

CATION DISTRIBUTION AND HIGH FIELD MAGNETIZATION STUDIES ON  $\text{SrFe}_{12-x}\text{Cr}_x\text{O}_{19}$ 

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Abstract

With the aim of a better understanding of both cationic distribution and magnetic properties of the uniaxial  $\text{SrFe}_{12-x}\text{Cr}_x\text{O}_{19}$  hexagonal ferrites, Mössbauer spectroscopy, neutron diffraction and high field magnetization measurements have been carried out. The  $\text{Cr}^{3+}$  ions occupy the octahedral sites of the M structure with a preference hierarchy within them. The magnetic measurements, together with the deduced cationic distribution, indicate that some sublattices have a random spin canting around the c-axis.

Introduction

M-type hexagonal ferrites have given rise to several studies because of their singular magnetic properties which are of considerable scientific and technological interest [1,2]. Particularly, the effect of Cr substitution on the magnetic properties of M-type hexagonal ferrites has been already studied by other authors [3,4]. However, the main problems connected with the cationic distribution are not completely solved. Therefore, we decided to undertake the study of the cationic distribution in the  $\text{SrFe}_{12-x}\text{Cr}_x\text{O}_{19}$  hexagonal ferrites by using Mössbauer spectroscopy and neutron diffraction measurements. High field magnetization measurements have been performed, as well, in order to analyze the consequences of the Cr substitution in the magnetic ordering of these oxides.

Experimental

Powder samples of  $\text{SrFe}_{12-x}\text{Cr}_x\text{O}_{19}$  oxides in the composition range  $0 \leq x \leq 8$  have been prepared by high temperature solid state reaction of  $\text{SrCO}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  stoichiometric mixtures. The purity of the samples was verified from X-ray powder patterns which were obtained with a Guinier camera by using Fe K as incident

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radiation.  $^{57}\text{Fe}$  Mössbauer spectra were obtained in the temperature range between 80 K and 800 K by using a constant acceleration spectrometer. A 10 mCi single line source of  $^{57}\text{Co}$  in Rh matrix was used. Neutron diffraction patterns of several compounds in the paramagnetic phase were obtained at different temperatures in the Laue-Langevin Institute. The isothermal magnetization curves in fields up to 150 KOe, in the temperature range from 4.2 K to 300 K were obtained by the axial extraction technique using a water cooled Bitter magnet of the Service National des Champs Intenses in Grenoble.

Results and discussion

a) Mössbauer spectroscopy: A first report of our Mössbauer spectroscopy results has been given before [5]. In figures 1 and 2 we show two typical spectra obtained in the paramagnetic and ferrimagnetic phases, respectively. The Fe content of the bipyramidal 4e sublattice was easily evaluated from the paramagnetic spectra because of the unusually high quadrupole splitting owing the Fe ions located at this position. The Fe content of the remaining sublattices was deduced from the magnetically split spectra in which the overlap is much less important. When Cr substitution is performed, a progressive broadening of the Lorentzian lines in the magnetic spectra is observed. This broadening is temperature dependent and it is interpreted as due to a hyperfine field distribution.

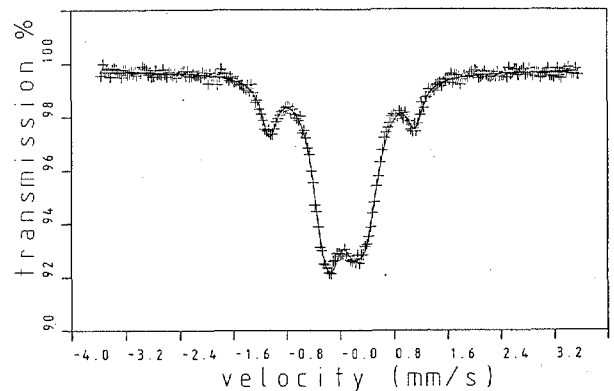


Fig.1. Paramagnetic Mössbauer spectra of  $\text{SrFe}_6\text{Cr}_6\text{O}_{19}$  hexagonal ferrite.

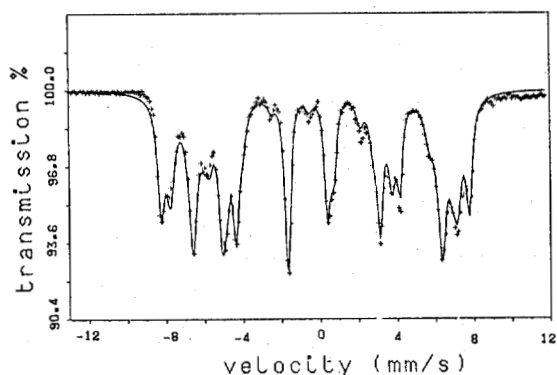


Fig.2. Room temperature Mössbauer spectra of  $\text{SrFe}_{10}\text{Cr}_2\text{O}_{19}$  hexagonal ferrite.

