Ferromagnetic Properties of SrFe$_{1-x}$Co$_x$O$_3$ Synthesized under High Pressure

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SrFe$_{1-x}$Co$_x$O$_{3-\delta}$ ($0 \leq x \leq 1$, $\delta \leq 0.06$) of the cubic perovskite type was prepared by treating mixtures of grossly oxygen-deficient samples obtained at ambient pressure with an oxidizer, KClO$_4$, at 6 GPa and 873 K. The lattice parameters were determined by X-ray diffraction measurements and their magnetic properties were characterized by measurements of magnetization and Mössbauer spectroscopy. The ferromagnetic Curie temperature has been found to be raised above 300 K for $0.4 \leq x \leq 0.9$ (340 K at $x = 0.6$) by the high pressure treatment, and the composition dependence of saturation magnetization for $x \geq 0.4$ is consistent with a simple picture in which Fe^{4+} ions with 4 μ_B and Co^{4+} ions with 1.8 μ_B align their moments ferromagnetically. The saturation magnetic hyperfine field, which is 330 kOe for SrFeO$_3$, decreases quickly at first ($x \leq 0.15$) and then slowly to about 290 ~ 300 kOe, or exponentially, as Co content increases, suggesting that the Co substitution tends to delocalize electrons of Fe parentage in a broadened σ^* band. SrFeO$_3$, an antiferromagnet with a relatively low T_N of 134 K, and Sr$_2$FeCoO$_6$, a ferromagnet with a high T_C of 340 K, seem to represent the two electronic phases switched from one to the other at $x = 0.1 \sim 0.15$. © 1996 Academic Press, Inc.

INTRODUCTION

3d-transition metal oxides have been studied extensively, since they offer many advantages including a variety of excellent physical and chemical properties, ease of fabrication, and chemical stability. However, proposal of a classification of electronic structures as Mott–Hubbard type ($U < \Delta$) or charge-transfer (CT) type ($U > \Delta$) (1) and the discovery of high-T_c superconductivity in complex cupric oxides (2) have shed a new light on the investigation of transition metal oxides, where U and Δ represent the d-d Coulomb energy and the ligand to metal electron-transfer energy, respectively. Of particular interest for us is to clarify the interplay of anions and cations under this new light, which becomes important for oxides of late-transition metals of the CT type. As a part of our systematic study of suitable systems characterized by small or even negative charge transfer energies, here we report magnetic proper-

ties of SrFe$_{1-x}$Co$_x$O$_3$. Both SrFeO$_3$ ($x = 0$) and SrCoO$_3$ ($x = 1$) contain transition metals with high oxidation numbers; Fe^{4+} and Co^{4+}, whose 3d levels are deep and close in energy to the oxygen 2p levels, have cubic perovskite structures in which metal–oxygen–metal interactions are enhanced, and are rather good conductors with resistivities (ρ) on the order of $10^{-1} \sim 10^{-4}$ Ω cm (3). We believe that the present system provides an opportunity to study how the electronic properties change as a function of d-electron density and oxygen content. The background is briefly described below.

SrFeO$_3$ is an antiferromagnet with a Neel temperature (T_N) of 134 K. The spin structure is of a screw type with a wave vector along the $\langle 111 \rangle$ axis. Assuming Heisenberg-type exchange interactions, Takeda et $al.$ estimated the magnitude as $J_1 = 1.2$ meV, $J_2 = -0.2$ meV, and $J_4 = -0.3$ meV from neutron paramagnetic scattering measurements, where J_i stands for the interaction of an Fe ion with the ith nearest neighbors (4, 5). The coexistence of the ferromagnetic nearest-neighbor interaction and the considerably strong antiferromagnetic second- and fourth-nearest-neighbor interactions leads to the specific spin structure. Various physical measurements including magnetization (6), Mössbauer spectroscopy (7), neutron diffraction (4, 5), photoemission (8), soft X-ray absorption spectroscopy (9), and also a theoretical calculation using a DV-Xα method (10) all showed that the Fe^{4+} ions are basically in high-spin state ($t_{2g}^3 e_g^1$). More exactly, however, the electronic configuration of the ground state is almost $d^5\underline{L}$ ($\underline{L}$: ligand hole), resulting from an O$_{2p} \rightarrow$ Fe$_{3d}$ electron transfer (8, 9, 10). The effective values of Δ and U estimated by the photoemission study (8) are -3.1 eV and 7.0 eV, respectively. According to MacChesney et $al.$ (11), a sintered pellet keeps a nearly temperature-independent resistivity of $\approx 10^{-2}$ Ω cm. This means that SrFeO$_3$ has a narrow conductive band to which the O$_{2p}$ levels contribute significantly.

