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# A Mössbauer study of Al and Ga substituted magnetite

M. Rosenberg, P. Deppe, and H. U. Janssen  
Ruhr-Universität, NB 03/34, 4630 Bochum, BR Deutschland

V. A. M. Brabers  
Eindhoven, University of Technology, The Netherlands

F. S. Li  
Lanzhou University, China

S. Dey  
Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

A Mössbauer study of  $\text{Fe}_{3-x}\text{Al}_x\text{O}_4$  and  $\text{Fe}_{3-x}\text{Ga}_x\text{O}_4$  has been undertaken. Measurements at low temperatures in magnetic fields enabled us to better separate the Fe(A) and Fe(B) subspectra and to determine the cation distribution on tetrahedral and octahedral sites. Whereas Al up to  $x = 1.4$  shows a strong preference for B sites, giving rise to a normalization of the spinel structure with  $\text{Fe}^{2+}$  located mainly in tetrahedral sites, Ga distributes over both A and B places without tendency towards normalization at least below  $x \leq 1.2$ .

## INTRODUCTION

Mössbauer studies of relatively broad compositional ranges of the spinel systems  $\text{Fe}_{3-x}\text{Al}_x\text{O}_4$  and  $\text{Fe}_{3-x}\text{Ga}_x\text{O}_4$  have been undertaken by Dehe *et al.*<sup>1,2</sup> According to their results  $\text{Al}^{3+}$  replaces mainly  $\text{Fe}^{3+}$  ions on the B sites of the spinel structure, whereas  $\text{Ga}^{3+}$  replaces only  $\text{Fe}^{3+}$  on the A sites for  $x < 0.3$  and then starts to distribute itself over both A and B sites.

In order to better characterize the cation distribution in the spinel lattice of Al and Ga substituted magnetite and its influence on the hyperfine fields HF(A) and HF(B) at the Fe(A) and Fe(B) sites, a Mössbauer study in which the emphasis was put on measurements in relatively high magnetic fields at low temperature, has been undertaken. In such a way it was possible to better separate the Fe(A) and Fe(B) Mössbauer subspectra and to determine the contribution of the different local environments of the Fe ions to the broadening of the Fe(B) subspectrum with increasing Al and Ga concentration.

## EXPERIMENT

Polycrystalline samples of  $\text{Fe}_{3-x}\text{Al}_x\text{O}_4$  ( $0.4 < x < 1.4$ ) have been prepared by sintering spray roasted mixtures of iron and aluminum sulfates at 1300 °C in an adjusted atmosphere to preserve the spinel structure; the partial oxygen pressures during the sinter process ranged from  $^{10}\log P_{\text{O}_2}$  (atm) = -4.9 for  $x = 0$  till -7.5 for  $x = 1.4$ . The gallium-ferrites  $\text{Fe}_{3-x}\text{Ga}_x\text{O}_4$  ( $0.1 < x < 1.2$ ) have been prepared by standard ceramic techniques; the final sintering process was carried out at 1370 °C in  $\text{CO}_2/\text{CO}$  mixtures with a partial oxygen pressure of  $10^{-8}$  atm.

Mössbauer spectra were taken with conventional equipment, using cryostats for measurements at 77 and 4.2 K and a superconducting coil for applying fields up to 50 kOe in the direction of the gamma rays. A Mössbauer Fe/Rh source with an activity of 25 mCi was used.

## RESULTS AND DISCUSSION

### $\text{Fe}_{3-x}\text{Al}_x\text{O}_4$

The room temperature Mössbauer spectra for  $x > 0.8$  show signs characteristic of relaxation spectra,  $x = 1.4$  is

already paramagnetic, in good agreement with the observations of Dehe *et al.*<sup>1</sup> Spectra taken at 4.2 K do not show relaxation effects. The Fe(A) and Fe(B) subspectra overlap each other, and the relative intensities of the second and fifth peaks increase anomalously with Al concentration.

In order to improve the separation of the Fe(A) and Fe(B) subspectra, and also to check the possibility of the existence of spin canting effects, Mössbauer spectra have been taken at 4.2 K in external fields of 10, 30, and 50 kOe applied parallel to the direction of the gamma rays. In the absence of any spin canting effects, the peaks corresponding to the Mössbauer lines 2 and 5 have to vanish.