In our fit procedure a Lorentzian hyperfine field distribution was assumed. Moreover, in some compounds the 12k octahedral subspectra are split in two inequivalent hyperfine fields displaying a different temperature dependence, as has been already observed in other substituted hexagonal ferrites [6]. In the computation of the Fe occupancy in the different sites it has been supposed that the recoil free fractions of the different

$^{57}\text{Fe}$  cations are the same within the 2a,  $4f_{\text{IV}}$ ,  $4f_{\text{VI}}$  and 12k sublattices. The Fe population of the 5-fold sublattice has been obtained from the relative change of the subspectrum area for the different compounds because the  $^{57}\text{Fe}$  ions located at this site have lower f-factors than those located at the other sites [7].

b| Neutron diffraction: The atomic content of the five cationic lattice sites of the M structure has been determined from a least squares refinement of the paramagnetic neutron diffraction data. Up to 80 Bragg reflections were measured in each neutron diffraction pattern. In order to determine the 12 positional parameters and the 5 Fermi lengths two different refinement methods have been used: the Rietveld method [8] and the integrated intensity method. The Fermi lengths (in units of  $10^{-12}\text{cm}$ ) of Fe (0.95) and Cr (0.352) are different enough to allow a correct assignment to each site. In figure 3 we show the resulting Fe population of each site as deduced from our neutron diffraction and Mössbauer spectroscopy studies. As can be seen in this figure, the  $\text{Cr}^{3+}$  ions do not occupy at all either the 5-fold 4e sublattice nor the tetrahedral  $4f_{\text{IV}}$  sublattice. Only the octahedral sublattices are simultaneously occupied by the  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  cations. Moreover, our results show that within these three octahedral sublattices a preference hierarchy, in the order 2a, 12k and  $4f_{\text{VI}}$  does exist (figure 4). The preference of  $\text{Cr}^{3+}$  ions for the octahedral sites can be well understood taking into

account the well-known crystal field stabilization of these ions in octahedral environments. The origin of the preference hierarchy within the three octahedral sites may be related to the different asymmetry degree and crystallographic features of these sites [9].

c| High field magnetization study: With the aim of a better understanding of the relationship between the magnetic structure and the  $\text{Cr}^{3+}$  location, isothermal magnetization curves have been obtained. Intrinsic magnetic parameters, such as saturation magnetization  $M_0$  and high field differential susceptibility  $\chi$ , have been deduced from a numerical analysis of the magnetization curves [10]. The composition dependence of the experimental  $M_0$  values at  $T = 0\text{K}$  is represented in figure 5, together

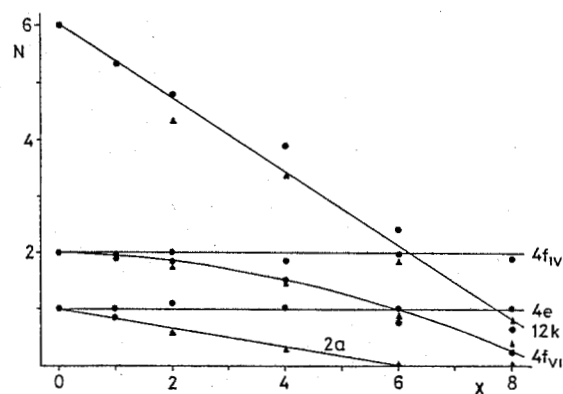


Fig.3. Iron content of the five sublattices of  $\text{SrFe}_{12-x}\text{Cr}_x\text{O}_{19}$  oxides; Mössbauer; neutron diffraction.

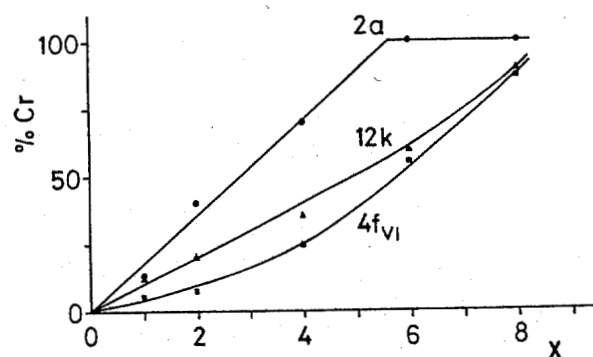


Fig.4. Chromium content of the three octahedral sublattices.

with the theoretical values obtained assuming a Gorter-type collinear magnetic structure and the cationic distribution deduced from our neutron diffraction and Mössbauer spectroscopy studies. Spin-only magnetic moments have been assumed in these calculations:

$\mu(\text{Fe}^{3+}) = 5 \mu_B$ ,  $\mu(\text{Cr}^{3+}) = 3 \mu_B$ . High field differential susceptibilities  $\chi$  were observed for all the compounds with  $x \neq 0$  in

in all the studied temperature range. The dependence of  $M_0$  on temperature for different compounds is represented in figure 6.