Takeda et $al.$ (6) reported that Co-substituted samples equilibrated at 623 K under an oxygen pressure of 0.14 GPa were ferromagnetic for $x \geq 0.2$. The Curie tempera-

ture (T_C) was $\approx$260 K for $x = 0.2 \sim 0.3$ and then decreased monotonically to $\approx$210 K for SrCoO$_3$. Magnetization (M) was not easily saturated, but the experimental values at 4.2 K in an external field (H) of 50 kOe were used to estimate the atomic moments approximately. The magnitude of M was also highest at $x = 0.2$ and then decreased quite linearly with increasing Co content, from which the atomic moments of 3.8 μ_B/Fe and 1.5 μ_B/Co were deduced. It was thus concluded that the Co^{4+} ions were nearly in low-spin state (t_{2g}^5, $S = \frac{1}{2}$), while it was also suggested that such a partial occupation of the up-spin band of e_g symmetry leads to the increased magnetic moment and also to metallic conductivity.

By the way, more recent measurements on electrochemically oxidized Sr$_2$FeCoO$_6$ ($x = 0.5$) and SrCoO$_3$ showed considerably higher T_C's of 325 and 280 K, respectively, and larger saturation moments of 5 μ_B/(Co + Fe) and 2.1 μ_B/Co, respectively (12, 13). Another intriguing issue raised more recently is the possibility of a new intermediate spin state for Co^{4+}. According to Potze et al. (14), a comparison of the experimental Co 2p X-ray absorption spectrum with theoretical calculations leads to an intermediate spin ground state with $S = \frac{3}{2}$ where a high-spin Co^{3+} (d^6, $S = 2$) ion is accompanied by a ligand hole carrying antiparallel spin. This possibility needs to be tested by making various physical measurements using well-characterized samples. The purpose of this paper is to clarify the composition dependence of electronic properties broadly using samples with minimized oxygen deficiency, before looking into physical properties in further detail.

EXPERIMENTAL

Samples with $x = 0$, 0.05, 0.1, 0.15, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8, and 1 were prepared as follows. SrCoO$_3$ and α-Fe$_2$O$_3$, Co$_3$O$_4$, each with a purity of 99.9%, were mixed at ratios of $2:1 - x:2x/3$, pelletized, and calcined at 900°C for 24 hr. The products were ground, mixed, pelletized, and heated at 1100°C for 24 h in air. This process was repeated again. The oxygen-deficient samples thus obtained were mixed with 10 wt% of KClO$_4$, sealed into gold cupsules, and treated under a pressure of 6 GPa at 600°C for 30 min using a cubic-anvil-type high-pressure apparatus.

X-ray diffraction (XRD) measurements on powdered samples were carried out using CuKα radiation (Rigaku Ru-200) at room temperature. Oxygen content was checked by iodometric titration using an aqueous solution of sodium thiosulfate as a standard solution. Magnetization was measured with a SQUID magnetometer (Quantum Design, MPMS2) between 5 and 350 K at $H = 10$ kOe and 10 Oe. The sign and the magnitude of the small magnetic field were determined by using a granular lead metal as a standard material. The Curie temperature was determined by a conventional $M^2 - T$ method
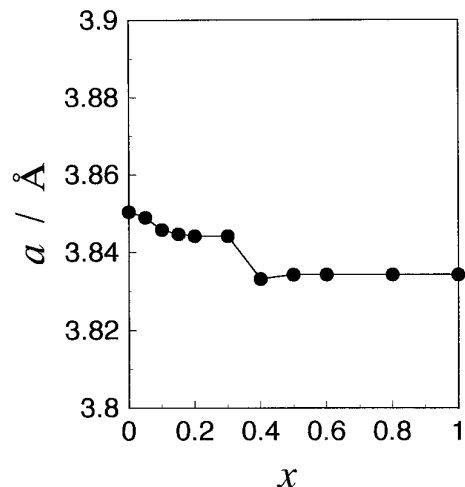

FIG. 1. Lattice parameter plotted against composition for SrFe$_{1-x}$Co$_x$O$_3$.

using the low-field data. For some typical compositions magnetic hysteresis curves were measured up to 50 kOe using another SQUID magnetometer (Quantum Design, MPMS). Mössbauer spectra were obtained at 4, 77, and 300 K using a ^{57}Co/Rh γ-ray source. The source velocity (V) was calibrated by using pure iron metal as a control material.