In fact, that is actually the trend taken from Fig. 1. Because of the broadening of the Fe(B) lines, a good separation of the Fe(A) and Fe(B) subspectra is reached only in a field of 50 kOe.

A most peculiar aspect is the presence of a Mössbauer subspectrum with HF values varying from about 300 to 230 kOe with increasing  $x$  in the range  $0.6 < x < 1.4$ . Its intensity is practically unaffected by the magnetic field, but increases strongly with  $x$  in the range  $0.8 < x < 1.4$ . This subspectrum overlaps with lines 2 and 5 of the Mössbauer spectrum taken without a field, and obviously its presence explains the already mentioned anomalously strong intensity of these lines with increasing  $x$ . Therefore this spectrum is not evidence for spin canting but, as we believe, for  $\text{Fe}^{2+}$  located at the A sites. A further argument for this interpretation is that in an external field it shifts to larger velocities, as the  $\text{Fe}^{3+}$ (A) lines do, because the outer field adds to the HF of Fe(A) ions. This trend changes for  $x = 1.4$ , where both the  $\text{Fe}^{3+}$ (A) and  $\text{Fe}^{2+}$ (A) lines shift to lower velocities. The reason is that slightly below  $x = 1.4$  the magnetizations of the Fe(A) and Fe(B) sublattices cancel each other and at  $x = 1.4$  the external field will be parallel to the magnetization of the Fe(A) sublattice and therefore antiparallel to HF at the Fe(A) sites.

Whereas the  $\text{Fe}^{3+}$ (A) lines remain relatively narrow even for high  $x$  values and HF at 4.2 K changes in the range  $0.6 < x < 1.2$  from 520 to 480 kOe, the Fe(B) lines considerably broaden, especially in the range  $0.6 < x < 1.0$ .

