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T. Shinjo, M. Takano, H. Taguchi, M. Shimada. MÖSSBAUER STUDY OF Fe⁴⁺ IN FERROMAGNETIC SrCoO₃. Journal de Physique Colloques, 1980, 41 (C1), pp.C1-157-C1-158. 10.1051/jphyscol:1980141 . jpa-00219710

HAL Id: jpa-00219710

<https://hal.science/jpa-00219710>

Submitted on 4 Feb 2008

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MÖSSBAUER STUDY OF Fe^{4+} IN FERROMAGNETIC SrCoO_3 T. Shinjo, M. Takano⁺, H. Taguchi* and M. Shimada**Institute for Chemical Research, Kyoto University, Uji, Kyoto, Japan.*⁺ *Department of Chemistry, Faculty of Science, Konan University, Kobe, Japan.*^{*} *The Institute of Scientific and Industrial Research, Osaka University, Osaka, Japan.*

A less-common valence state, Fe^{4+} , is found in such oxides as Sr-Fe-O, Ca-Fe-O and Ba-Fe-O. The compounds with 100% Fe^{4+} can be prepared under high oxygen pressure. Recently, Takano et al./1-4/ studied stoichiometric CaFeO_3 and observed that the charge disproportionation, $\text{Fe}^{4+} \rightleftharpoons \text{Fe}^{3+} + \text{Fe}^{5+}$, takes place below the Neel temperature (115K). In the case of SrFeO_3 , which is known to be an antiferromagnet with a screw spin structure ($T_N = 134\text{K}$)/5/, a single hyperfine field of Fe^{4+} state was observed at 4.2K/6/. Namely no charge disproportionation has occurred. Mössbauer spectroscopic measurements so far carried out show that the typical hyperfine field of Fe^{4+} state at 0K is between 300 and 350kOe. However, the sign of the hyperfine field has not been determined since all the compounds were antiferromagnetic.

The Co^{4+} compounds, SrCoO_3 , which is also prepared under high oxygen pressure, is of great interest because it is ferromagnetic (T_C ; about 220K). SrCoO_3 is isomorphous with SrFeO_3 and the solid solution was investigated by Takeda and Watanabe/7/. A part of their results is reproduced in Fig. 1. The magnetization measured at 77K with applying 6kOe is not exactly equal to the saturation magnetization at 0K but the followings are clearly shown.

- (1) The dilute Fe in SrCoO_3 couples ferromagnetically with the ferromagnetic matrix.
- (2) Magnetization of the system has a maximum around the middle, $X=0.5$.

We have measured the Mössbauer spectra for the samples of $\text{SrCo}_{0.99}\text{Fe}_{0.01}\text{O}_3$ and $\text{SrCo}_{0.5}\text{Fe}_{0.5}\text{O}_3$. Both samples were prepared by a thermal treatment at 300°C for 3 days under 1000atm. O_2 pressure. Results on dilute Fe in SrCoO_3 will be useful not only for the study of electronic structure but also to determine the sign of the Fe^{4+} hyperfine field.

Figure 2 shows the Mössbauer spectra of SrCoO_3 including 1% ^{57}Fe . At 300K, the spectrum is a single line whose isomer shift is 0.05mm/sec (vs.Fe)

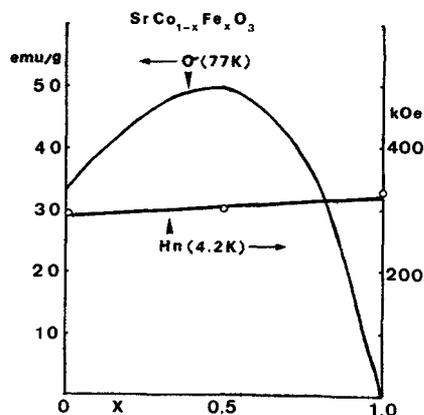


Fig. 1 : Magnetization of $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_3$ as a function of x , measured at 77K with applying 6kOe. Hyperfine fields at 4.2K for $X=0.01$ and 0.5 (present results) and $X=1.0$ (Ref.6) are also shown.

which is typical of Fe^{4+} state. The line width at half maximum is 0.67mm/sec. This value is fairly large but meaningful analysis seems to be impossible. At 4.2K, a magnetic hyperfine field of 296kOe was observed. All Fe ions are confirmed to be in a single Fe^{4+} state. When an external magnetic field (45kOe) was applied in parallel to the gamma ray direction, the No.2 and No.5 lines disappeared nearly completely and the effective field was decreased. It is thus clear that the sign of the Fe^{4+} hyperfine field is negative. This result is the first observation of Fe^{4+} ion in a ferromagnetic substance. The spin structure of pure SrCoO_3 is suggested to be collinear by the fact that the magnetic spin of impurity Fe has been oriented to the direction of external field.