RESULTS AND DISCUSSION

The oxygen content for a series of samples estimated by iodometry ranged from 2.94 ($\delta = 0.06$) to 2.99 ($\delta = 0.01$) within experimental error of $\pm$0.03. The rather large uncertainty was caused by the limited sample quantity of about 60 mg. On the other hand, the structural and magnetic properties to be described below were confirmed using several series of samples.

SrFe$_{1-x}$Co$_x$O$_3$ keeps cubic perovskite structure for the whole composition range. Figure 1 shows the composition dependence of the lattice parameter, a. The values for the end members agree well with the literature values (4, 7, 11, 12, 13). However, the change at intermediate compositions is not simple; there seems to be a gap at $x = 0.3 \sim 0.4$ in Fig. 1.

Plotted in Fig. 2a are typical M vs T curves measured at $H = 10$ kOe on cooling. It is evident that the Co substitution induces ferromagnetism as reported by Takeda et al. (6). Shown in Fig. 2b are the first quadrants of typical $M–H$ hysteresis curves measured at 5 K, which are raw data without any correction of demagnetizing effects. Compositions with $0.2 \leq x \leq 1$ are soft ferromagnets with coercive fields of $\leq$0.1 kOe. However, Fe-rich compositions with $0.05 \leq x \leq 0.1$ showed complex behavior suggesting the existence of ferromagnetic islands which were coupled
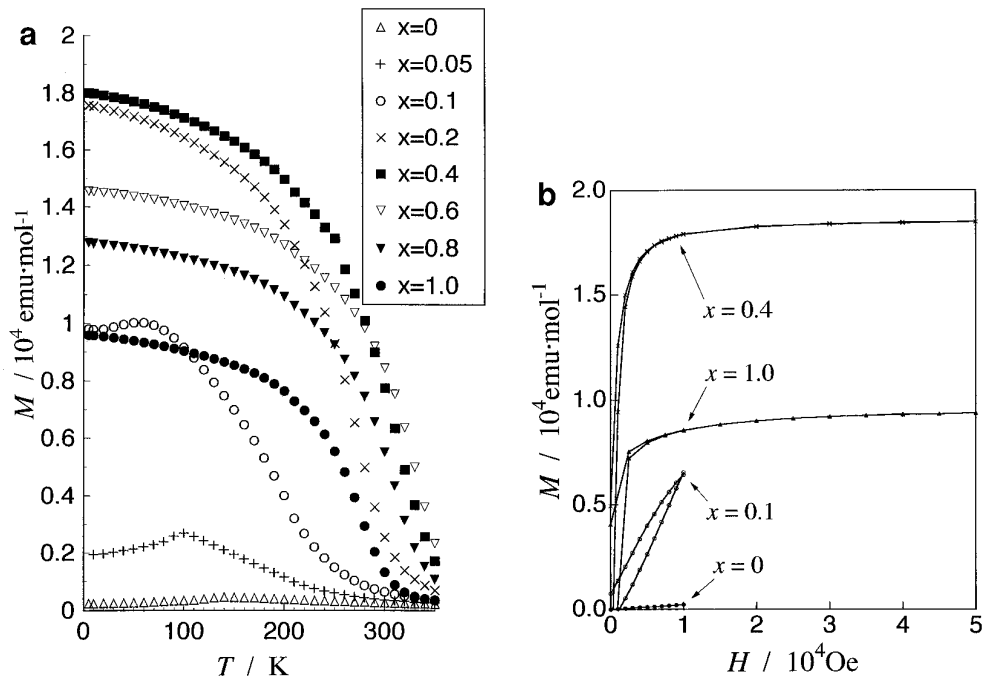
FIG. 2. Temperature dependence of magnetization at $H = 10$ kOe (a) and magnetization vs applied field curves at $T = 5$ K (b).