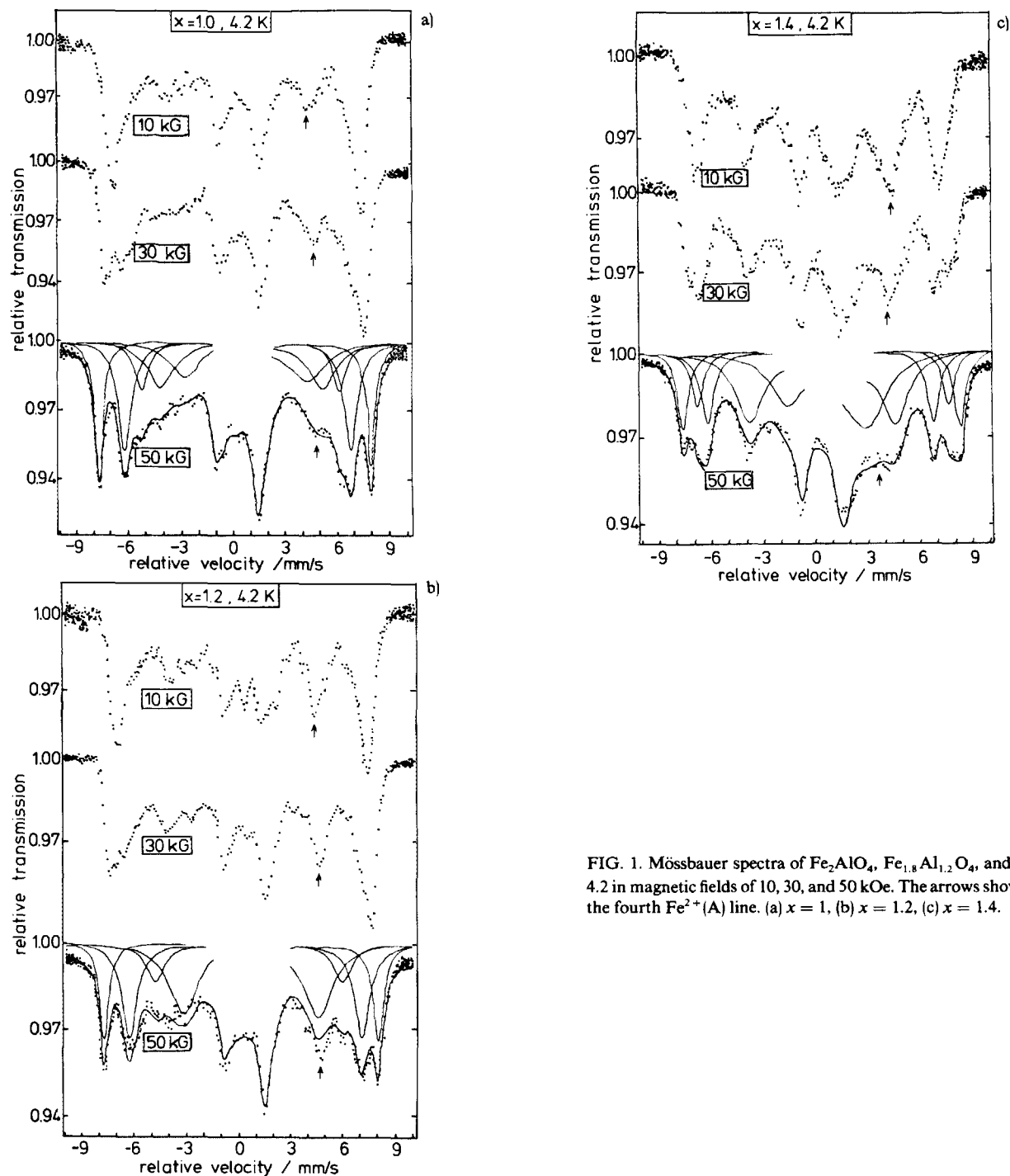


FIG. 1. Mössbauer spectra of  $\text{Fe}_2\text{AlO}_4$ ,  $\text{Fe}_{1.8}\text{Al}_{1.2}\text{O}_4$ , and  $\text{Fe}_{1.6}\text{Al}_{1.4}\text{O}_4$  at 4.2 K in magnetic fields of 10, 30, and 50 kOe. The arrows show the position of the fourth  $\text{Fe}^{2+}(\text{A})$  line. (a)  $x = 1$ , (b)  $x = 1.2$ , (c)  $x = 1.4$ .

Tentative fits to the Mössbauer spectra at 4.2 K in 50 kOe are shown in Fig. 1. The  $\text{Fe}(\text{B})$  hyperfine field component with the highest value shifts from about 500 kOe for  $x = 0.6$  down to 445 kOe for  $x = 1.4$ .

The clear separation of the  $\text{Fe}^{3+}(\text{A})$  and  $\text{Fe}^{2+}(\text{A})$  subspectra shows that no fast relaxation  $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$  takes place for  $\text{Fe}(\text{A})$ , in contrast to  $\text{Fe}(\text{B})$  where the asymmetrical broadening of the lines can be explained by the migration of  $\text{Fe}^{2+}$  ions from B towards A sites with the increasing random substitution of Fe with Al, giving rise to a distribution of environments with different numbers of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  nearest neighbors.<sup>3</sup> The magnetic dilution of the  $\text{Fe}(\text{B})$  sublattice will lead to the observed continuous small decrease of the  $\text{Fe}(\text{B})$  hyperfine fields.

An analysis of the dependence of the intensities of the  $\text{Fe}^{3+}(\text{A})$  and  $\text{Fe}^{2+}(\text{A})$  subspectra on  $x$  shows that up to  $x = 1.2$ , because of a strong preference for octahedral sites<sup>4</sup> Al substitutes practically only  $\text{Fe}^{3+}(\text{B})$  ions in good agreement with other authors.<sup>1</sup>

#### $\text{Fe}_{3-x}\text{Ga}_x\text{O}_4$

The room temperature Mössbauer spectra for  $x \geq 1.0$  show the presence of strong relaxation effects. For  $x < 0.7$  no relaxation occurs and in the negative velocity range the first  $\text{Fe}(\text{A})$  line is relatively well separated from the  $\text{Fe}(\text{B})$  one. This advantage is lost at 77 K but at this temperature no more relaxation effects for  $x \geq 1.0$  occur. In order to better separate the  $\text{Fe}(\text{A})$  and  $\text{Fe}(\text{B})$  subspectra Mössbauer spectra

