Preparation and Mössbauer Effect of $Cr_{1-x}Fe_xOOH$ (0 ≤ x ≤ 1.0) with the InOOH-Type Structure

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The complete solid solutions of $Cr_{1-x}Fe_xOOH$ with the InOOH-type structure were synthesized under high pressures. They were antiferromagnetic with Néel temperatures of 570 K for FeOOH, 454 K for $Cr_{0.2}Fe_{0.8}OOH$, 332 K for $Cr_{0.4}Fe_{0.6}OOH$, and 160 K for $Cr_{0.6}Fe_{0.4}OOH$ as determined by the Mössbauer effect measurements.

Introduction

β-CrOOH and ϵ-FeOOH are oxyhydroxides with the InOOH-type structure and are prepared under high pressures (*1, 2*). CrOOH is antiferromagnetic, T_N = 120 K, and its magnetic structure was determined by Christensen and Hansen (*3*). From Mössbauer effect measurements (*4*) and neutron diffraction analysis (*5*) of ϵ-FeOOH, the spin structure of ϵ-FeOOH with a Néel temperature of 570 K was determined. β-CrOOH and ϵ-FeOOH are antiferromagnetic, but the two spin structures are different. To study the magnetic properties of the solid solutions, an attempt to prepare $Cr_{1-x}Fe_xOOH$ with InOOH-type structure was made. We report here the preparation and Mössbauer effect of $Cr_{1-x}Fe_xOOH$ compounds. By thermal decomposition of the present solid solution series, it is expected that CrO_2 doped with iron may be easily produced (*6*).

Experimental

The solid solution of the oxyhydroxide was prepared as follows. Solutions of 1 *M* chromium nitrate and 1 *M* ferric nitrate were mixed to 100 ml in a required ratio in a 500-ml beaker and 1 *M* ammonia was added to the solution with stirring to pH = 9.0. The fact that no chromium and ferric ions were detected in the filtrate by chemical analysis using diphenylcarbazide and ammonium thiocyanate indicated that the composition of the precipitate was equal to that of the solution. The precipitate was dried at 65°C for a day and ground. The amorphous powders obtained in this way were charged in a cylindrical gold tube 3 mm in diameter and 5 mm long. The tube was placed in the high-pressure cell assemblage and subjected to high temperature–

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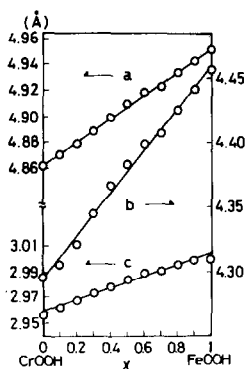
FIG. 1. Lattice parameters as a function of mole fraction X.

	Isomer shift (mm/sec)		Internal magnetic field at 90 K (kOe)
X	300 K	90 K	
0.2	0.36	0.48	—
0.4	0.35	0.50	412
0.5	0.38	0.50	462
0.6	0.40	0.50	497
0.8	0.40	0.40	517
1.0	0.30	0.50	521

[a] Isomer shift is relative to Fe metal.

pressure conditions using a cubic anvil apparatus. The magnitudes of pressure generated inside the cell were calibrated on the electrical transitions of Bi (25.5 and 77 kbar) and Ba (55 kbar). The temperature of the sample was measured by a Pt–Pt · Rh 13% thermocouple. The reactions were performed at 20–80 kbar and 300–600°C for 30 min. The sample was quenched to room temperature prior to release of the applied pressure.

The products were identified by X-ray powder diffraction. Cell dimensions were calculated using a least-squares method from the powder patterns taken with Ni-filtered CuK_α radiation. Silicon was used as an internal standard.
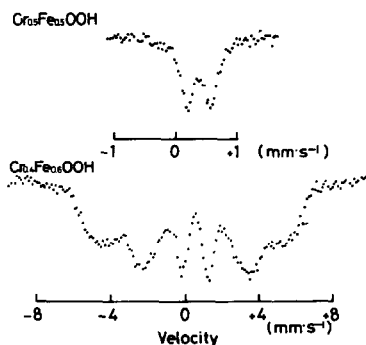
The Mössbauer spectra were measured from 90 to 500 K using a 400-multichannel analyzer and the radiation from ^{57}Co in Pd. The γ-ray source was always kept at room temperature. Calibration of the velocity scale was made using the iron metal as a standard absorber.

