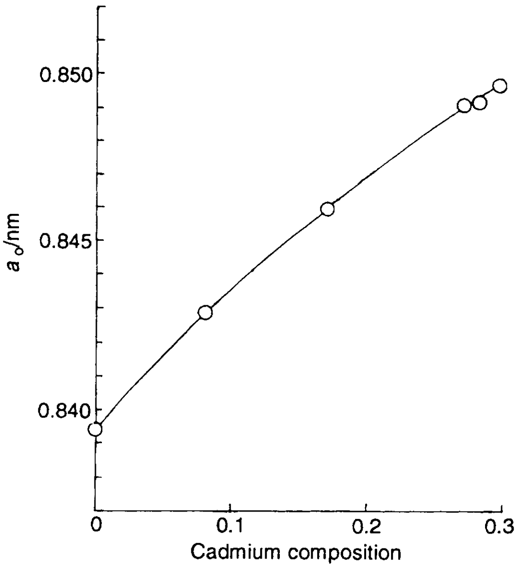

**Fig. 5** Variation of the lattice constant $a_0$ of the cadmium-bearing ferrites with cadmium composition. Error for the lattice constant ± 0.0001 nm

limiting amount of cadmium is incorporated into the lattice sites of a spinel structure.

The variation of the lattice constants $a_0$ of the Cd-bearing ferrites with the cadmium compositions (Fig. 5) is in good agreement with that of Cd-bearing ferrites, $Cd_xFe_{3-x}O_4$, prepared by a solid-state reaction.[6]

Mössbauer spectra at room temperature of the Cd-bearing ferrites with cadmium compositions of $\leqslant 0.17$ showed two hyperfine splitting patterns A and B arising from $Fe^{3+}$ ions on the tetrahedral sites and from $Fe^{3+}$ and $Fe^{2+}$ ions on the octahedral sites, respectively. Ferrites having cadmium compositions of 0.27–0.30 showed a paramagnetic pattern B′ arising from $Fe^{3+}$ ions on the octahedral sites together with the two hyperfine splitting. The Δ values for the paramagnetic patterns (0.071–0.077 cm $s^{-1}$) are in good agreement with that (0.080 cm $s^{-1}$) for $CdFe_2O_4$ prepared by a solid-state reaction.[6] These results are explained by consideration of the random distribution of $Cd^{2+}$ and $Fe^{3+}$ ions among tetrahedral sites.[9]

The area fractions for the hyperfine splitting pattern A arising from $Fe^{3+}$ ions on the tetrahedral sites estimated from the Mössbauer spectra decreased with increasing cadmium composition and were lower than the values calculated from the chemical compositions by assuming that the sum of the cations (sum of the compositions of $Cd^{2+}$ and $Fe^{3+}$ ions) on the tetrahedral sites are equal to 1.00 (results for a cadmium composition of 0.27 are listed in Tables 2 and 3). These facts also suggest that $Cd^{2+}$ ions are incorporated into the tetrahedral sites in a spinel structure but that vacancies are also present at these sites.

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