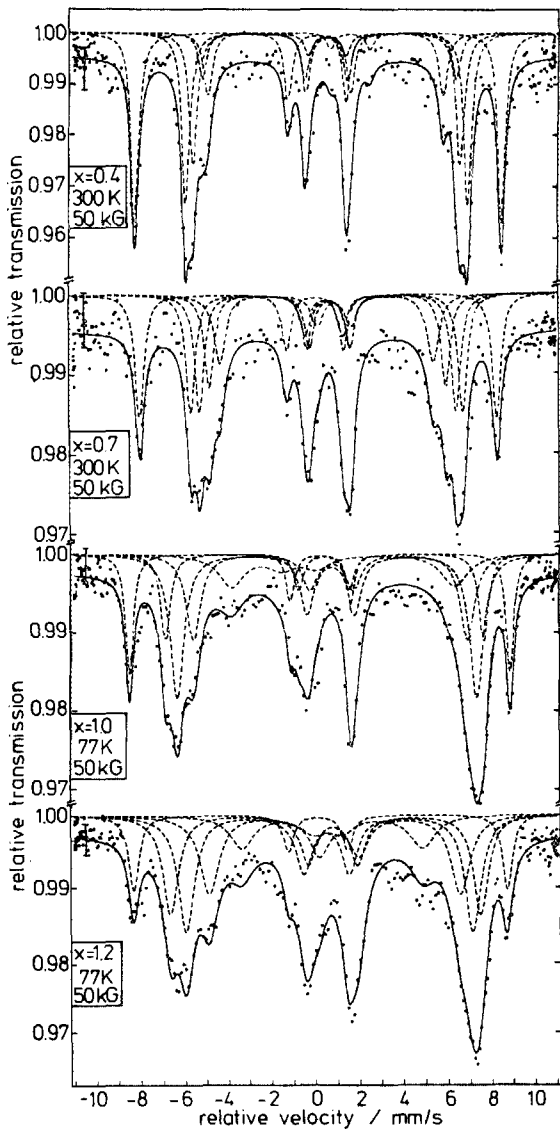
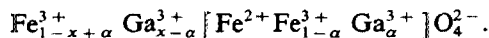


FIG. 2. Mössbauer spectra of  $\text{Fe}_{3-x}\text{Ga}_x\text{O}_4$  with  $x = 0.4$  and  $0.7$  at  $300\text{ K}$  and  $x = 1.0$  and  $1.2$  at  $77\text{ K}$  taken in a magnetic field of  $5\text{ kOe}$ . Besides the Fe(A) subspectrum a fit with 4 Fe( $B_i$ ) subspectra to the broadened Fe(B) spectrum is shown.

in an external field of  $50\text{ kOe}$  have been taken at room temperature for  $x < 0.7$  and  $77\text{ K}$  for  $x = 1.0$  and  $1.2$ , as shown in Fig. 2.

In contrast to  $\text{Fe}_{3-x}\text{Al}_x\text{O}_4$  there is no evidence for  $\text{Fe}^{2+}$  on A sites, i.e., the substitution with Ga at least up to  $x = 1.2$  does not displace  $\text{Fe}^{2+}$  from B to A sites and the cation distribution formula can be written as follows:



From the intensities of the Fe(A) and Fe(B) subspectra a linear dependence of the form  $\alpha = 0.376x$  has been derived, showing that  $\text{Ga}^{3+}$  distributes on both A and B sites even at very low concentration as  $x = 0.1$  for instance.

Whereas the width of the Fe(A) Mössbauer lines does not change too much with  $x$ , a strong asymmetrical broadening of the Fe(B) lines increasing with  $x$  takes place. The number of Fe(B) subspectra fitted changes from one for  $x = 0.1$  up to four for  $x > 0.4$ . The room temperature values of  $\text{HF}(B_i)$  for the subspectra indexed with A and  $B_i$  ( $i = 0, 1, 2, 3$ ) for  $x < 0.7$  and the  $77\text{ K}$   $\text{HF}(B_i)$  values for  $x = 1.0$  and  $1.2$  are