antiferromagnetically with each other at low temperatures. For example, as seen in Fig. 3a, the $M–T$ curve for $x = 0.1$ measured at 10 Oe exhibited a well-defined cusp at 80 K which might well be taken as reflecting the onset of antiferromagnetic transition, but the $M–H$ curves at higher temperatures of 90 and 150 K were not linear but were both S-shaped, as shown in Fig. 3b, revealing the presence of ferromagnetic islands. On the other hand, the data for $x = 0.15$ showed a rather well-defined ferromagnetic transition at 235 K accompanied by a very broad low-temperature anomaly.

Figure 4a shows the composition dependence of the magnetic transition temperature determined from the measurements at 10 Oe, where the T_N's for $x = 0.05$ ~ 0.1 correspond to the cusp temperatures mentioned above, while plotted in Fig. 4b is the composition dependence of M at 5 K and 10 kOe measured on cooling from 300 K. For $x \geq 0.2$, the magnitude of M is almost coincident with the saturation magnetization, being smaller by less than 5%. It is evident that M increases rapidly with increasing x around $x = 0.1$, reaching a maximum (1.80×10^4 emu/mol) at $x = 0.4$. And the experimental values for $x \geq 0.4$ are near the calculated sum of atomic moments of 4 μ_B/Fe and 1.8 μ_B/Co as compared in Fig. 4b. The corresponding literature data are also included in Figs. 4a and 4b.

In comparison with the previous systematic data (6), the present result is distinguished by the following points. First, the T_C is considerably higher for $x \geq 0.4$. Second, the

magnetization is much more easily saturated. Third, the composition dependence of saturation magnetization peaked at $x = 0.4$. For $x > 0.4$ it decreases with increasing Co content simply because Co carries a small magnetic moment, while for $0.2 \leq x < 0.4$ it decreases with increasing Fe content probably because antiferromagnetic Fe–Fe interactions cause a partial and local cancellation of the atomic moments. Electrochemically oxidized Sr_2FeCoO_6 and $SrCoO_3$ have similar T_C's as those of the present samples (12, 13).

Another point to be remarked here is the possibility of magnetovolume effect, i.e., the correlation between unit cell volume and magnetism. There is a gap of about 0.28% in the a vs x curve between $x = 0.3$ and 0.4 in Fig. 1, where the magnetic properties at room temperature change from paramagnetic to ferromagnetic with increasing x. It is known that Fe and Ni metals show a positive and a negative magnetovolume effects, respectively (15). That is, the normal tendency of cell volume to decrease with decreasing temperature is suppressed for Fe in its ferromagnetic state, while it is enhanced for Ni. For either case, the change in the coefficient of thermal expansion due to this effect is maximized in the vicinity of T_C where dM/dt is sharp. In the case of the present system the magnetism at 300 K changes both at $x \approx 0.35$ and 0.9, while the magnetovolume effect would be more important at the former composition because both dT_C/dx and dM/dx are sharper. This possibility of a negative magnetovolume effect should, however, be
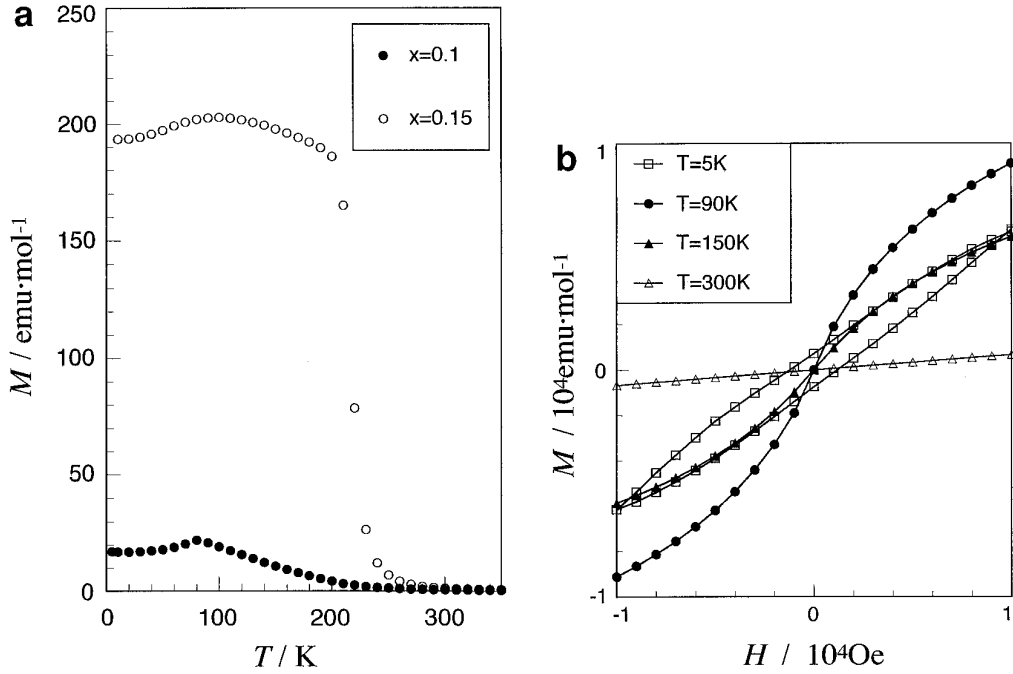
FIG. 3. Temperature dependence of magnetization for Fe-rich compositions with $x = 0.1$ and $x = 0.15$ in a small external field of 10 Oe (a) and magnetization vs applied field curves for $x = 0.1$ measured above and below the cusp temperature (b).