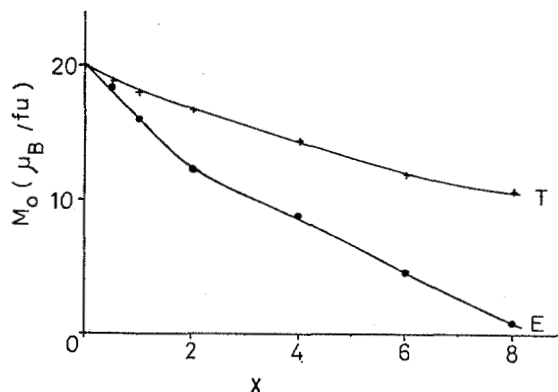


Fig.5. Saturation magnetization at  $T = 0\text{K}$  as a function of the Cr content,  $x$ ; E: experimental values; T: theoretical values.

Both the low  $M_0$  values experimentally obtained and the appearance of a high field differential susceptibility indicate that the magnetic structure of these compounds is not collinear. Nevertheless, neutron diffraction patterns obtained below  $T_C$  [3,11] have shown that the long range ferrimagnetic ordering remains collinear and directed along the  $c$ -axis. Therefore, the results of our thermomagnetic study can only be interpreted in terms of a random canting of the spins around the  $c$ -axis. In this way, the  $c$ -axis component of the magnetic moments has a long range ferrimagnetic ordering while the planar components are disordered within the  $a$ - $b$  plane. The observation of a high field differential susceptibility excludes the possibility of a random spin reversal [3,12,13].

As a matter of fact, from the strong decrease of the  $T_C$  values [3,4] and the selective distribution of  $\text{Cr}^{3+}$  cations it becomes clear that some intersublattice exchange interactions are strongly diminished. Moreover, previous studies on mixed oxides [12-14] suggest that when  $\text{Cr}^{3+}$  ions are introduced in the lattice the near  $180^\circ$  antiferromagnetic superexchange interactions are strongly decreased, or even change sign, while the  $90^\circ$  interactions remain strongly antiferromagnetic. Therefore, the appearance of localized spin canting may be expected as a consequence of the relative increase of the competing interactions [15,16]. Due to the fact that the difference

$M_0^{\uparrow}(\text{OK}) - M_0^{\downarrow}(\text{OK})$  remains positive throughout the solid solution, it can be concluded that the spin canting appears mostly in the spin up sublattices, namely 12k, 2a and 4e. Among these sublattices the 12k has the higher degree of frustration being in this way strongly affected by the decrease of the  $12k - 4f_{\text{VI}}$  interaction [6,17]. Therefore, a canted state will immediately appear for some 12k Fe ions. This magnetic inequivalency of the Fe 12k ions leads to the observed splitting of their hyperfine field in the Mössbauer spectra.

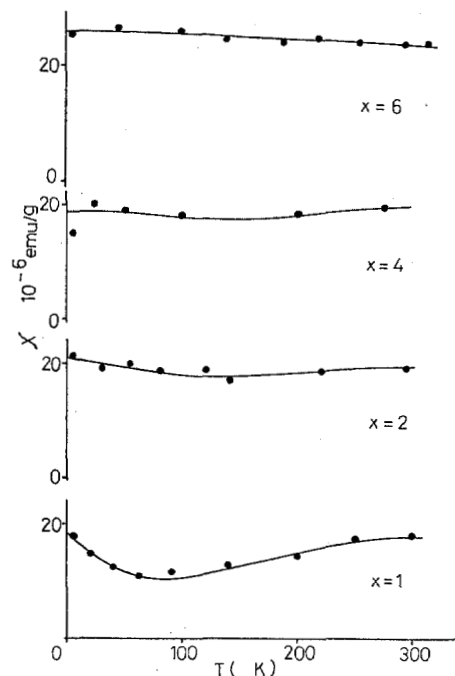


Fig.6. Temperature dependence of the high field differential susceptibility, for different  $x$  values.

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