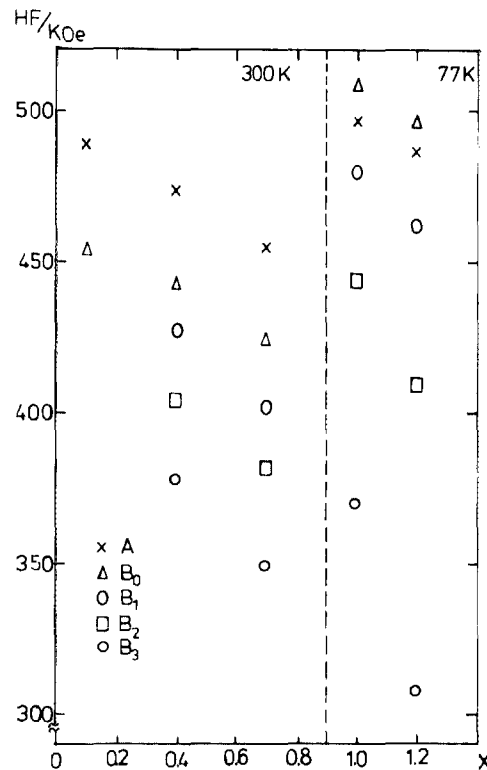


FIG. 3. Fe(A) and Fe( $B_i$ ) hyperfine fields of  $\text{Fe}_{3-x}\text{Ga}_x\text{O}_4$  vs  $x$  at  $300\text{ K}$  (for  $x = 0.1, 0.4, 0.6$ ) and  $77\text{ K}$  (for  $x = 1.0$  and  $1.2$ ).

shown in Fig. 3. The trend is similar to that observed in the case of low Cr substitution in the  $\text{Fe}_{3-x}\text{Cr}_x\text{O}_4$  system.<sup>5</sup> The main reason for the occurrence of 4 Fe(B) subspectra is in our opinion the increasing ratio of the number of  $\text{Fe}^{2+}$ (B) to that of the  $\text{Fe}^{3+}$ (B) nearest neighbors with increasing  $x$  and  $\alpha$ , because of the random distribution of  $\text{Ga}^{3+}$  ions on the B sites. Whereas the A and  $B_0$  subspectra describe pure  $\text{Fe}^{3+}$  states, the subspectra  $B_1$ ,  $B_2$ , and  $B_3$  arise because of the increasing with  $x$  probability of finding environments with 2  $\text{Fe}^{3+}$  and 3  $\text{Fe}^{2+}$ , 1  $\text{Fe}^{3+}$ , and 3  $\text{Fe}^{2+}$  and only 3  $\text{Fe}^{2+}$  iron nearest neighbors. The decrease of  $\text{HF}(B_i)$  in the sequence  $B_0 \rightarrow B_3$  results from the increasing  $\text{Fe}^{2+}$  character of the hyperfine field. The general decreasing trend of all  $\text{HF}(B_i)$  values with  $x$  is due to the weakening of A-B exchange interaction because of the substitution of  $\text{Fe}^{3+}$ (A) magnetic active ions with the nonmagnetic  $\text{Ga}^{3+}$ .

The intensities of the Fe( $B_i$ ) subspectra are in agreement with the expectations of a model in which one ascribes the  $\text{HF}(B_i)$  values to the types of environments mentioned before, assuming that their populations are given by the binomial distribution of the fraction  $\alpha$  of  $\text{Ga}^{3+}$  ions on the B sites.

According to this model,  $\text{HF}(B_3)$  has the quasipure  $\text{Fe}^{2+}$  character, whereas  $\text{HF}(B_0)$  has to derive from an admixture of equal amounts  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  states as in the case of the Fe(B) subspectrum of  $\text{Fe}_3\text{O}_4$ .

<sup>1</sup>G. Dehe, B. Seidel, K. Melzer, and C. Michalk, *Phys. Status Solid A* **31**, 439 (1975).

<sup>2</sup>G. Dehe, J. Suwalski, E. Wieser, and R. Kabisch, *Phys. Status Solid A* **65**, 669 (1981).

<sup>3</sup>H. Franke and M. Rosenberg, *Physica B* **86-88**, 965 (1977).

<sup>4</sup>A. Miller, *J. Appl. Phys.* **30**, 245 (1959).

<sup>5</sup>H. Franke and M. Rosenberg, *J. Magn. Magn. Mater.* **9**, 79 (1979).