examined carefully in the furture by measuring the cell volume as a function of M and T in detail.

Typical Mössbauer spectra for $x = 0$, 0.2, 0.4, and 0.6 measured at 300 and 4 K are shown in Figs. 5a and 5b, and the hyperfine parameters determined by fitting to Lorentzian lines are summarized in Table 1. The spectrum of SrFeO$_3$ at 300 K shows a single peak the width (Γ) of which, 0.33 mms^{-1}, is near the resolution limit of the present spectrometer, 0.28 mms^{-1}. This shows good stoichiometry of the present sample (16). On the other hand,
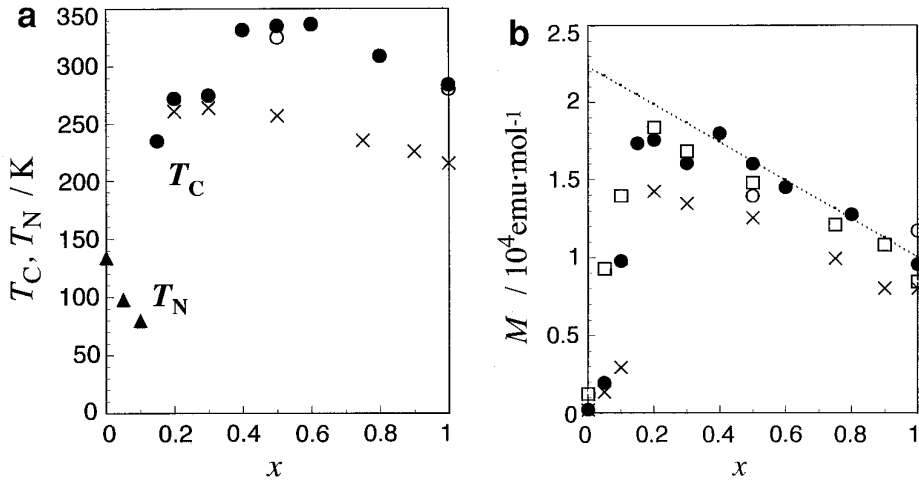