The spectra of $\text{SrCo}_{0.5}\text{Fe}_{0.5}\text{O}_3$ are shown in Fig. 3. The single line spectrum at room temperature certifies the whole Fe atoms being in an Fe^{4+} state. The isomer shift is nearly the same as the previous one. In all $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_3$ system, the isomer shift at room temperature is $+0.05 \pm 0.02$ mm/sec.

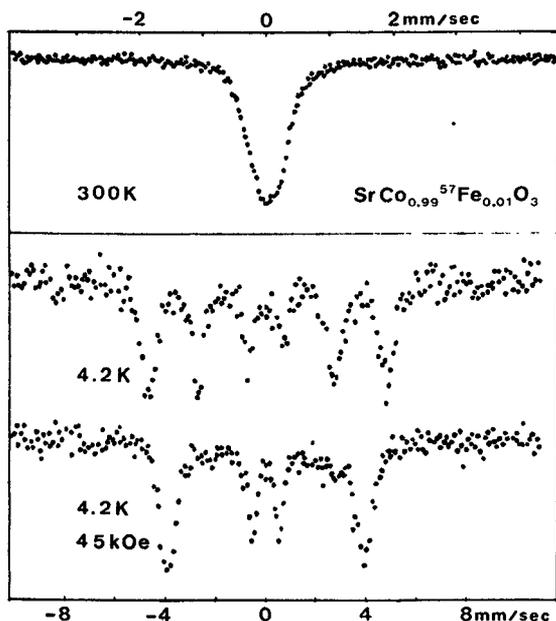


Fig. 2 : Mössbauer spectra of $\text{SrCo}_{0.99}\text{Fe}_{0.01}\text{O}_3$ at 300K and at 4.2K without external field and at 4.2K with an external field of 45kOe.

At 4.2K, a rather sharp six-line spectrum was obtained and the hyperfine field was derived to be 302kOe. The hyperfine field is varying monotonously as a function of the composition. The change of the magnetization shown in Fig. 1 is interpreted as follows. When the concentration of Fe in SrCoO_3 is dilute, the Fe's spin couples ferromagnetically with the ferromagnetic matrix. With increase of Fe concentration, antiferromagnetic coupling between Fe atoms becomes significant. Then the spin structure must be complicated. Partially or entirely, canted spin configuration might be realized and the magnetization curve eventually shows a maximum around $x=0.5$.

The change of the hyperfine field is rather small and the electronic structure of Fe^{4+} ion itself is almost the same in the whole composition range.

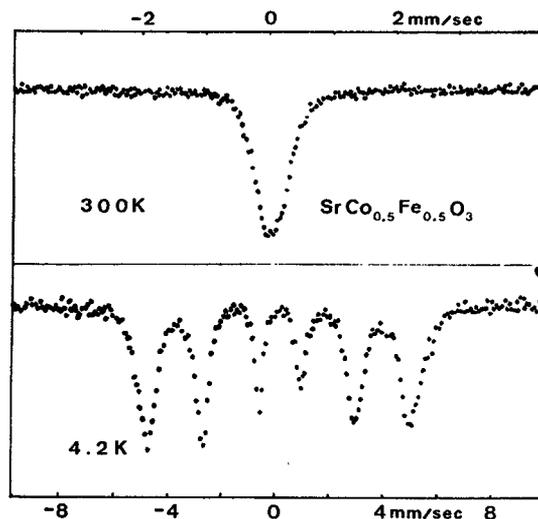


Fig. 3 : Mössbauer spectra of $\text{SrCo}_{0.5}\text{Fe}_{0.5}\text{O}_3$ at 300K and 4.2K.

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