Results and Discussion

The complete series of solid solutions of $Cr_{1-x}Fe_xOOH$ were synthesized and their

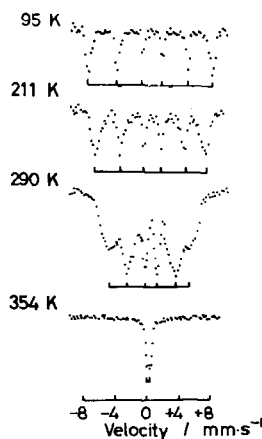FIG. 2. Mössbauer spectra of $Cr_{0.5}Fe_{0.5}OOH$ and $Cr_{0.4}Fe_{0.6}OOH$ at 300 K. Velosity scale is relative to Fe metal.

FIG. 3. Mössbauer spectra of $Cr_{0.4}Fe_{0.6}OOH$ at various temperatures. Velosity scale is relative to Fe metal.
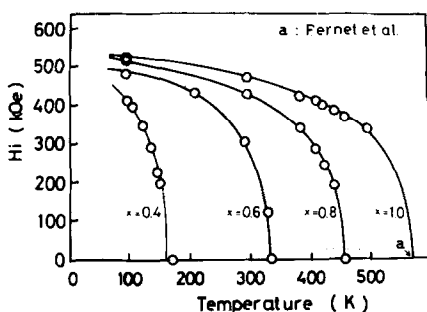
FIG. 4. Temperature dependence of the internal magnetic field of $Cr_{1-x}Fe_xOOH$ with InOOH-type structure.

X-ray powder patterns were indexed on the basis of the InOOH-type structure. Figure 1 shows the lattice parameters as a function of the mole fraction X. In the present system, the compounds with $x \leq 0.6$ were prepared at 380°C and 60 kbar, and for $x \geq 0.7$ higher pressure-temperature conditions of up to 500°C and 82 kbar were required to synthesize the single phase. This fact reflected the synthetic conditions for β-CrOOH (1) and ϵ-FeOOH (2). As seen in Fig. 1, the lattice parameters increased liberally with X, and those of both terminal compounds were in good agreement with the values already reported (1, 2).

Mössbauer absorption spectra of $Cr_{0.5}Fe_{0.5}OOH$ and $Cr_{0.4}Fe_{0.6}OOH$ at 300 K are shown in Fig. 2.

At 300 K, the samples with $x \leq 0.5$ showed only the paramagnetic quadrupole splitting spectra, but magnetic hyperfine spectra were found down to 90 K for all samples, except for the specimens CrOOH and $Cr_{0.8}Fe_{0.2}OOH$. Each hyperfine spectrum for $Cr_{1-x}Fe_xOOH$ ($x \geq 0.4$) at 90 K consists of only one set of a six-line spectrum. The values of the isomer shift and the internal magnetic field are listed in Table I. The quadrupole splitting of $Cr_{0.6}Fe_{0.4}OOH$ was 0.35 mm/sec at 300 K. Since the distance (S_1) between the two lines located at the left side of the pattern is greater than that (S_2) at the right side at 90 K, the

parameter $\Delta S = S_1 - S_2$ was positive and was nearly equal to the quadrupole splitting in the paramagnetic state, indicating that the internal field was perpendicular to the Z axis of the efg tensor. It is evident that a correct quantitative exploitation of these results is probably complex due to the distribution of Fe and Cr ions and the poorly known direction of the principal axis of the efg.

The temperature dependence of the Mössbauer absorption spectrum of $Cr_{0.4}Fe_{0.6}OOH$ is shown in Fig. 3. It is assumed that the measured values ranging between 0.3 and 0.4 mm/sec for the isomer shift relative to the iron metal were due to the high-spin Fe^{3+} ion.

The temperature dependence of the internal magnetic field is illustrated in Fig. 4. The display shows that the H_{eff} versus T curves almost follow a Brillouin function. The magnetic ordering temperature was determined to be 160 ± 5 K for $Cr_{0.6}Fe_{0.4}OOH$, 332 ± 10 K for $Cr_{0.4}Fe_{0.6}OOH$, and 454 ± 10 K for $Cr_{0.2}Fe_{0.8}OOH$. Since ϵ-FeOOH begins to decompose to α-Fe_2O_3 at about 500 K, its Néel temperature was not directly determined by Mössbauer effect measurement. From the extrapolation of the results obtained by the Mössbauer effect measuremens of ϵ-FeOOH up to 500 K, the Néel temperature was estimated to be about 570 K. This value was in good agreement with that reported by Permet et al. (4). The Néel temperature of β-CrOOH was assumed to be approximately 120 K. However, no magnetic hyperfine spectrum of $Cr_{0.8}Fe_{0.2}OOH$ was observed down to 90 K.

Acknowledgments

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