FIG. 4. (a) composition dependence of the Curie temperature (T_C) (●, ○, ×) and the Néel temperature (T_N) (● and ▲, the present work; ○, from Refs. (12) and (13); ×, from Ref. (6)). (b) The magnetization at 5 K and 10 kOe (●, ○, ×) and 50 kOe (□) (●, the present work; ○, from Refs. (12) and (13); × and □, from Ref. (6)). The T_N's for $x = 0.05 \sim 0.1$ correspond to the cusp temperatures measured at 10 Oe (see text) in (a). The dotted line in (b) represents the calculated magnetization for the Fe^{4+} ions with 4 μ_B and the Co^{4+} ions with 1.8 μ_B aligning their moments ferromagnetically.
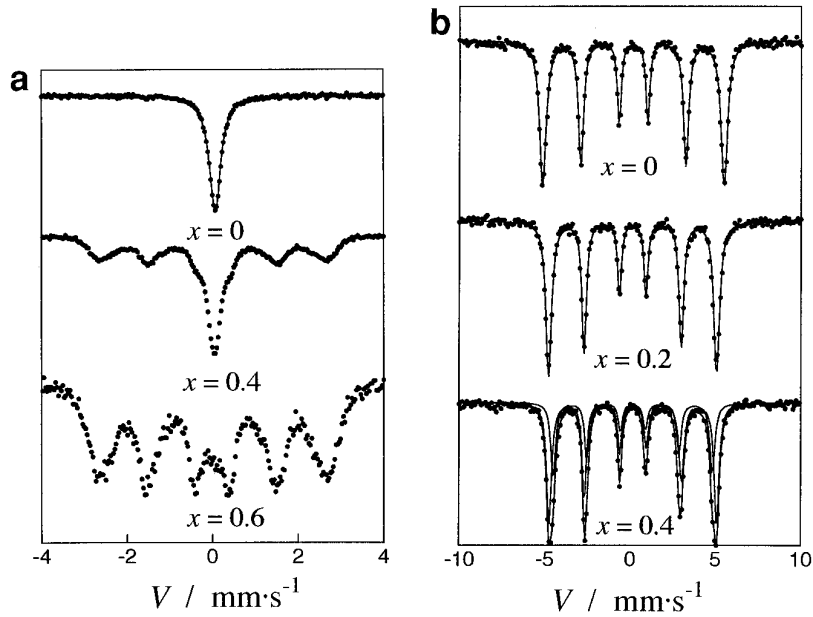
FIG. 5. Typical Mössbauer spectra at 300 K (a) and 4.2 K (b). The solid lines are the computed spectra. The velocity scale was calibrated against pure iron metal.

magnetic hyperfine interactions appear in the spectra for $x = 0.4$ and 0.6. This is consistent with the magnetization data revealing the ferromagnetic ordering above room temperature. However, the spectrum is considerably broadened for either sample, and, moreover, a sharp paramagnetic component is mixed for $x = 0.4$. Local statistical inhomogeneity in the Fe : Co ratio within a crystal seems to contribute to the smearing. As shown

in Fig. 4a, T_C remains above 300 K for $0.35 \leq x \leq 0.9$. So, a local fluctuation in Co content of, say, ± 0.1 would lead to the coexistance of a paramagnetic component for $x = 0.4$, but not for $x = 0.6$.

An inhomogeneity effect appears also at low temperatures, as seen in Fig. 5b. None of the magnetic spectra for $x = 0.4$ and 0.6 at 77 and 4 K could be fitted to a single magnetic pattern, but they could be resolved into two components with a composition-dependent relative intensity (I) of 63 : 37 for $x = 0.4$ and 44 : 56 for $x = 0.6$ (see Table 1). Component 1 is characterized by a larger hyperfine field (HF). If it is assumed that the d-electron density and, therefore, the magnitude of HF of an Fe ion depends upon the Fe : Co ratio at neighboring sites, components 1 and 2 would be assigned to a relatively Fe-rich and a Fe-poor configurations, respectively. This assignment is consistent with the composition dependence of I and also with the tendency of HF to decrease from SrFeO$_3$ (330 kOe) (17) to SrFe$_{0.01}$Co$_{0.99}$O$_3$ (296 kOe) (18). Here, it should be stated, however, that the resolution of the spectra into the double components was made for convenience, or for the purpose of clarifying tendency, neglecting the probability of a wide distribution in the local Fe : Co ratio.

Shown in Fig. 6 is the composition dependence of HF at 4 K. It is remarkable that HF decreases quickly or exponentially as x increases to ~ 0.2. The change from antiferromagnetism to ferromagnetism found by the magnetization measurements can thus be considered to be parallel to the change in HF reflecting microscopic elec-
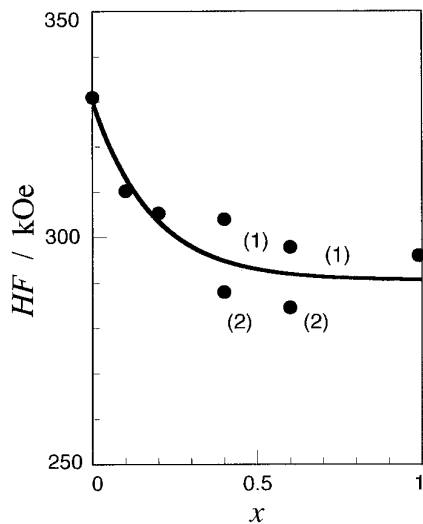
TABLE 1
Mössbauer Data for the Fe^{4+} Ions in SrFe$_{1-x}$Co$_x$O$_3$ at 300 K and 4 K

x	T (K)	IS (mm·s^{-1})	HF (kOe)	I (%)	Γ^a (mm·s^{-1})
0	300	0.066	0	100	0.33
	4.2	0.11	334	100	0.36
0.2	300	0.045	0	100	0.35
	4.2	0.145	310	100	0.33
0.4	300	—	~165	—	—
	4.2				
	Component 1	0.12	304	63	0.32
	Component 2	0.11	288	37	0.31
0.6	300	—	~165	—	—
	4.2				
	Component 1	0.12	305	44	0.30
	Component 2	0.11	290	56	0.29
0.99^b	4.2	0.19	296	100	—

^{a} Full peak width at the half maximum.
^{b} See Ref. (18).

FIG. 6. Dependence of the magnetic hyperfine field at 4 K on Co content (see Table 1). The solid line is an exponential function, $HF/\text{kOe} = 291 + 39.5 \exp(-5.56x)$, reproducing the experimental composition dependence approximately.

ried out with great interest and will be published soon elsewhere. Interpretation of the relation among various experimental results and theoretical calculations, including the atomic moments of 4 μ_B/Fe and 1.8 μ_B/Co, the *HF* values of 330 ~ 290 kOe, and the description of the ground state as $d^5\underline{L}$ for Fe^{4+} and as $d^6\underline{L}$ for Co^{4+}, needs to be established in the future.

CONCLUSION

SrFe$_{1-x}$Co$_x$O$_{3-\delta}$ with its oxygen deficiency minimized by using a high-pressure technique shows ferromagnetism with T_C above 300 K for $0.4 \leq x \leq 0.9$. In relation to this, a possibility of negative magnetovolume effect has been raised for the composition dependence of the lattice constant at 300 K. The composition dependence of the magnetic hyperfine field suggests that the Co substitution makes Fe$_{3d}$ electrons more delocalized. From these experimental results a phase change in the σ^* band properties from the SrFeO$_3$ type to Sr$_2$FeCoO$_6$ type has been proposed.

tronic properties. If we follow the usual assumption that the magnetic hyperfine interaction is due to the polarization of *s*-electrons and is linear to the localized electron density (19), we can say that the Co substitution delocalizes about 10% of electrons of Fe parentage in a broadened σ^* band.

The Mössbauer results can thus be summarized as follows. First, there is no trace of Fe^{3+} ions resulting from oxygen deficiency within experimental error. Second, the high T_C's above 300 K around $x = 0.5$ concluded from the magnetization data are supported by this microscopic measurement. Third, however, it has been suggested that a statistical fluctuation in the Fe : Co ratio can affect the magnetism locally. Fourth, the density of *d*-electrons localized at an Fe ion seems to decrease by about 10% at relatively low Co content.

It is intriguing and, at the same time, constructive for a further study to interpret these results as follows. The σ^* band made of d_σ and p_σ orbits switches its properties from the SrFeO$_3$ type to the Sr$_2$FeCoO$_6$ type. The former one is featured by the screw spin structure with a low T_N of 134 K and the latter by ferromagnetism with a high T_C of 340 K. The initial tendency of T_N to decrease with increasing Co content up to $x \sim 0.1$ and the sudden appearance of ferromagnetism with much higher T_C's for $x \geq 0.15$ suggests that the boundary between these two electronic phases is $x = 0.1 \sim 0.15$. The decrease in localized electron density at the Fe site found by Mössbauer spectroscopy suggests that the σ^* band is broadened in the Sr$_2$FeCoO$_6$-type phase. In this respect a study of electric conductivity as a function of temperature and Co content is being car-

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